Ordered nanostructures by colloidal self-assembly

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ORDERED NANOSTRUCTURES BY COLLOIDAL SELF-ASSEMBLY

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SUMMARY

This research is focused on the fabrication of optically active three-dimensional (3D) ordered nanostructures by the cost-effective colloidal self-assembly (CSA) approach, and their applications in high performance photonic microlasers and efficient light sources for the next era of integrated optoelectronics. This includes detailed consideration essential to the building of high-quality 3D photonic crystals (PhCs) for the control of light in the ultraviolet (UV) and visible regimes, methods for measuring photonic bandgap (PBG), and the engineering of defects. The colloidal PhCs (a. k. a. *artificial opals*) should have sufficient dielectric contrast for opening a complete PBG, low defect density for extending long range crystallinity and the possibilities to introduce intentional defects.

The thesis begins with a study on growth imperfections in polystyrene (PS) opals grown by the widely-used vertical convective self-assembly approach. Here, the growth pattern is attributed to the *dynamic* balance between surface tension forces due to the change in the contact angle with time, which results in a “stick-slip” motion of the meniscus growth front. These macroscopic imperfections have been reduced to produce single-crystal opals over centimeter-square areas. This forms the basis for the realization of functional PBG materials.

The PS opals then serve as templates for the fabrication of two different optically active 3-D PhCs, (i) ZnO inverse opal (ii) and the lattice-matched ZnO-PS hetero-opal. Both systems have been prepared by infiltrating PS opaline templates using the cost-effective, vacuum-less, and aqueous-based electrodeposition technique, which produces highly dense materials for high filling fraction. Unlike most previous studies on incorporating light-emitting elements into the body of an opal or over a small fraction of the opal surface, this research introduces an “emissive” PhC, where the light emitters

(ZnO) constitute the dielectric framework of the PhC. These PhCs possess photonic pseudogaps tunable in the UV to visible spectrum, while effective photonic pseudogaps emerge in the hetero-opal.

To reveal the key factors for enhanced photonic pseudogap characteristics, this thesis presents the first systematic comparative study, both experimentally and theoretically, on the optical characteristics of opals and inverse opals. The electrodeposited inverse opals with complete infill give rise to superior photonic pseudogaps: blue-shifted, widen, and more importantly, non-dispersive, approaching omni-directionality within a specific range of directions. While these are only partial PBG, they are strong enough to suppress unfavorable spontaneous emission upon appropriate design. Interestingly, this work has demonstrated an effective photonic pseudogap effect on suppressing the spontaneous emission in the emissive hetero-opal, a linear superposition of individual effects from its component opals with no noticeable interaction effect.

One of the key accomplishments of this work is the demonstration of room temperature UV lasing under optical pumping in *electrodeposited* ZnO inverse opal. Lasing occurs above an excitation threshold of 0.38 MW/cm^2 , among the lowest in polycrystalline ZnO films. Tuning the primary photonic pseudogap of inverse opals to gain maximum leads to a two-fold reduction in lasing threshold. Independently, at an excitation just above the threshold, discrete lasing modes resembling that of whispering gallery mode (WGM) with an emission linewidth less than 0.1 nm and a zero background was observed. The ZnO air-spheres form high quality factor ($Q \sim 6500$) resonators. This suggests that 3D periodic dielectric macroporous structures can be exploited as alternative miniaturized WGM-based laser light sources.

This thesis also highlights a novel “anti-infiltration” approach for introducing nanocrystals (NCs) as optically active planar defects into colloidal PhCs. The method

relies on the retention of an aqueous suspension droplet from infiltrating a porous network and the convective self-assembly of nanoparticles to form a continuous suspended NC sheets upon evaporation. This method should be applicable for any uniform nanocolloids and opens up an opportunity for introducing a wide variety of planar defects with new functionalities derived from the collective properties of self-assembled NCs. More importantly, the ability to fabricate a suspended layer covering patterned/porous surfaces holds promises for a wide variety of applications other than optoelectronics, especially for sensors or molecule-separation membranes.

In summary, this thesis describes the development of *optically active* 3-D colloidal PhCs and demonstrates the use of emissive PhCs to realize low threshold PBG lasing. These photonic nanostructures could act as turnkey PBG systems for the study of complex flow of light in a PhC. More importantly, the experimental advances accomplished in this work will have direct impact on the global effort of building revolutionary photonic devices.

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Chapter 1:

INTRODUCTION

1.1 Background Information

Ordered nanostructure has emerged as an important research focal point for a wide variety of niche applications that range from optoelectronics, advanced catalysis to nanopatterning technology. These useful functionalities are derived from the feature size and periodicity rather than directly from its constituent materials. The most remarkable is to obtain photonic crystals (PhCs), which encompass a fascinating approach to the manipulation of electromagnetic (EM) radiation and hold promises for optoelectronics revolution.

Photonic crystals [1, 2] are materials with a periodic modulation in their dielectric constant on a length scale in the same order of the wavelength of EM radiation it interacts with. The dispersion of light is linear in vacuum and isotropic materials but forms photonic bands in PhCs, akin to electronic energy bands in semiconducting materials. Photonic band structures can lead to a vast variety of useful EM phenomena, ranging from birefringence in the lowest frequency range, the photonic bandgap (PBG), to superprism and anomalous dispersion in the higher frequency range above the PBG. Among these, the PBG, which prohibits the propagation of specific wavelengths of light, is of primary importance. Applying PBG for suppression of spontaneous emission, reduction of group velocity of light at the band edge, and localization of defect states within the gap (analogous to doping in semiconductors) allows high performance reflection-type photonic devices to be envisioned, such as low threshold microlasers, high extraction efficiency light-emitting diodes (LEDs), low loss waveguides, ultra-fast optical

switches, sensors, etc. Such revolutionary photonic devices harnessing the modified flow of light should be exploited for miniaturized, densely integrated all-optical circuits, while providing novel and low power operation. The characteristics of PhCs are scalable with the dimensions of the periodicity. This further opens up the possibility for “PBG engineering” to design devices for application wavelengths ranging from ultraviolet (UV) to microwave regimes, not possible for electrons in silicon.

A full control of EM radiation requires an omnidirectional PBG in three-dimensional (3D) PhCs with 3D periodicity and sufficient dielectric contrast. While the theoretical predictions of the unique physics associated with PhCs are well-established [3-6], the experimental investigation of 3D PhCs and their device prototypes remains an issue too complex to face. The sub-micron scale lattice for applications in the optical regime imposes great fabrication challenges limited by the lithographic resolution of state-of-the-art micro-fabrication processes. Moreover, this top-down layer-by-layer approach to pattern intricate 3D lattices is highly serial and complicated. On the other hand, the “bottom-up” colloidal self-assembly (CSA) approach lends itself very well to produce large area 3D photonic lattice in the UV to infrared regime at low cost. This involves the spontaneous organization of monodispersed sub-micrometer colloidal spheres to form ordered face-centered cubic (fcc) colloidal crystals, though this also implies limited variability in photonic lattice symmetry. In nature, this process leads to sparkling gemstone opals (see Fig. 1.1). Hence, the colloidal crystals are also widely known as “artificial” or “synthetic” opals. Opals have incomplete PBG – it is not effective in every direction – but they still reflect iridescent colors. Theory has predicted that an “inverted” opal, which is obtained by infiltrating the interstitial spaces between the spheres with another dielectric material and subsequent etching of the spheres, can have a complete PBG at a refractive index contrast (RIC) ≥ 2.8 [4].

Figure 1.1: Natural photonic crystals: opal, butterfly, seamouse.

The self-assembled colloidal crystals, however, possess intrinsic disordering [7, 8] and various types of defects [9, 10]. These are extremely difficult to eliminate and currently limit the use of colloidal crystals as practical 3D PBG materials. The PBG is extremely sensitive to the presence of defects because they act as perturbations in the periodicity of the nanostructures and introduce defect states in the bandgap.

1.2 Motivation

Although the highly parallel CSA is potentially appealing in terms of cost and manufacturability, its full development to reach its potential in core industrial applications is considered a formidable task. The current materials engineering challenges for photonic nanostructures by CSA include:

1. To fully develop CSA into a simple, reliable technique for growing large area defect-free photonic nanostructures

The CSA process is highly efficient but suffers from the drawback of native defects. Many fabrication strategies have been developed to form perfect crystals, with the vertical deposition method [11] most widely used to produce single-crystal fcc colloidal films with the (111) close-packed plane oriented parallel to the substrate. However, there have been limited reports providing guidelines for extending long range crystalline quality in CSA due to the lack of understanding on the underlying growth mechanism and the origins of growth defects.

2. To realize 3D PhCs with an omnidirectional PBG at optical wavelengths

It is extremely challenging to satisfy the requirement on $\text{RIC} \geq 2.8$ to obtain a complete PBG in colloidal crystals, since few materials simultaneously have a high refractive index and negligible absorption at optical wavelengths. The first evidence of a complete PBG at $1.5 \mu\text{m}$ has been achieved in Si inverse opals [12]. However, these structures are inappropriate for wavelengths shorter than $1.1 \mu\text{m}$ due to the absorption of Si. To reach the visible part of the spectrum, one promising class of materials is wide bandgap semiconductors with electronic bandgaps above 2 eV and sufficiently high refractive index. On the other hand, the infiltration of opals has been proven to be a non-trivial process since the interstices of the opals are interconnected by small channels. Due to incomplete infilling, so far, effective RICs between 1.9 and 2.7 have been realized experimentally.

3. To innovate new approaches for the controlled introduction of defects into 3D PhCs as optical “doping”

While extending the regions of periodicity and lowering defect density are obvious immediate goals, the ability to retain the possibility to introduce intentional defects at desired locations is equally important. Unlike the incorporation of defects in typical micro-fabrication approaches which is relatively straightforward, it requires new external methods for inserting defects in colloidal crystals. Despite the relatively well-documented normal, passive defects, the demonstration of functional defects has been lacking, which further deferred the widespread implementation of PhCs for a wide range of truly useful and practical applications.

1.3 Objectives and Scope

This thesis aims to develop optically active 3D PhCs by CSA for molding the flow of light. This enables the realization of high-efficiency, miniaturized light emitting devices at UV and visible wavelengths. Two optically active 3D PhCs, differing in the manner of light emitter incorporation are described: (a) inherently optically active and (b) optically active planar defect. The research is organized in a sequence of milestones:

1. Process development of colloidal self-assembly

It is of primary importance to establish a process capability to produce large area 3D colloidal crystals with minimum defects prior the development of optically active PhCs. In this study, the growth pattern of 3D polystyrene (PS) colloidal films produced by vertical convective self-assembly under different experimental conditions (e.g., colloidal concentration and temperature) is investigated. This is analyzed in terms of the dynamic balance of surface tension forces and the convective transport of spheres at the meniscus growth front, based on a relatively well-explained mechanism for horizontal deposition. The optical response of the films is also correlated with the crystallinity to identify the optimum growth conditions to achieve high quality, large area photonic lattices.

2. Realization of inherently optically active 3D photonic crystals

In the quest to achieve a complete PBG, much of the research to date has focused on obtaining large dielectric contrast using passive dielectric materials (e. g., Si [12, 13], Ge [14, 15], or TiO₂ [16-19]). This work is focused on the development of two *inherently* optically active 3D PhCs, (i) ZnO inverse opal (ii) and the lattice-matched ZnO-PS hetero-opal. Since the light emitters (ZnO) constitute the dielectric framework of the PhC, this architecture has the advantages of minimizing the spatial uncertainty in the emitter position while retaining the dielectric contrast. This could serve as a proper model system for the experimental study of modified emission in 3D PhCs by which the effects of the

emitter's spread configuration on decay kinetics can be curtailed to avoid the discrepancies among some pioneering experiments. The inherently optically active 3D PhCs are achieved by employing aqueous-based electrodeposition as an infiltration route. Electrodeposition offers several advantages over gas-phase deposition techniques for the infiltration of complex 3D lattices: relatively dense and uniform deposits are obtainable, high deposition rate, vacuum-less, and low cost. ZnO is a direct, wide bandgap (3.3 eV) semiconductor and a transparent (in the visible region) conductive oxide with a large exciton binding energy (~ 60 meV) much greater than the thermal energy at room temperature (26 meV). In this respect, ZnO is a promising candidate for ultraviolet (UV) optoelectronic applications as an efficient emission material stable at room temperature. Although its refractive index (~ 2.45) is too low for formation of a complete PBG, the dielectric contrast is large enough for strong directional pseudogaps.

3. Comparative study of the directional pseudogaps in opals vs inherently optically active opals

Although the fabrication of 3D PhCs by colloidal templating has been widely explored, there is still a dearth of systematic assessment of the angular dispersion (i.e., directionality) of pseudogaps in opaline PhCs. While the opening condition of a complete PBG and its fragility against disorder are well-investigated, the effect of topology of the dielectric/air network and RIC on the dispersion of the pseudogap remains relatively unclear. In this thesis, it is postulated that electrodeposition assumes a different mode of infiltration as compared to other forms of infiltration methods and results in exceptional photonic characteristics. This is evaluated by a systematic study on the pseudogaps among different opals by performing angle-resolved reflection measurement and photonic bands calculation. Their impact on controlling light emission is examined by acquiring

the respective photoluminescence spectra. The insights gained help to elucidate general conditions for obtaining strongly photonic crystals and ways to ‘engineer’ light emission.

4. Demonstration of inherently optically active 3D photonic crystal laser

One of the first PBG devices envisioned is an efficient thresholdless laser proposed by Yablonovitch [1]. Most of the electric current consumed to produce lasing is wasted as spontaneous light emission, and it is believed that the PBG could suppress that waste: atoms cannot spontaneously emit light when they are part of a material that forbids light propagation. Unfortunately, many hurdles lie ahead for the realization of thresholdless lasers due to the unresolved fabrication issues in 3D PhCs with complete PBG. More background on PhC lasing will be provided in Chapters 2 and 6. Nevertheless, this thesis reports, for the first time, PhC lasing in *electrodeposited* ZnO inverse opals under optical excitation at room temperature. Since there exists only pseudogaps in these PhCs, spontaneous emission is not exclusive to the lasing mode and thus a finite pumping threshold is expected before lasing occurs. The PBG effect on the reduction of lasing threshold is examined by tuning the primary pseudogap of inverse opal to the gain spectrum of ZnO. In addition, it is hypothesized that the periodicity in inverse opals induces structural changes to the constituent dielectric infills. Since this work involves emissive inverse opals, it is imperative to address the impact of periodicity on structural characteristics of the constituent dielectric infills, which will consequently affect their optical characteristics.

5. Controlled introduction of optically active defects into opaline photonic crystals

Defects of various architectures (point, line and bend, or planar) have been incorporated into 3D opaline PhCs by both top-down and bottom-up micro-fabrication approaches [20, 21]. This thesis proposes a new fabrication scheme for creating optically active planar

defects in opals using uniform aqueous nanocolloids. The nanocrystals themselves serve both as the optically active species as well as the defect layer sandwiched between two opal films. In comparison with other techniques, this technique is simple and applicable for both organic and inorganic opals. Both optical reflectance and photoluminescence measurements are carried out to substantiate the successful introduction of the NCs defect layer for light modulation.

1.4 Organization of the Report

This report is divided into eight chapters and each chapter is briefly discussed as follows:

Chapter 1 gives a brief introduction of background information related to this research and presents the motivation and objective.

Chapter 2 deals with a literature review covering various topics related to this research work, such as PBG formation, state-of-the-art PhC fabrication techniques and basic concepts of photonic crystal lasers.

The original work accomplished in this research is presented in Chapters 3 to 7.

Chapter 3 serves to establish the growth of colloidal crystals. The issues involved and approaches employed to optimize the growth are discussed.

Chapter 4 presents the fabrication and preliminary characterization of inherently optically active 3D ZnO PhCs via colloidal templating with electrodeposition, while Chapter 5 provides a comprehensive study on the optical characteristics of these structures.

Chapters 6 reports the first demonstration of lasing in electrodeposited ZnO PhCs.

Chapter 7 describes a novel fabrication scheme for introducing nanocrystals as optically active planar defects into opaline PhCs.

Finally, Chapter 8 summarizes the important conclusions and major findings of this research and proposes potential areas for future research.

Chapter 2:

FABRICATION & CHARACTERISTICS OF PHOTONIC CRYSTALS – A REVIEW

2.1 Overview of Photonic Crystals

Despite the long existence of one-dimensional periodic structures such as Fabry-Perot resonators and Bragg reflectors, it was not until the idea proposed by Yablonovitch [1] and John [2] independently in 1987 that periodic structures are identified as photonic crystals (PhCs) or photonic bandgap (PBG) materials for inhibition of spontaneous emission and localization of light. Since then, these structures have attracted great research interest in both theoretical and experimental study for their ability to control radiation field and light propagation.

2.1.1 The Basic Concept

Photonic crystals are materials with a periodic modulation in refractive index (RI) designed to block the propagation of specific wavelengths of light. This range of wavelength in which no light is allowed to propagate due to a minimum in local electromagnetic density of states (DOS) within the frequency range is called the photonic bandgap (PBG). The PBG arises not by absorption, but as a consequence of the refractive index contrast (RIC) between the two dielectric materials. Light incident on the material will be scattered and/or diffracted off the dielectric surfaces resulting in the combination or cancellation of certain wavelengths of light. Perfect cancellation of the light waves results in the PBG, thus removing the pathways for light propagation.

Depending on the periodicity, PhCs can be classified as one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D). An example of a 1D PhC is the Bragg stack, which consists of alternating layers of high and low dielectric material in one direction as shown in Fig. 2.1(a). A 2D PhC is a structure that has periodicity in two directions, such as an ordered arrangement of dielectric rods. The inverse structure which is fabricated by etching a periodic array of holes in a dielectric slab [see Fig. 2.1(b)], or by formation of a PhC fiber are also considered as 2D PhCs. A 3D PhC is realized by the creation of a material with periodicity in all three directions as in the “Yablonovite” structure, which consists on an overlapping array of air spheres arranged in a diamond lattice as shown Fig. 2.1(c).

Figure 2.1: Examples of (a) 1D, (b) 2D, and (c) 3D photonic crystals.

The PBG is considered as a “full” or “complete” bandgap when the propagation of light is inhibited in all directions, i.e., omnidirectional. This can be achieved in 3D PhCs. A PBG that prohibits the propagation of light in only some directions is referred to as an “incomplete” PBG or “pseudogap”. The naturally occurring gemstone opals, which consists of a close-packed arrangement of sub-micron sized silica spheres, has pseudogaps. While the bandgap is incomplete, it does produce iridescent colors.

2.1.2 Photonic Bandgap Formation

The PBG is the optical analogue of the electron energy bandgap in semiconductors, whereby the air-band is equivalent to the conduction band and the dielectric band is equivalent to the valence band. Figure 2.2 illustrates the typical band diagrams or dispersion curves for semiconductor crystals and PhCs. The x-axis represents the wavevector k , the y-axis represents frequency (or energy), and the curves indicate the allowed energies or states at given k -vectors. The yellow boxes indicate the bandgaps.

Figure 2.2: Semiconductor analogy [22].

Just as the arrangement of atoms in a semiconductor that acts as a periodic potential to electrons, the periodic dielectric in PhCs acts as a periodic potential for incident light.

$$\varepsilon(x) = \varepsilon_0 + \varepsilon_{fluct}(x)$$

While the periodic arrangement of atoms in semiconductor crystals is determined by nature, the periodic structure of dielectric materials in PhCs is artificially designed by

researchers. The PBG is thus tunable. This exciting new class of materials possess novel properties not present in their bulk natural state.

In a semiconductor the motion of electrons in a scattering potential is described by Schrödinger's equation, and analogously the interaction of light is described by Maxwell's equations

$$-\nabla^2 \vec{E} + \vec{\nabla}(\vec{\nabla} \cdot \vec{E}) - \frac{\omega^2}{c^2} \epsilon_{\text{fluct}}(x) \vec{E} = \frac{\omega^2}{c^2} \epsilon_0 \vec{E}$$

The first two terms on the left resembles the kinetic energy terms in Schrodinger's equation, while the third term plays the role of scattering potential. Calculations have shown that the gap at a location arises due to the difference in frequency as low-frequency modes concentrate their energy in the dielectric band while high-frequency modes concentrate their energy in the air-band. One-dimensional bandgaps always appears so long as there is a dielectric contrast.

The most promising structure for new devices is the 3D PhC, since it can result in complete confinement of light. From theoretical calculations, a lattice of dielectric spots [Fig. 2.3(a)] has a bandgap in the TM modes (magnetic field in plane), while a connected lattice [Fig. 2.3(b)] has a bandgap in the TE modes (electric field in plane) only. Therefore, in order to obtain a complete PBG for all polarizations along all directions, the most useful structure is a connected network of dielectric spots [Fig. 2.3(c)].

Figure 2.3: (a) Spots: TM gap; (b) Veins: TE gap; (c) FCC structure with sphere-like Brillouin zone: complete gap.

Initially, it was thought that the high symmetry face-centered cubic (fcc) lattice would have a full PBG. The fcc structure has a sphere-like Brillouin zone (BZ) in reciprocal space, thereby reducing the chance of overlap of a forbidden gap. However, the calculations of Ho *et al.* [3] showed that an fcc lattice with dielectric spheres will only have a pseudogap between the 2nd and 3rd photonic bands centered around $\omega a/2\pi c = a/\lambda = 0.6$, where a is the lattice parameter [see Fig. 2.4 (a)]. This pseudogap is due to a symmetry induced degeneracy at the W point in the first BZ as shown in Fig. 2.5. The degeneracy between the 2nd and 3rd bands is independent of the RIC and filling ratio of the spheres. The 2nd and 3rd photonic bands also cross at the U point of the fcc BZ.

Figure 2.4: Calculated photonic band structures for a dielectric fcc structure composed of (a) polystyrene spheres ($n = 1.59$) in air and (b) air spheres in a dielectric matrix ($n = 3$).

Sozuer *et al.* [4] showed that the inverse fcc structure has a full PBG between the 8th and 9th bands, in addition to pseudogaps between the 2nd and 3rd bands and the 5th and 6th bands. The full PBG between the 8th and 9th bands opens up for crystals with a RIC

greater than 2.8. The photonic band structure for an inverse fcc arrangement of air spheres in a dielectric matrix is shown in Fig. 2.4 (b). Since the RI of air is 1.0, materials with an index greater than 2.8 are required in order to fabricate an inverse fcc PhC with a complete PBG. For optical application, these materials must also be transparent in the visible part of the light spectrum.

Figure 2.5: First Brillouin zone of the fcc crystal structure.

On the other hand, the degeneracy at the W point can be avoided by using a non-spherical basis [5] or a diamond lattice [3] that retains the fcc BZ with a basis of two atoms. The diamond cubic lattice introduced by Ho *et al.* [3] was the first structure theoretically predicted to have a full PBG as shown in Fig. 2.6. Theoretical calculations for structures with a filling fraction of 34% dielectric spheres in air and 81% air spheres in dielectric predict that the diamond structure exhibits a PBG for RIC greater than 2. While the diamond structure is exciting because it has a complete PBG at relatively small refractive index contrast, it is very difficult to fabricate at the sub-micron scale.

Figure 2.6: Calculated photonic band structure for a diamond dielectric structure consisting of dielectric spheres of refractive index 3.6 in an air background [3].

The semiconductor analogy also applies to the introduction of intentional defect modes, i.e., dopants, into the PhC structure. The presence of defects in the PhC structure results in the creation of allowed states within the bandgap. The defects can be in the form of point defects, line defects, or planar defects. For example, one lattice point in a 3D PhC could be replaced with a different dielectric material, either higher or lower in RI. Introducing dielectric defects in the PhC structure can result in light localization and thus many exciting applications such as optical microcavities for light trapping or confinement resulting from point defects and 2D waveguides associated with the introduction of line defects with no reflection or scattering losses. The ‘defect’ can act as a resonator that picks up a particular frequency and route it to a specified destination, like the case in a photonic crystal fiber.

2.1.3 Modification of Light Emission by Photonic Bandgap

The DOS of photons $\rho(\omega)$, i.e., the number of modes per unit volume with frequencies between ω and $\omega+d\omega$ in vacuum or free space is given by

$$\rho(\omega)d\omega = \frac{\omega^2}{\pi^2 c^3} d\omega$$

According to the well-known Fermi's Golden Rule, the transition rate of emission is proportional to $\rho(\omega)$.

It is important to note that a DOS completely different from that in free space can be obtained in a PhC. Thus, the spontaneous emission from an embedded emitter inside a PhC can be suppressed if the transition frequency lies within a stop-band [1]. The modification of light emission can also be accomplished in defect modes within a PBG, which serve as high quality microcavities where light can be spatially localized [6]. Such cavities have the potential to exhibit an ideal cavity for ultimate control of spontaneous emission. As spontaneous emission is a current sink, the possibility of complete manipulation of emission would have deep implications in realizing ultralow threshold lasers, or so-called thresholdless lasers.

Another effect that is often overlooked is the “group velocity anomaly”. Within the photonic band diagram, often at the band edge, there are clearly bands that display smaller slopes than other bands, and are labeled as “flat” or “heavy” bands. The slope of the dispersion curve, $d\omega/dk$, is equal to the group velocity v_g . When the curves flatten out, the PhC has a slow v_g for that frequency range. The DOS is inversely proportional to v_g since the wavevector span dk for a given $d\omega$ increases with the decrease of the curvature. Since v_g is equal to the radiation energy velocity in a PhC, this has the effect of increasing the interaction time between the radiation mode and the PhC, increasing coupling between them, and potentially enhancing optical processes including stimulated emission, and absorption [23]. The amplitude amplification factor for stimulated emission is inversely proportional to v_g . This can lead to a large reduction in the lasing threshold at the band edge where v_g goes to zero or other flat-band regions [24].

2.2 State-of-the-Art Fabrication Techniques

The synthesis of 3D PhCs on the nanometer scale has been the subject of considerable research in the past decade. Three-dimensional PhCs with a full PBG have been fabricated for operation in the microwave and near-infrared (NIR) regimes. However, a complete PBG in the visible light regime has not yet been demonstrated.

2.2.1 Fabrication Issues of 3D Photonic Crystals in the Visible Regime

In order to produce 3-D PhCs in the visible region, it is necessary to synthesize a material with dielectric periodicity in the sub-micron range. If the wavelength of interest is in the visible range of light ($\sim 400 - 700$ nm) then the periodicity must be on the order of $\lambda/2n$, which is $150 - 300$ nm or lower, meaning the minimum feature sizes are in the tens of nanometer. These dimensions complicate processing, since they are at the limits of traditional photolithography, which has proven to be exceedingly difficult for fabrication of 3D PhCs.

The first PhC exhibiting a full PBG was fabricated by Yablonovitch in 1991 [5]. The structure, called “Yablonovite”, was fabricated by mechanically drilling holes into a bulk dielectric material. Three intersecting arrays of holes were drilled at an angle of 35.26° from the vertical into the top of the dielectric material in order to create a fcc structure with a non-spherical lattice basis. A schematic of Yablonovitch’s fabrication method as well as a picture of Yablonovite is shown in Fig 2.7. However, this PhC has millimeter scale feature sizes that exhibited a full PBG at microwave wavelengths, which are substantially longer than the wavelength of visible light. Furthermore, past research work creating the “Yablonovite” structure using focused ion beam [25], X-ray lithography [26] and holographic lithography [27] techniques has proven that this technique would be very difficult to use for forming structures with the small dimensions required for visible wavelength applications. It should be mentioned that lithography

based structures result in insufficient dielectric contrast for a PBG because the resist typically has a refractive index of approximately 1.5-1.6. However, they might prove useful as templates for infiltration of a higher index material.

(a)

(b)

Figure 2.7: (a) Schematic of fabrication of Yablonovite [5]. (b) Picture of Yablonovite [28].

Another method for fabricating 3-D PhCs is to create a “woodpile” structure, as shown in Fig. 2.8. This structure was successfully formed by micro-machining silicon wafers and stacking them up to successfully form a PhC with a PBG in the millimeter range [29]. While this process is desirable because it uses traditional microelectronic techniques, research groups have only been able to fabricate a few layers of this structure. Lin *et al.* [30] constructed a five-layer, 180 line width structure that exhibited a PBG in NIR regime.

Figure 2.8: (a) 3-D Log pile Structure [29]. (b) Silicon 3-D photonic crystal [30].

2.2.2 Fabrication of 3D Photonic Crystals by Colloidal Self-Assembly

In general, the use of micro-fabrication techniques to make 3D PhCs is limited by the fabrication technology and it is tedious and expensive as well. To produce 3D PhCs in the visible region, “bottom-up” colloidal self-assembly (CSA) is a more promising approach as it relies on natural self-assembly forces to grow a 3D structure using spherical building blocks and is thus more cost effective and less time consuming.

In this method, monodispersed colloidal sub-micron spheres are first used to create an artificial opal using self-assembly based on capillary forces, resulting in an fcc lattice of ceramic (e.g., silica) or polymer spheres (e.g., polystyrene and polymethylmethacrylate) that can then be used as a template for making PhCs. A variety of techniques can be used to form this template, ranging from pure sedimentation to forced sedimentation in a confinement cell [31]. Among these, it has been found that vertical deposition utilizing evaporation-induced self-assembly driven by capillary forces [11] produces single-crystal fcc colloidal films with (111) close-packed plane oriented parallel to the substrate, presumably due to the directional nature of crystallization in the meniscus. Certain defects, including point defect, stacking faults, and lattice distortions are consistently observed in colloidal crystals. While point defects can be reduced by

using colloidal spheres with small size polydispersity, stacking faults are found to be inevitable in colloidal crystals [10, 32]. This is because the energy difference between the fcc and hexagonal close-packing (hcp) structure is small, typically 10^{-3} kT per particle in a hard sphere model [33]. Stacking faults has been shown to widen the PBG in fcc structures due to Anderson localization occurring at frequencies near the band edges [10]. Another growth defects that are consistently observed are macroscopic cracks in the colloidal crystals. The growth of the crack in colloidal suspension has been observed in various other studies [34, 35]. However, the microscopic origin of cracking of colloidal crystal is still not well understood.

After growth of the 3D opaline template, a high refractive index material (HRIM) is then infiltrated in the space between the spheres by some form of chemical or physical deposition, followed by removal of the spheres using chemical etching or burnout, thus creating an "inverse" or "inverted" opal. This route is illustrated in Fig. 2.9. As predicted theoretically and demonstrated experimentally in the IR regime, the inverse opal is one of a few known 3D structures that exhibit a full PBG, as previously shown in Fig. 2.4. This structure does require a high RIC in order to obtain a full bandgap, with the minimum RIC predicted to be ~ 2.8 . This method of 3D PhC fabrication was used for the structures described in this thesis. The next section details some of the recent work on PhC fabrication using this method.

Figure 2.9: Schematic outline of the experimental procedure that creates “inverse” opal.

2.2.3 Recent Progress in Colloidal Templating with Infiltration of Semiconductors

It has been reported that a PBG at optical wavelength will arise if the periodic nanostructure has sufficient RIC (≥ 2.8), negligible absorption at optical wavelengths (transparent), appropriate porosity ($\sim 80\%$ air), lattice spacing and lattice symmetry [36]. One suitable class of materials is semiconductors. This has prompted several groups to explore the infilling of semiconductor particles inside opal using vapor phase synthesis, e.g., CdS [37, 38], or InP [39, 40]. However, in most of these early efforts, the interstitial voids of the opal were incompletely filled and resulted in limited effective RI. So far effective RIs between 1.9 and 2.7 have been realized experimentally. In addition, since small clusters of nanoparticles tend to grow inside the opal, the filling was inhomogeneous and consequently, the semiconductor structure collapses after template removal.

the voids without obstructing these channels. To overcome these difficulties, various new approaches have recently been reported [41]. The pros and cons for each method are discussed as follows:

a) Chemical Vapor Deposition

Chemical vapor deposition (CVD) has been used for InP [16, 40], GaP [42] (<32% of void space), and TiO₂ [16] (4% volume fraction). These early attempts failed to achieve full infiltration due to the difficulties to avoid porosity because the film growth tends to fill the interstices in the top few layers. Recently, low pressure CVD has been successfully used for infiltration of Si [12] and Ge [43] with high filling fractions. In this approach, disilane gas has been used as a precursor to uniformly infiltrate the corresponding nanoclusters throughout interior surfaces of the template. This is followed by annealing of the nanoclusters at relatively moderate temperature (e.g., 600°C to obtain polycrystalline Si). This method has been claimed to be one of the best infiltration techniques reported so far that produces conformal films and high infiltration control. Unfortunately, due to the absorption of Si, these structures are inappropriate for wavelengths shorter than 1.1 μm .

In addition, a modified CVD process known as atomic layer deposition (ALD) has also been used for TiO₂ [19] and ZnO [44]. The key distinction between ALD and CVD is that ALD is driven by surface reaction, which highlights the need for surface modifications and flat surfaces. Main concerns with ALD are its slow deposition (0.14 nm/cycle for ZnO) and the use of special organometallic compounds. There is a decreasing interest for ALD in applications that require more than 500 nm thick films.

b) Nanocrystal Sintering

Nanocrystal sintering has been demonstrated for CdSe [45] and TiO₂ [18]. It begins by synthesis of nanocrystals and dissolution of the nanocrystals in a solvent. The nanocrystals are then infiltrated into the voids while slowly evaporating away the solvent. Subsequently, the nanocrystals are sintered at moderate-to-high temperature (e.g., 750°C for CdSe nanoparticles). This approach is extendable to any materials that can be synthesized as colloidal particles. However, it is potentially difficult to obtain complete infiltration of the HRIM due to the condensation of the nanocrystals during sintering. Thus, this method yields a low filling fraction (<50% of void space) and high porosity.

c) Oxide Reduction

This method involves first the formation of semiconductor oxide inside the template by hydrolysis of an organic-based semiconductor gas precursor. After the reduction of the oxide with H₂ at high temperature (e.g., 550°C for reducing GeO), pure semiconductor can then be obtained. This method is still at an infancy stage, and the possibility to extend this method to other semiconductors is still questionable.

d) Electrodeposition

Electrodeposition is emerging as one promising infiltration method. This method has been successfully used to form inverse opals of II-VI semiconductors which exhibit high filling fractions, conformal layers, and good crystalline quality [46-51]. Braun *et al.* [48] first reported the successful use of electrodeposition to construct CdS and CdSe replicas of colloidal crystals with greater robustness and a higher RI than had been achieved with other methods. This method has also been demonstrated in higher RI materials, such as Ge [50] and GaAs [47]. Efforts to extend this method to optically interesting semiconductors with RI greater than 3, such as GaP and Si, are currently in progress.

A critical advantage of electrodeposition over other infiltration techniques is that it can produce dense infiltrated materials within the voids of the template and leads to volume templating of the structure, as opposed to templating of materials around the surface of the template. By placing the template directly on a conductive substrate which acts as the cathode of an electrochemical cell, this bottom-up deposition method improves the possibility of complete infilling of the voids within the template. The electrodeposits nucleate at preferential sites on the substrate around the template and grow to “flood” the void space within the template, giving rise to smooth deposits in which the template finally becomes immersed. As a result, there is insignificant shrinkage of the material during template removal. Furthermore, it can be performed at a temperature well below those that polymeric resists or colloidal templates can withstand without mechanical collapse or chemical alteration. Thus, the resulting 3-D periodic inverted structure will be an exact replica of the initial template and the size of these spherical macro-pores within the film is directly determined by the size of the template spheres used.

It should be highlighted that electrodeposition can be used to prepare materials from aqueous, non-aqueous and molten salt solutions under conditions which are compatible with the template materials. This method also allows fine control over the thickness of the resulting inverted structure through control of the total charge allowed to pass through.

For the work performed here, electrodeposition was employed for the infiltration step. Chapters 4 and 5 will further discuss in detail the use of the electrodeposition as an efficient infiltration method.

2.3 Optical Characterization of Colloidal Crystals

Optical studies of opals as PhCs were launched in 1995 [37, 52]. Bragg diffraction first proposed for atomic crystal structure analysis in X-ray diffraction forms the basis for determining the angular dependent iridescent colors in natural and artificial opaline PhCs as well. The Bragg conditions for the scattering of waves in a periodic lattice are as follows:

1. angle of incidence = angle of scattering
2. the path-length difference = an integer number of wavelength

The wavelength of the Bragg peak λ_B is given by

$$m\lambda_B = 2d_{hkl} \sin \Theta$$

where d_{hkl} is the interplanar spacing between (hkl) planes and m is the order of the Bragg diffraction.

Figure 2.10: Illustrations of (a) Snell's Law and (b) Bragg's Law.

To derive the modified Bragg condition, the reduced angle with respect to the normal at which light travels in the opal is taken into account. Thus, according to Snell's Law of refraction as shown in Fig. 2.10(a),

$$n_1 \sin \theta = n_2 \sin \phi$$

where n_2 is the refractive index of the material and n_1 of the medium of the incoming wave or in this case air, thus $n_2 > n_1$. θ is the angle between the incident wave and the surface normal and ϕ the angle between the ray in the higher index media (opal) and the normal. According to the illustration in Fig. 2.10(b), the Bragg's equation becomes:

$$m\lambda_2 = 2d \cos \phi$$

By combining Snell's Law and Bragg's Law one obtains:

$$\frac{\lambda_B}{\lambda_2} = \frac{\sin \theta}{\sin \phi} = \frac{n_{eff}}{n_{air}}$$

$$m\lambda_B = 2d_{hkl} n_{eff} \cos \phi$$

and Snell's Law yields the relation:

$$\sin \phi = \frac{1}{n_{eff}} \sin \theta$$

$$1 - \sin^2 \phi = 1 - \frac{\sin^2 \theta}{n_{eff}^2} = \cos^2 \phi$$

After rearranging, the modified Bragg's equation thus becomes:

$$\lambda_B = \frac{2d_{hkl}}{m} \sqrt{n_{eff}^2 - \sin^2 \theta}$$

The n_{eff} is the effective refractive index of the lattice.

The position of the resonance is approximated by the modified Bragg's condition. Its position can be varied by changing the lattice parameter d , the angle of incidence θ and the effective index of the refraction n_{eff} . For an fcc lattice, the peak obtained at normal incidence corresponds to first order Bragg diffraction of the fcc (111) planes. The n_{eff} can be determined by an effective medium approach:

$$n_{eff}^2 = n_p^2 V_p + n_m^2 V_m = 0.74n_p^2 + 0.26n_m^2$$

where n_p and n_m are the refractive indices of spheres and surrounding medium, respectively; V_p and V_m are the volume fractions of spheres and surrounding medium, and

are approximately 74% and 26%, respectively for (111) planes in fcc lattice. The interplanar spacing d_{111} is given by:

$$d_{111} = \sqrt{2/3}D$$

where D is the center-to-center distance of the spheres or equivalent to the diameter of the spheres in this case. As the diameter of the spheres increases, the wavelength of light reflected also increases.

Reflection and transmission measurements are commonly used to probe the crystalline structure of PhCs. They are performed by illuminating the surface of the specimen with white light and collecting the reflected or transmitted spectrum. As shown in Fig. 2.11, the optical transmission and reflectance spectra of opals contain diffraction resonances, which appear at the same frequency either as dip or maximum [Fig. 2.11(a)].

Figure 2.11: Typical reflectance and transmission spectra of opal-based PhCs at normal incidence. (b) Angular resolved reflectance measurements [53].

The following parameters of this diffraction resonance can be defined: the resonance frequency ($E_B = \hbar\omega_B$), the full width at half maximum (FWHM), the depth of the transmission minimum and the resolution of the reflectance maximum. Another

important parameter is the overlap of these diffraction resonances recorded at different angles of observation [Fig. 2.11(b)], which can be used to characterize the completeness of the PBG structure.

Approximately 30 layers of colloidal spheres, which can be controlled through the colloidal concentration and sphere size, are needed to approach the infinite crystal limits predicted theoretically [54, 55]. However, disordering [7, 8] and various types of defects [10, 32] intrinsic to the colloidal crystals remains a challenge for the widespread implementation of CSA. A critical size distribution of 6% has been reported beyond which the optical quality deteriorates [8] mostly in the form of increased light scattering and results in diffused light [7]. The main source of scattering has been found to be from point defects.

2.4 Photonic Crystal Lasers

The potential applications of PhCs include zero-threshold semiconductor lasers, single-mode light-emitting diodes, resonant cavity enhanced detectors, highly directional resonant antennas, planar waveguides, filters, and optical limiters. This thesis focuses on 3D photonic crystal lasers.

2.4.1 Basic Laser Theory

a) Stimulated Emission

Lasers are unique sources of light that do not behave like conventional thermal light sources. For atomic systems in thermal equilibrium, emission of light is the result of two main processes: absorption and spontaneous emission of energy. A third mechanism also exists, which is known as stimulated emission. Although not a dominant process in thermal systems at room temperatures, it is crucial to the formation of laser action.

As schematically shown in Fig. 2.12, in stimulated emission, atoms in an upper energy level can be triggered or stimulated in phase by an incoming photon of a specific energy corresponding to the energy difference between the upper and lower states. The incident photon is not absorbed by the atom but it actually vibrates the pair of energy levels with whom its energy coincides. The atom de-excites with the consequent release of photons of the same energy as the incident photon. The stimulated emission process thus results in coherent radiation, since the waves associated with the stimulating and stimulated photons have identical frequency (wavelength), are in phase, have the same state of polarization and travel in the same direction.

Figure 2.12: Stimulated emission.

The key to the above behavior lies in the probability that an optical transition will occur. Not all transitions, upwards or downwards, occur with equal probability. For spontaneous emission of a photon, the probability of occurrence is inversely related to the average length of time that an atom can reside in the upper level of the transition before it relaxes, which is known as the spontaneous lifetime. Typically, the spontaneous lifetime is some tens of nanoseconds. The shorter the spontaneous lifetime, the greater is the probability that spontaneous emission will occur. For some pairs of energy levels in certain materials, the spontaneous lifetime can be of the order of microseconds to a few milliseconds. We call this a metastable state. The probability that a spontaneous transition will take place between these levels is relatively low.

As the probability of spontaneous emission decreases, the conditions which favour stimulated emission are enhanced. If an atom is excited into a metastable state it can stay there long enough for a photon of the correct frequency to arrive. This will stimulate the emission of a second photon, and thus the amplification of light (one photon in and two out) at the expense of spontaneous emission. Unlike the random and incoherent emitted photons from spontaneous emission, all the emitted photons from stimulated emission possess the same wavelength and vibrate in phase with the incident photons. The stimulated emission forms the basis of laser action and gives us the origin of the name **LASER** (*L*ight *A*mplification by *S*timulated *E*mission of *R*adiation).

b) Population inversion

Stimulated emission is the premise of coherent light amplification. In a two energy level system (e.g. a direct bandgap semiconductor), if the stimulated emission is greater than the absorption process, the amplification of coherent light can be expected. Unfortunately, at thermal equilibrium, atoms tend to be at their lowest energy level, thus in all natural situations, the number of atoms at lower energy level is greater than that at higher energy level, which means that there is more absorption than stimulated emission. The number of atoms at each energy level is called population; the population decreases as the energy level increases, which is schematically shown in Fig. 2.13.

Figure 2.13: Schematic diagram of relative population of energy levels.

In order to achieve “population inversion”, i.e., when more atoms are in a higher energy state than the lower one, a four-level system can be used, as schematically shown in Fig. 2.14. Firstly, ground level (E_0) atoms are excited to the 3rd level (E_3) by pump energy (E_0-E_3). Secondly, let the transition between E_3 and E_2 be very fast, so Level 2 (E_2) becomes populated. Let E_1 to E_0 transition be also extremely fast, so Level 1 (E_1) is effectively always unpopulated. Thus, it causes a population inversion between E_2 and E_1 , which is easily sustained without high pump rates. Finally, E_2 is metastable, so laser action occurs between E_2 and E_1 . Most modern semiconductor lasers are four-level system.

Figure 2.14: Schematic diagram of population inversion in the four-level system.

c) Radiative and non-radiative decay: the quantum efficiency

There are two different ways in which decay or recombination that can occur between the conduction and valence bands of the semiconductor: radiative and non-radiative. As discussed in Section 2.4.1a, the three radiative recombination processes important in semiconductor lasers are absorption, spontaneous emission, and stimulated emission. For full radiative decay, the quantum efficiency (QE) is 100%, which is rarely the case. The QE is defined as the fraction of emission processes in which emission of light is involved:

$$QE = \frac{\Gamma_{rad}}{\Gamma_{rad} + \Gamma_{nr}}_{ad}$$

where Γ_{rad} is the radiative decay rate and Γ_{nrad} the non-radiative decay rate.

$$\Gamma_{tot} = \Gamma_{rad} + \Gamma_{nrad}$$

where Γ_{tot} is the total decay rate.

In non-radiative recombination, the energy is released as phonons, more commonly known as heat. Non-radiative recombination occurs when the energy difference between the levels is very small, such as those in semiconductors featuring indirect bandgap, and these typically occur on a much faster time scale than radiative transitions. Large non-radiative transitions do not occur frequently because the crystal structure generally can not support large vibrations without destroying bonds (which generally doesn't happen for relaxation). If non-radiative decay rate is too high, no material will lase.

d) Laser components

The basic requirements of any laser are similar, they all comprise:

- an **active medium** (gain medium) with a suitable set of energy levels to support laser action. It can be a solid, a liquid, or a gas. In a neodymium YAG (Nd:YAG) laser, the laser medium is a rod of yttrium aluminium garnate (YAG) containing neodymium ions. In a laser diode, it is a thin layer of semiconductor material sandwiched between other semiconductor layers.
- a source of **pumping** energy in order to excite the active medium and establish a population inversion. For solid laser media, the pumping is usually achieved by irradiation with an intense light source, i.e., optical pumping. Laser diodes are pumped by passing an electric current across the junction where the two types of semiconductor within the diode come together.
- an **optical cavity** to introduce optical feedback and so maintain the gain of the system above all losses. In order to sustain stimulated emission for light amplification,

photons need to be confined in the system to allow the number of photons created by stimulated emission to exceed all other mechanisms. This can be achieved by bounding the laser medium between two mirrors. This forms an optical resonant cavity in which one mirror is totally reflecting and the other partially reflecting. The reflectivity of the partial reflector is normally between 10 to 90 %. This is necessary to ensure that some laser light can escape and provide useful optical power.

e) Laser action

A laser medium positioned between two mirrors is schematically shown in Fig. 2.15. The cavity provides a method of optical feedback such that the stimulated beam is made to pass backwards and forwards several times and it stimulates further emission as it goes. Stimulated photons can bounce back and forth along the cavity, creating more stimulated emission as they go. Photons which do not travel along the optical axis and which are not of the correct frequency are lost. When the number of photons produced by stimulated emission exceeds that produced randomly, the system gain exceeds the losses and laser action can be sustained.

Figure 2.15: Schematic diagram of the basic components of a laser system.

2.4.2 Motivation and Recent Progress in Photonic Crystal Lasers

In semiconductor lasers, spontaneous emission is the major sink for threshold current, which must be surmounted in order to initiate lasing. Low threshold lasing has been realized in vertical cavity semiconductor lasers (VCSELs), but VCSELs can only be made in a select few laser materials.

Based on the light enhancement discussed in Section 2.1.3, ultralow threshold photonic crystal lasers may be classified into two categories: one utilizing a particular point in the BZ where v_g is small, and the other in a PhC microcavity. However, this dream of achieving a thresholdless laser has been postponed by more than a decade due to the difficulty of fabricating 3D PhCs with a complete PBG to interact with the electromagnetic waves in the visible range. Instead, a number of prototype 2D photonic crystal lasers have been designed and tested.

Figure 2.16 depicts two distinct types of micro-lasers. The first shown in Fig. 2.16 (a) is a “band edge micro-laser” in which light emission from electrically injected electron-hole pairs in a multiple quantum well array occurs near the band edge of a 2D PBG. It has been predicted that strong feedback and memory effects accompany collective light emission near the photonic band edge [56]. Near a true 3-D photonic band edge, this would lead to lasing without a conventional distributed feedback (DFB) optical cavity [57]. A precursor to this effect is seen in the 2D band edge micro-laser in which lasing occurs preferentially at the 2D photonic band edge [58] even though the emission from the active region has a broad frequency distribution.

The second type of micro-laser shown in Fig. 2.16(b) utilizes a localized state defect mode as a laser cavity [59]. Here, the localized electromagnetic mode is associated with a missing hole in the 2D triangular lattice. This particular structure has been proposed as the “world’s smallest micro-laser” with a cavity volume of $0.03 \mu\text{m}^3$. Spontaneous emission from electron-hole pair recombination in the multiple quantum

well active region occurs preferentially into the localized state. Since the photonic crystal is two-dimensional, spontaneous emission is not exclusive to the lasing mode. This results in a finite pumping threshold before lasing occurs.

Figure 2.16: Architectures of 2-D photonic crystal micro-lasers. (a) Band-edge micro-lasers [58]. (b) Defect mode micro-laser [59].

Other investigations report band-edge DFB lasing for an ordered colloidal suspension in a mirror-aided DFB cavity, band-edge amplified spontaneous emission for semiconductors embedded in 3D PhCs, and band edge lasing for cholesteric liquid crystals.

Chapter 3:

PROCESS DEVELOPMENT OF COLLOIDAL SELF-ASSEMBLY

3.1 Introduction

For this thesis, a vertical convective self-assembly method [11] was employed to fabricate 3D, single-crystal, face-centered-cubic (fcc) colloidal crystal films with the (111) close-packed plane oriented parallel to the substrate. Despite its popularity, these colloidal films often display macroscopic defects: growth bands and cracks. The growth bands consist of alternating thinner and thicker film, which results in uneven deposition along the growth direction. In addition, this method is limited to smaller colloidal spheres that sediment more slowly than the solvent (water in this case) evaporates. Recently, many approaches were developed for preventing sedimentation of large spheres in the suspension during the deposition process [13, 60-65]. These studies are concerned mainly with the final crystal quality, rather than the crystal growth process itself. The vertical deposition method is essentially developed based on the comprehensive work of Nagayama's group [66] on continuous convective assembling of fine particles into two-dimensional (2D) arrays on horizontal solid surfaces. They have illustrated that the main factors governing the array ordering are the attractive capillary forces and the convective transport of particles towards the ordered region [67]. At the same time, they also explained the mechanism of stripe formation on a horizontal solid surface during droplet evaporation to be a consequence of competition between the droplet's surface tension, the wetting film's surface tension, and the friction force at the contact line [68]. While colloidal crystal growth characteristics on horizontal surfaces are relatively well-understood, an extension

of such understanding to vertical surfaces is clearly lacking. Furthermore, although colloidal crystals contain large amounts of defects and disordering, as a consequence of the very small entropy difference between fcc phase and hexagonal close-packed (hcp) phase [33], there has been limited studies on improving their crystalline quality [62, 69]. There are only a few reports on the role of evaporation temperature on crystalline quality and its effect on optical properties [62, 70].

This chapter presents a study on the band formation during 3D colloidal crystal growth from vertical deposition, and analyzes the macroscopic growth imperfections in terms of the dynamics of convective mass transport at the meniscus. A correlation of optical response in different growth zones with the quality of the structures is also provided. Understanding the origin of macroscopic non-idealities should provide guidelines for the conditions to achieve high quality colloidal crystals over large areas.

3.2 Experimental Procedure

The vehicle for this study is 3D colloidal crystallization of polystyrene (PS) latex spheres on a silicon substrate by vertical deposition. Monodispersed PS spheres dispersed in water were synthesized following the micro-emulsion method [71]. Sub-micrometer PS spheres with diameter 148 nm (polydispersity of 7.4%) were used in the experiment. Colloidal crystals were deposited on a silicon wafer using the widely-used convective self-assembly technique [11] with the wafer inserted vertically into a vial containing the colloids. The vial is kept in a temperature-controlled oven with controlled ventilation. The colloidal crystals were fabricated at 50°C and 90°C. Colloids with volume fractions of 2.96%, 0.59%, 0.30%, 0.15%, and 0.10% were used.

To examine the formation of growth patterns and the photonic lattice of the colloidal crystals, the samples produced under different experimental conditions were observed under a field-emission scanning electron microscope (FESEM) (JEOL JSM-

6340F). The optical properties of these colloidal crystals were studied by means of optical reflectance measurements using a UV-visible spectrometer (Shimadzu UV-2501PC).

3.3 Growth Imperfections in 3D Colloidal Self-Assembly

Typical growth patterns of colloidal crystals built up from diluted PS latex spheres at an evaporation temperature of 90°C are shown in Fig. 3.1(a). The films are not continuous and are separated into many individual ‘grains’ and gaps (i.e., cracks).

Figure 3.1: (a) Schematic of a typical colloidal film with three growth zones, (b) Colloidal film of 0.15 vol.% grown at 90°C, showing bands and crack orientation. Interfaces between (c – e) Zone II and III, and (f-h) Zone I and II for different volume fractions.

Three growth zones can be observed. The growth begins with the formation of bands parallel to the liquid/substrate interface (Zone I). As shown in Fig. 3.1(b), the film in this region is thin and exhibits alternating bands of deposited and empty regions. In general, the area of deposited bands widen with concentration at the expense of the empty regions [see Figs. 3.1(c) – (e)]. Further along the growth direction, the undulation ends and the film becomes translucent and more uniform in thickness, although very fine cracks running parallel to the growth direction can be seen (Zone II). With further growth, the film becomes thick, white and opaque with cracks separated further apart (Zone III) [see Figs. 3.1(f) – (h)]. In this region, adhesion to the substrate becomes very poor, and the film flakes off into rectangular pieces. For higher concentrations (e.g. 2.96 vol.% and 0.59 vol.%), Zone I is either very short-lived or not visible at low magnifications.

The relative extent of the growth zones is a function of colloidal concentration. The length of each zone was measured and the corresponding concentration changes in the colloidal suspension during evaporation were calculated based on the volume of solvent lost to evaporation, assuming negligible solute loss from crystallization. The results are tabulated in Table 3.1.

Table 3.1: Length of different zone for each concentration at 90°C.

Initial vol. %	Length (mm)			Total length (nm)	vol. %	
	I	II	III		at end of I	at end of II
0.06	10.0	4.5	-	14.5	0.19	-
0.10	9.0	1.5	5	15.5	0.24	-
0.15	4.5	3.5	4.5	12.5	0.23	0.41
0.30	0.5	4.5	7.0	12.0	0.31	0.51
0.59	-	1.0	12.5	13.5	-	0.64
2.96	-	-	15.0	15.0	-	-

The data suggests that the tendency for the colloidal suspension to form bands is affected by its concentration, which increases during crystallization. The uneven growth and banding of the film occurs at low colloidal concentrations, approximately <0.31 vol.%, while uniform growth (Zone II) takes place between 0.31 and 0.64 vol.%.

Figure 3.2 presents typical micrographs of the observed crack pattern. The cracks observed in the film vary in each zone. In Zone I, the cracks intersect hexagonally, resembling the equiaxed grains of an unworked metal. Further down the film, there is a transition from hexagonal cracks to elongated cracks. Here, in Zone II, the cracks are parallel to each other and to the growth direction (longitudinally). When examined closely, these cracks are intersected by other perpendicular (transverse) cracks which break the strips of the compact spheres into rectangular blocks or ‘grains’ (secondary branching). The longitudinal cracks are mainly continuous, although some may terminate, thus merging two rectangular blocks into one.

Figure 3.2: Crack patterns at different zones: (a) hexagonal cracks, (b) parallel cracks, and (c) rectangular blocks.

3.3.1 Growth Bands

The growth band is postulated to be a consequence of the dynamic balance of surface tension forces due to the oscillation of the contact angle with time, which results in a “stick-slip motion” of the meniscus growth front.

At the initial stage of growth, the colloidal solution rides up to the substrate, forming a concave meniscus at the substrate-suspension-air contact line, which is at a short distance above the bulk liquid surface. At the contact line, the cosine component of the suspension's surface tension, $T_s = \gamma_o \cos \theta$, is in competition with the wetting-film's [68] surface tension, γ_f . At this point, it is the deformation of the meniscus which accommodates the growing gap between the contact line and the suspension level.

As the solution recedes slightly upon evaporation, the thickness of the wetting film starts to shrink. A flux of spheres is transported towards the meniscus and generates a capillary force to assemble the spheres, forming a thin layer of ordered spheres on the substrate. At this stage, γ_f is greater than T_s ($T_{s1} < \gamma_f$). As the solution recedes further, the wetting film becomes thinner. Correspondingly, T_s increases with the decrease of the wetting angle, θ . When T_s exceeds γ_f , the contact line "slips" downwards to a new, lower level. At this point, T_s is again lower than γ_f ($T_{s3} < \gamma_f'$). The stick-slip motion [68] repeats itself for some distance as the film grows and the fluid recedes. Figure 3.3 shows the schematic of one cycle of stick-slip motion.

Figure 3.3: Schematic of one cycle of stick-slip motion.

γ_f' should be higher than Ts_3 since the stick-slip motion would bring the contact line to a level lower than its equilibrium. However, the excessive “sticking” force may be affected by the presence of an initial thin layer deposited before slipping, which could act as a source of friction at the contact line. The fact that the banding of the film diminishes as growth proceeds suggests that this modification is a decrease in magnitude, i.e., $\gamma_f' < \gamma_f$.

In addition, the distance of this slip should also be taken into consideration. If the slip occurs over a distance longer than the width of the thin layer already deposited, this deposited layer becomes an isolated band of spheres, as illustrated in Fig. 3.1(b). In between islands, we would thus see regions of substrate with no spheres. Finally, γ_f would be progressively modified by the presence of increasingly thicker films of deposited spheres. In effect, the interface between the colloidal suspension and the substrate surface would be disrupted by the deposited films of spheres. The distance of the slip will also be reduced as growth proceeds, i.e., the film growth process becomes smoother so that the stick-slip motion of the meniscus would cease at a particular critical film thickness deposited.

3.3.2 Crystalline Quality

Figure 3.4 shows SEM surface images in different growth zones of the colloidal crystals with intermediate initial concentration (0.15 vol.%) prepared at 90°C. There are no major differences between the ordering of the spheres in all cases, but the crystalline quality deteriorates in terms of packing density as growth proceeds. A recent report by Braun *et al.* [72] which shows that colloidal crystals may be non-close-packed with a pore volume of 4 – 15% larger than the expected for close-packed fcc crystals complements our observations. Here, we infer that the crystalline quality depends on the colloidal concentration and evaporation rate (which causes a change in colloidal concentration).

Figure 3.4: Ordering in three zones observed in the film of 0.15 vol.%, grown at 90°C: (a) Zone I, (b) Zone II, (c) Zone III.

The dynamic surface tension forces proposed in the previous section is extended here to evaluate the crystalline quality of the colloidal crystals. In the beginning of growth, the solution recedes gradually, which leads to a decrease of wetting angle, θ as well as the flux and accumulation of colloidal spheres as a result of a large capillary force. A small region of suspension near to the meniscus is now depleted of spheres due to the relatively low initial concentration. The capillary force at this stage is sufficient to assemble the spheres in close proximity into a well-ordered close-packed structure in Zone I. On the other hand, in Zone III, the increase in concentration upon evaporation leads to a larger wetting angle, θ . The initial thin layers deposited in Zone I and II may also act as a source of friction and further increase the angle θ . This in turn lowers the capillary force for assembling the spheres, thus the poorer packing density. Furthermore, there is insufficient time for the spheres to settle to the most favorable lattice sites due to the rapid evaporation, i.e., the flux of spheres in the region near to the meniscus is too high for array formation, hence a poorer crystalline quality.

3.3.3 Growth Cracks

Under higher magnification (Fig. 3.5), it was noted that the crystalline order on the top layer of the colloidal film resembles the (111) plane in fcc structure. The crystalline order is preserved across the crack and the boundaries mirror each other, indicating that the different ‘grains’ are not the result of independent nucleation but rather post-growth cracking. This implies that prior to cracking, the initial domain size of colloidal crystallinity is much larger, estimated to be on the order of 50 – 100 μm wide, consistent with other reports on similar methods [11, 62]. If cracks had not formed, this would have been a good large colloidal crystal with long-range ordering.

Figure 3.5: The orientation of nanospheres remains unchanged across cracks.

For the hexagonal cracks at the starting regions (Zone I), the preserved orientation of spheres across the crack edges suggests that these cracks are the result of fractures caused by the volume shrinkage of wet films during the drying process. At the starting edge of the film, for low concentrations, the spheres are far apart. Since the solution has not receded very much, the supply of water to this region at this time is high. As the spheres attract each other to form ordered arrays, therefore, there is a large amount of water in between them even though evaporation continues, and their separation is larger

than in a dry film. The stick-slip motion of the meniscus results in the abrupt loss of the supply of water required to maintain this inter-sphere water film as water is lost to evaporation. As drying and further compaction occurs, the spheres are pulled closer together by the capillary force as the water film between them disappears. Here, the capillary force acts in all directions so that the resulting cracks form hexagonal networks with no propagation preference in any direction.

The hexagonal cracks then elongate so that the crack-edges parallel to the growth direction become longer. The gravitational force, which may impart a surface-tension induced shear force, could have promoted the elongation in the vertical growth direction. This elongation causes the domains to grow more strip-like, ultimately becoming long, narrow bars parallel to the direction of film growth. Further down the grown film, recession of the fluid becomes smoother, and the colloidal solution is able to maintain continuous contact with the growing front. This means that the supply of colloidal spheres to the growth film is uninterrupted. This inhibits the drying film from forming cracks in the direction perpendicular to the growth direction, because as spheres move closer, more spheres are supplied to ensure that the vacated volume is occupied. This supply however, does not happen for cracks in the direction of growth, which are caused by compaction perpendicular to growth. These cracks therefore propagate throughout the film, in the direction of growth, as observed.

A linear thermal expansivity (CTE) differential between the substrate and the film may also be a contributor to the cracks. However, from the calculations of the magnitude of the differentials, using known CTE of silicon and polystyrene, this cannot be a significant contributor. From the micrographs of the films taken at 90°C, the crack/film lengths ratio was found to be one order of magnitude higher taken along the length and width of the rectangular blocks.

3.4 Guidelines to Reduce Growth Imperfections

The presence of growth bands and cracks in colloidal films produced from vertical deposition is not desirable from the perspective of device fabrication. Some possible means of their reduction is presented here.

The preceding sections deduce that growth band arises as a result of dynamic competition between surface tension forces at the contact line. For self-assembly with lower colloidal concentration, the cosine component of the suspension's surface tension is higher due to a smaller wetting angle, which leads to band formation. When this surface energy is close to or higher than that of the substrate, wetting is poor and recession of meniscus takes place in steps upon evaporation. The surface tension of the solution decreases in magnitude with temperature and the addition of surfactant [73], while increases with concentration of the colloidal solution [74]. Therefore, growth bands may be eliminated by proper selection of the types and amount of surfactant, volume fraction of colloidal solution and temperature to reduce the surface tension of the colloidal solution in order to improve its wetting on substrates. Alternatively, this can also be achieved by chemically functionalising the substrate surface. For the subsequent work in this research, the substrates were chemically treated with a "Piranha" solution (a 3:1 mixture of concentrated sulfuric acid with 30% hydrogen peroxide) to obtain a hydrophilic surface.

On the other hand, the crystalline quality of the colloidal crystal is believed to be related to the magnitude of the capillary force, which is again a function of the surface tension forces and wetting angle of the meniscus at the substrate-suspension-air contact line. Based on the conventional wisdom that crystalline quality deteriorates when a fast deposition rate gives self-assembly insufficient time to work [62, 75], a compromise between the supply of colloidal spheres at a region near to the meniscus and the evaporation rate is important for the growth of crystal with good crystalline quality.

The formation of hexagonal cracks arises mainly from abrupt water loss, with minor contribution from the CTE mismatch. Parallel cracks in turn follow from the propagation of cracks originating in the hexagonal regions. Therefore, the elimination of further densification or shrinkage in the initial regions of the film is crucial for crack reduction in the film. A suitable approach to reduce cracks is to dry the film slowly in a humidity chamber or wet environment to reduce the evaporation rate. This allows the spheres to reposition themselves more tightly as drying occurs, possibly reducing the extent of hexagonal crack formation and increasing its domain size. Once a thin band of ordered film has been deposited, spheres transported to the growth front subsequently would find well ordered sites to deposit themselves. From this point onwards, growth rate may be accelerated without the formation of parallel cracks. For all the experiments in this research, the deposition has been performed in an oven controlled under mild ventilation. The actual value of the relative humidity is unknown though, since it depends on the relative volume of the colloidal solution and the oven used.

3.5 Correlation of Optical Properties to Crystal Quality

Optical reflectance measurement was carried out to evaluate the postulations above. The reflection spectra obtained at normal incidence to the colloidal films prepared at two different temperatures are shown in Fig. 3.6. For the optical setup used in this study, the diameter of the illumination beam was approximately 5 mm. However, in Zone I, the width of the deposited regions is <1 mm and they are well-separated from the empty regions. Therefore, optical reflectance from Zone I could not be resolved. As such, the measurements were taken on Zone II or Zone III or a combination of these, depending on their relative proportion within each sample. For example, the spectrum was collected on Zone III for colloidal films with initial volume fraction of 2.96%.

A reflection peak corresponds to first-order Bragg diffraction of the fcc (111) planes can be observed in all samples. It can be seen that the reflectance peak is more distinct for samples prepared at 50°C ($\Delta\lambda/\lambda_{\text{peak}} \approx 0.09$) than at 90°C ($\Delta\lambda/\lambda_{\text{peak}} \approx 0.13$). The broadening is a result of increased light scattering from disorder and various types of defects in the colloidal crystals. This shows that an evaporation temperature of $\sim 50^\circ\text{C}$ should provide sufficient time necessary for self-assembly to work and results in better crystalline quality for the range of colloidal concentrations used in this study.

Figure 3.6: Optical reflectance of colloidal films prepared at different concentrations at (a) 90°C and (b) 50°C. The spectra were measured in the [111] direction.

Interestingly, the reflectance peak position shifts toward longer wavelength with colloidal concentration (Fig. 3.7), which implies lattice distortions [72]. Since colloidal concentration increases as growth proceeds, the same can be conjectured from growth zones I to III along the growth direction. In principle, the reflectance peak should stabilize at a fixed position; in this case ~ 346 nm calculated using the modified Bragg's condition for a true close-packed structure. This suggests that a true close-packed structure can only be obtained at 0.1 – 0.15 vol.%, in accordance with the deterioration of packing density during the self-assembly process described in the previous section. It is believed that the

degree of the lattice dilation can be attributed to the capillary force, which is determined by the curvature of the meniscus, i.e., wetting angle θ . For low colloidal concentration, similar to the beginning of growth, there is a strong physical confinement of the spheres within the thin meniscus and the resultant high capillary force is sufficient to assemble the spheres into a well-ordered close-packed structure. On the other hand, the increase in concentration leads to an increase in θ . This in turn lowers the capillary force within the relatively thicker meniscus that provides weaker physical confinement for assembly, thus the poorer packing density.

Figure 3.7: Optical reflectance peak position changes with colloidal concentration.

3.6 Chapter Summary

In this study, the growth imperfections in 3D colloidal crystals produced from vertical deposition manifested as growth zones were found to depend on colloidal concentration. This growth pattern can be explained by the competition between the surface tension forces at the substrate-suspension-air contact line, which results in a “stick-slip” motion. The packing density deteriorates upon evaporation, which may be controlled by the

colloidal sphere supply at a region near to the meniscus and the evaporation rate. Furthermore, we demonstrate that the cracks observed in the initial regions of growth were the result of the presence of water films in between spheres immediately after assembly and the subsequent loss of this water film upon drying. Beyond this region, the cracks tend to follow the growth direction of the film, which can be explained by the continuous supply of spheres to the growth front that made up for shrinkage in this direction. We deduce that substrate wettability, colloidal concentration, temperature, and humidity are crucial requirements for producing the highest quality colloidal crystal films. Specifically, it was found that colloidal crystals with good crystalline quality can be achieved on cleaned hydrophilic substrates over areas as large as $\sim 2 \times 1 \text{ cm}^2$ at colloidal concentrations ranging from 0.10 – 0.15 vol.% at a temperature of $\sim 50^\circ\text{C}$ under controlled ventilation. Figure 3.8 shows the crystalline quality of a typical 3D PS colloidal crystal film grown using the optimum conditions deduced above and its corresponding optical reflectance.

Figure 3.8: Ordering (a) and optical reflectance (b) of a 3D PS colloidal crystal (sphere diameter $\sim 148 \text{ nm}$) prepared under the optimum growth condition of 0.10 vol% at 50°C . The arrow at $\sim 290 \text{ nm}$ indicates the point where PS starts to absorb, which does not affect the optical properties of the colloidal crystal above $\sim 300 \text{ nm}$.

Chapter 4:

INHERENTLY OPTICALLY ACTIVE 3D PHOTONIC CRYSTALS BY ELECTRODEPOSITION

4.1 Introduction

Photonic crystals (PhCs) offer rich possibilities for light manipulation to achieve high extraction efficiency light-emitting diodes and low threshold lasers. The study of light generation and propagation in PhCs requires the presence of light sources embedded in PhCs with a photonic bandgap (PBG) overlapping with the emission spectrum. Several groups have incorporated light-emitting components (e.g. semiconductors quantum dots [38], dye molecules [76], rare earth ions [77], etc.) into the body of opals or decorated over a small fraction of the opal surface. However, the refractive index contrast (RIC) of such PhC systems is weak, thus limiting the associated PBG effect on modifying light emission. Recently, inhibition of spontaneous emission from ZnSe-coated CdSe quantum dots has been demonstrated in strongly photonic titania inverse opal [78]. Nevertheless, the incorporation of emitters in passive PhC could lead to degradation of the emitters due to interaction with the dielectric backbone.

On the other hand, there have only been a few reports on the fabrication of an emissive PhC, i.e., the emitters and the dielectric backbone constituting the opal body are one and the same materials [79]. This simplifies the fabrication process without the need of introducing external emitters and avoids the reduction of RIC. This chapter reports the fabrication of two inherently optically active 3D PhCs, (i) ZnO inverse opal (ii) and the lattice-matched ZnO-polystyrene (ZnO-PS) hetero-opal. As a direct and wide electronic

bandgap (3.3 eV) semiconductor, ZnO is a widely used optoelectronic material due to its potential as an efficient UV light source. Although its refractive index (~ 2.45) is too low for formation of a complete PBG in a face-centered cubic (fcc) lattice, it is high enough to produce a pseudogap (stop gap).

4.2 Recent Advances in ZnO Photonic Crystals

Synthesis and self-assembly of monodispersed ZnO colloidal spheres[80] has also been reported to produce 3D ZnO PhCs. Unfortunately, the uniformity of the ZnO spheres is far inferior to silica or polystyrene colloidal spheres and their refractive index is relatively low compared to bulk ZnO (due to the porous polycrystalline substructure). As such, the PBG effect in these opals is weak.

Later, ZnO-infiltrated opals produced by spray pyrolysis [81], chemical deposition [82], and sol-gel [83] have been reported. However, the RIC of such infiltrated opal is weak and the infiltration introduces significant disorder into the PhCs.

Recently, ZnO inverse opals have been fabricated by colloidal templating with gas-phase deposition techniques, such as atomic layer deposition (ALD) [44] and chemical vapor deposition (CVD) [84]. The main concerns with ALD are its slow deposition (0.14 nm/cycle for ZnO) and the use of special organometallic compounds. Meanwhile, both methods involve complex processes and require the use of pressure and thus more costly infrastructure.

Fabrication of ZnO inverse opals has, in fact, first been demonstrated with electrodeposition [49], but optical studies were not reported at the time. An exciting feature of electrodeposition is that it allows complete infiltration of the voids since the growth proceeds from the bottom to the top of the template. Furthermore, this method is simple and highly cost effective, since it does not require vacuum and has a high deposition rate.

In this work, ZnO was infiltrated into opals by electrodeposition. At almost the same time, Yang et al. [51] have independently obtained ZnO inverse opals by electrodeposition, but the pseudogap in these samples was far apart from the emission spectrum of ZnO in the red (large spheres were used). Moreover, their work was focused on the electronic structure and optical properties [85, 86] of the structure instead of the PBG effect.

4.3 Electrodeposition of ZnO

4.3.1 Principles of Electrodeposition

Figure 4.1 shows the schematic diagram of the experimental setup for galvanostatic electrodeposition. There are a few components: electrolyte containing metal ions, electrodes (substrate and counter electrode), and current or voltage source. When a current flows through the electrodes, a charge transfer reaction takes place at the electrodes and results in deposition.

Figure 4.1: Schematic representation of a simple galvanostatic electrodeposition setup.

Quantitative aspects of electrochemistry are governed by Faraday's laws of electrolysis:

(1) Faraday's 1st Law

The total amount of chemical change produced by an electric current is proportional to the total charge passing through the electrolyte.

(2) Faraday's 2nd Law

The quantity of substance liberated in the electrolysis is proportional to its weights for a given quantity of electricity.

Mathematically, Faraday's laws are summarized by:

$$m = \frac{QM}{zF} = \frac{I}{zF} Mt$$

where m is the mass of the substance produced at the electrode, $Q = I(\text{Amperes}) \times t(\text{seconds})$ is the total electric charge passed through the solution, z is the valence number of ions of the substance (electrons transferred per ion), $F = 96\,485 \text{ C/mol}$ is the Faraday constant, and M is the molar mass of the substance. The term, I/zF will give the growth rate of the electrodeposits.

Simply, an electrochemical reaction involves transport of ions to the substrate, followed by a charge transfer at the interface and finally transport of the products back to the bulk material [87]. The required deposition current density is derived from the knowledge of the faradaic efficiency and maximum permissible growth rate for a good crystal. The latter can be obtained from the available crystal growth data, whereas the former is to be obtained from a series of preliminary deposition experiments.

4.3.2 Electrodeposition Growth Mechanism of ZnO

Unlike metals, the electrochemistry of semiconductors can be very complex. The window for stoichiometric deposition is typically very narrow. Fortunately, thanks to the large free energy of formation of ZnO (1.64 V), the electrodeposition of ZnO has been successful.

ZnO films can be electrodeposited via two different routes, namely the nitrate route and (b) oxygen route. The former was used in this work.

Starting from a precursor solution containing both Zn^{2+} and NO_3^- ions, the electrodeposition of ZnO proceeds cathodically [88]. The first electrochemical step is the electrochemical reduction of NO_3^- ions:

This reduction reaction causes an increase in the pH close to the electrode such that metal deposition does not take place. On the other hand, the metal ion deposits in the form of a hydroxide on the cathode and spontaneously dehydrates into ZnO:

The overall expression of the reactions for the formation of ZnO is therefore:

4.4 Fabrication of ZnO Photonic Crystals

4.4.1 Experimental Procedure

(1) Fabrication of Opal Templates

Colloidal polystyrene (PS) spheres with diameter, $D = 200$ nm to 300 nm (polydispersity $\sim 6\%$) were synthesized following the emulsion polymerization method [89]. The PS opaline film was then deposited on an indium-tin oxide (ITO) coated glass substrate at 50°C by the vertical convective self-assembly technique [11]. The resulting PS-opal had an average thickness of $20\ \mu\text{m}$ with an area of $1\ \text{cm}^2$, i.e., ~ 100 layers of PS spheres with typical optical reflectance of $\sim 50\%$.

(2) Wetting of Opal Templates

The as-synthesized PS spheres were hydrophobic, thus blocking the aqueous precursor solution from infiltrating the interstices of the PS templates. To improve their wettability,

the templates were treated with a solution containing 5.2 g of polyethylenimine in 100 ml of ethanol.

(3) Infiltration with ZnO

ZnO was infiltrated into the voids of the opaline template by a simple two-electrode galvanostatic cathodic deposition method using 0.1 M aqueous zinc nitrate electrolyte maintained at 65°C without stirring [88]. The cathode was an ITO substrate (30 – 60 Ω/cm^2) with PS-opal deposited on top of it, while a zinc sheet was used as active anode. The electrodeposition was performed at a cathodic current density ranging between 5 to 20 mA/cm^2 . Homogeneous ZnO films were also deposited under the same conditions as reference samples.

(4) Removal of Templates

The template was removed by heating at 600 °C in air for 1 h, forming a macroporous 3D ZnO inverse opal.

(5) Characterization

The quality of the ZnO PhCs was examined by a field-emission scanning electron microscopy (FESEM) and an optical microscope (OLYMPUS). The presence of PBG in these structures was evaluated by means of optical reflectance measurements using a UV-visible recording spectrophotometer (Shimadzu, UV-2501PC) recorded in the direction perpendicular to the sample surface. The (atomic) crystal structure was evaluated by X-ray diffraction measurements using monochromatic Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) operated at 40 kV and 40 mA flux. The photoluminescence (PL) spectra were acquired at room temperature under the excitation by a 325 nm line of a continuous wave 30 mW He-Cd laser, a 0.55 m spectrometer, a PMT detector, and a lock-in amplifier. The collection was performed in the normal direction from the sample surface.

4.4.2 ZnO Inverse Opal

The top-view of ZnO inverse opals with $D = 200$ nm obtained at various cathodic current densities are shown in Fig. 4.2. As shown in Figs. 4.2(a) and (b), the ZnO films prepared at cathodic current densities of 5 mA/cm^2 and 10 mA/cm^2 are smoother with longer range of ordered pores. On the other hand, the macroporous films deposited at cathodic current densities of 15 mA/cm^2 [Fig. 4.2 (c)] were found to consist of nodular structures. The morphology of the macroporous films resemble that of their corresponding electrodeposited homogenous films (results not shown).

Figure 4.2: Top view of ZnO inverse opals with $D = 200$ nm prepared at (a) 5 mA/cm^2 , (b) 10 mA/cm^2 , (c) 15 mA/cm^2 , and (d) 10 mA/cm^2 at high magnification.

The enlarged micrograph in Fig 4.2 (d) reveals that the air spheres in ZnO inverse opal are well ordered in a close-packed structure with center-to-center distance within the size disparity of the PS spheres used, indicating a direct replica of the PS-opal template. The three dark holes inside each sphere correspond to the air spheres at the underlying layer. The solid frame surrounding the air spheres suggests the effective infilling of ZnO by electrodeposition.

Figure 4.3 shows the cross-section of a typical ZnO inverse opal with a thickness of more than 30 layers, which is sufficient for optical measurements. Opals of approximately 30 layers thick are needed to approach the infinite crystal limits predicted theoretically [54, 55].

Figure 4.3: Cross-section of ZnO inverse opal fabricated using a PS template with $D = 200$ nm. The ZnO was deposited at 10 mA/cm^2 followed by firing in air at 600°C .

The x-ray diffraction patterns of the electrodeposited films prepared at cathodic current densities from 5 mA/cm^2 to 15 mA/cm^2 show that the electrodeposited ZnO

inverse opals have a hexagonal wurtzite structure (see Fig. 4.4). The preferred (101) orientation was weakened with the increase in current density. The same behavior was observed in the as-deposited homogeneous films. These results are consistent with an early report [88] on galvanostatic electrodeposition of ZnO films for the same range of current density values. While the as-grown ZnO films from ALD [44] and CVD [84] were amorphous, the as-deposited ZnO films prepared in this work were crystalline.

Figure 4.4: X-ray diffraction patterns for electrodeposited ZnO inverse opals prepared at different current densities.

The crystallite size can be obtained by the calculated full-width-at-half-maximum (FWHM) of the diffraction peaks using the Scherrer equation,

$$\text{Average crystallite size, } T = [0.9 \cdot \lambda / (B \cdot \cos \Theta_B)]$$

where T is the average crystal size ($\text{\AA}$),

λ is the wavelength of the X-rays ($\text{Cu K}\alpha = 1.54 \text{ \AA}$),

B is the observed FWHM for the material in radians, and

Θ_B is the Bragg's angle in degrees.

The Scherrer equation is valid by assuming that only a single crystallite size is present in the film. With an increase in cathodic current density, the crystallite size decreases slightly from 27 to 23 nm in both ZnO inverse opals and their respective homogeneous films. This shows that the heat treatment for template removal did not cause significant sintering and grain growth.

The unit-cell parameters can be obtained by the calculated lattice spacing for a (hkl) plane, d_{hkl} using the following relationship,

for hexagonal crystals, $a = b \neq c$,

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + hk^2 + k^2) + l^2\left(\frac{a}{c}\right)^2}}$$

The unit-cell parameters were found to be $a \approx 3.25 \text{ \AA}$ and $c \approx 5.20 \text{ \AA}$, while the axial ratio c/a was about 1.60 for the ZnO inverse opals, without any noticeable dependence on the deposition current density. Again, the heat treatment for template removal did not cause significant change in lattice constant.

The SEM and XRD results suggest that cathodic current density of $5 - 10 \text{ mA/cm}^2$ are optimum for fabricating ZnO inverse opals, since both the ZnO inverse opals deposited under these conditions are the most uniform and well ordered while maintaining the preferred orientation for efficient UV emission [90].

The optical reflectance peaks taken at normal incident angle show the positions of the pseudogap in the [111] direction. Figure 4.5 compares the pseudogaps of the PS opals and ZnO inverse opals made of 200 nm spheres (see Appendix I for different sphere sizes). These films exhibit bright opalescent colors, demonstrating their excellent optical quality with % reflectance of $\sim 10\%$. The bright iridescence in reflected light observed through a microscope corresponds to the pseudogaps of the opals, with the PS opal appearing green-blue (485 nm) and the ZnO inverse opal being violet (410 nm) in color. Due to the reduced effective refractive index in the inverse structure, the pseudogap in

ZnO inverse opals is blue-shifted as compared to their PS opal templates. The positions of the pseudogaps are in good agreement with the Bragg condition as well as the photonic band diagram (see Appendix I for detailed calculations). The cracks observed in the optical pictures are caused by volume shrinkage of the colloidal crystal film during drying. The pseudogap shifts to the red when larger PS spheres were used. For smaller spheres (≤ 200 nm), the determination of pseudogaps in ZnO inverse opals would not be possible since the expected pseudogaps would have blue-shifted, approaching the absorption band edge of ZnO (at approximately 385 nm in this work).

Figure 4.5: The pseudogaps for 3D PhCs made of 200 nm spheres. (a) Optical reflection spectra (dotted lines: PS opals; solid lines: ZnO inverse opals) measured in the [111] direction; (b) Optical microscope images (magnification of 5x) of the PS opal (green-blue) and ZnO inverse opal (violet).

As shown in Figure 4.6, the PL spectrum of the ZnO inverse opal electrodeposited at 10 mA/cm^2 exhibits characteristic UV emission of ZnO. The PBG effect on

modification of emission as well as lasing characteristics will be described in the following chapters.

Figure 4.6: PL spectrum of ZnO inverse opals with $D = 200$ nm prepared at 10 mA/cm^2 followed by firing in air at 600°C . The spectrum is independent of the sphere size, D .

4.4.3 Lattice-Matched ZnO-PS hetero-opal

Photonic crystal heterostructures, similar to their electronic counterpart, generate many exciting functions from simple building blocks. Devices such as low loss PhC waveguides and high-efficiency add-drop filters have been demonstrated in heterostructures [91]. Most of the previous published work on hetero-opals was focused on the fabrication of heterostructures by repeating the self-assembly process with different sphere sizes [63, 92, 93]. A few groups have also explored lattice-matched hetero-opals using non-uniform infiltration [94, 95].

In this work, the deposition conditions were controlled such that the infiltration was incomplete, resulting in a lattice-matched heterostructure. As shown in the cross-section in Fig. 4.7(a), the unfilled PS opal is stacking on top of the ZnO-infiltrated PS opal to form a multilayer. While the infiltration was incomplete through the thickness of

the entire sample, the interstices regions are completely filled and adjoining to form solid frameworks around the PS spheres, features of the electrodeposition infiltration technique. The ordered structure remained robust after the infiltration process.

Figure 4.7: (a) Cross-section of ZnO-PS hetero-opal with $D = 200$ nm; (b) Enlarged view of the ZnO-PS component opal. The ZnO was deposited at 10 mA/cm^2 for 20 mins.

Figure 4.8 shows the reflection spectra of ZnO-PS hetero-opal deposited at 10 mA/cm^2 for different duration. The peak at 485 nm corresponds to the pseudogap of the PS template. A pseudogap at 548 nm peak position appears only after 60 mins of deposition. As such, the stop gap corresponding to the PS template was still visible. The red-shifted peak at 548 nm wavelength corresponds to the ZnO-PS opal as a consequence of the change in effective refractive index (n_{eff}) from 1.49 for the PS-opal to 1.69 for the ZnO-PS opal. The presence of two Bragg resonances at different wavelengths shows that a hetero-opal with an effective photonic pseudogap consisting of the pseudogap in each of the component opals has been formed. The results here complement an earlier study on the additive PBG properties of colloidal multilayers fabricated from colloids with different sphere sizes [92]. This additive property extends to lattice-matched hetero-opals

formed from different RICs. We can thus generalize that hetero-opals have additive PBG properties, whether the component PBGs differ by lattice constant or by RIC.

Figure 4.8: The optical reflectance for ZnO-PS hetero-opal deposited at 10 mA/cm^2 for various duration. The inset shows the incomplete infiltration scenario during electrodeposition of ZnO into the interstices of PS template.

For the ZnO-PS hetero-opal, the reflectance appears to increase dramatically at longer wavelength. This is believed to be a consequence of scattering, possibly due to non-homogeneous distribution of the particles (PS sub-micron spheres and ZnO nanocrystallites) and rough interfaces in the composite opal samples. Typically, the scattering is non-uniform and the effect is more pronounced at the longer-wavelength end of the spectrum.

As shown in Fig. 4.9, the PL spectrum of the as-deposited ZnO before heat treatment for template removal shows a broad visible defect-related band at around 510 nm (green) [96, 97]. The absence of UV excitonic emission of ZnO at 385 nm could be attributed to the presence of a high concentration of non-radiative recombination centers

in the as-deposited films. An effective photonic pseudogap effect suppressing green emission from the ZnO-PS hetero-opal will be discussed in the following chapter.

Figure 4.9: Photoluminescence spectrum of as-deposited ZnO. The deposition current density was 10 mA/cm^2 .

4.5 Chapter Summary

Three-dimensional ZnO photonic structures were prepared using a galvanostatic electrodeposition route and via colloidal templating with PS colloidal crystal template. Current densities ranging from 5 to 10 mA/cm^2 were found to be optimum for attaining ordered 3D ZnO PhCs. Both lattice-matched ZnO-PS hetero-opal and ZnO inverse opal were successfully obtained. These PhCs possess photonic pseudogaps tunable in the UV to visible spectrum, while effective photonic pseudogaps which are sums of the component pseudogaps emerge in the hetero-opal. The resulting structures are polycrystalline and exhibit efficient photoluminescence, which shows potential for studying the modification of emission in photonic crystals. Such photonic crystals constructed from direct bandgap semiconductor may act as an optically active material to achieve lasing action in solid state device enhancing the optical gain.

Chapter 5:

COMPARATIVE STUDY OF THE DIRECTIONAL PSEUDOGAPS: OPALS VS OPTICALLY ACTIVE OPALS

5.1 Introduction

Having fabricated the inherently optically active three-dimensional (3D) photonic crystals (PhCs), a comprehensive discussion on their optical characteristics is now presented. Special emphasis has been placed in understanding how the mode of infiltration is related to the angular dispersion of the pseudogaps, as well as the effect of an effective pseudogap on suppression of spontaneous emission.

5.2 Angular Dispersion of Primary Photonic Pseudogap

In an artificial opal of dielectric spheres, the low refractive index contrast (RIC) opens a photonic pseudogap between the 2nd and 3rd bands in the photonic band diagram. [3] The inverse opal, on the other hand, exhibits a complete photonic band gap (PBG) between the 8th and 9th bands for sufficiently high RIC (>2.8). [98, 99] Theoretical simulations have shown that the opening of the PBG is a function of the infiltration degree while the gap width is dependent on the RIC. [100] The band gap is extremely sensitive to geometrical non-uniformities such as size and site randomness. [101]

One approach to experimentally probe the existence of a PBG in the opal is the collection of transmission/reflection spectra along high symmetry directions of the first Brillouin zone (BZ) by varying the angle of incidence. This reveals the angular dispersion of the stop-band, which is an important factor towards a complete PBG. The overlapping

of the stop-bands for all directions corresponds to an omnidirectional (complete) PBG. Due to the complexity in correlating the high energy spectral features to the high-order bands, [102] most work focus on investigating the evolution of the low-energy pseudogap with the incident angles. Despite its implication on the omnidirectionality of PBG, only several attempts [42, 103, 104] have been made to access the angular dispersion of an inverse opal.

In this work, we report an improvement in the stop-band characteristics, i.e., a *non*-dispersive pseudogap in the blue region near the *L* point in the face-centered-cubic (fcc) BZ, in an electrodeposited ZnO inverse opal. Although the refractive index (RI) of ZnO (~ 2.0) is insufficient for the opening of a complete PBG, the RIC is high enough to produce pseudogaps. While the opening condition of a complete PBG in an inverse opal and its fragility against disorder are well-investigated, the effect of topology of the dielectric/air network and RIC on the dispersion of the pseudogap has not been addressed. Here, we present the calculated photonic bands along the *LW* direction in the BZ with the aim to investigate the difference in the dispersion of the low-energy pseudogap between opal and inverse opal periodic structures. The results allow us to identify the condition to obtain a non-dispersive pseudogap along certain directions.

5.2.1 Methodology

The angle-resolved reflection measurements were made using the variable-angle reflection sampling system (Ocean Optics) to determine the optical Bragg diffraction peak from the colloidal crystal planes arising due to the existence of PBG.[37, 105] The incident light is from an optical fiber (200 μm diameter) that is coupled to a UV-Vis light source (Deuterium Tungsten-halogen type). The light is deflected onto the sample by a series of mirrors that can be rotated to measure the reflectance spectra at various incident

angles (up to 45°). The reflected light is collected with another similar optical fiber to a spectrometer.

In angle-resolved measurements, the experiment is such that the incident and reflected beams, as well as the normal to the sample surface, are contained in a plane perpendicular to the rotation axis and the sample surface (see Fig. 5.1). It should be highlighted that, when carrying out these measurements, if the sample is placed in such a way that the rotation axis is perpendicular to the growth direction but parallel to the sample surface, it is the plane spanned by the Γ , L , and W points in the fcc BZ that must be considered [55].

Figure 5.1: The sample (S) is denoted by the dark gray region of the substrate (M). The incident (k_{in}) and reflected (k_{out}) beams as well as the normal to the sample surface (N) are contained in a plane. The growth direction is indicated by an arrow.

The dispersion of the stop-gaps can be extracted by plotting the normalized frequency (a/λ) of the resonances versus the wavevector parallel to the (111) surface, $k = (\omega/c)\sin\theta$. The photonic band structures were computed in a planewave basis using a freely available software package [106].

5.2.2 Isotropic Photonic Pseudogap in Electrodeposited ZnO Inverse Opal

Optical reflection spectra at different angle of incidence ($0^\circ - 45^\circ$) to the close-packed plane of the polystyrene (PS) opals are displayed in Fig. 5.2. This allows the investigation

of the photonic band structure along a specific k -direction as determined by the incidence angle. For instance, the reflectance maxima at normal incidence (0°), i.e., the (111) Bragg's peak, corresponds to the pseudogap in the Γ - L direction in the opal. In general, the peak position can be defined by the modified Bragg's condition: $\lambda_B = 2d\sqrt{n_{eff}^2 - \sin^2 \theta}$,²⁰ which is dependent on the incidence angle θ , the effective refractive index n_{eff} , and the lattice parameter d ($d_{111} = \sqrt{\frac{2}{3}}D$, where D = center-to-center distance of the spheres or equivalent to the sphere diameter in this case). The full width at half maximum (FWHM) of the peak, on the other hand, generally increases with the RIC of the opal.

Figure 5.2: Reflection spectra of (a) PS-opal and (b) ZnO inverse opal as a function of angle of incidence. The inset shows the peak positions for PS-opal (squares) and for ZnO inverse opal (dots) along with Bragg's fit.

The reflectance spectrum of the PS-opal at normal incidence shows an asymmetric Bragg peak at 485 nm corresponding to the Bragg diffraction of the fcc (111) plane [see Fig. 5.2(a)]. This peak is blue-shifted to 410 nm and widened as a result of the change in n_{eff} of the structure, as shown in Fig. 5.2(b). The n_{eff} can be calculated by the modified

Bragg's condition at normal incidence, which gives $n_{\text{eff}}=1.49$ for PS-opal and $n_{\text{eff}}=1.27$ for ZnO inverse opal. Hence, the inverse structure should exhibit Bragg's peak at shorter wavelength compared with the bare opal. In addition, an approximation of the RI of ZnO n_{ZnO} from the expression $n_{\text{eff}} = \sqrt{0.74n_{\text{air}}^2 + 0.26n_{\text{ZnO}}^2}$ indicates that the ZnO prepared by electrodeposition is dense and has a RI close to the bulk value. While the peak position at normal incidence for both the PS-opal and the ZnO inverse opal is in good agreement with that calculated using Bragg's condition, the dependence of peak position with incidence angle in the ZnO inverse opal can no longer be explained by the modified Bragg's law. The inset in Fig. 5.2(b) also depicts that, in comparison with the PS-opal, the peak shift with angle for the ZnO inverse opal is negligible, indicating an isotropic pseudogap in the inverse structure. This means that, while the color of the PS-opal changes rapidly with the viewing angle, the color of the ZnO inverse opal remains unchanged. The absolute intensity of the Bragg peak was lower in the ZnO inverse opal, possibly a result of light diffusion [9, 107] from roughness and fabrication imperfections. The diffusion effects are stronger at higher incidence angles and it almost disappears at 45° .

Figure 5.3(a) shows the relation of the relative stop-band width of $\Delta\lambda/\lambda_B$ (determined from the FWHM of the Bragg peak) with the angle of incidence. It is worth mentioning that the asymmetric peaks observed in the ZnO inverse opal are wider ($\Delta\lambda/\lambda_B \approx 0.10$) than the peaks typical of good quality PS-opal ($\Delta\lambda/\lambda_B \approx 0.08$). This is attributed to the increase in RIC resulting from the removal of opaline template as well as the effective infilling by electrodeposition. In addition, the fraction of space forbidden of light propagation is larger in the ZnO inverse opal than the PS-opal, as can be seen from the large extent of the overlap of the Bragg peaks when the external incidence angle sweeps from 0° to 45° , which covers the range of directions in the vicinity of the L point of the

fcc BZ [see Fig. 5.2(b)]. This can be further quantified by the relative shift of the stop-gap with the angle of incidence ($\lambda_{\text{shift}}/\Delta\lambda$) that characterizes the rate of approaching complete PBG (for complete PBG, $\lambda_{\text{shift}}/\Delta\lambda < 1$).²² Figure 5.3(b) shows that, when compared to the PS-opal, the relative shift for the ZnO inverse opal is less than 1 at all the examined angles. This indicates clearly a non-dispersive pseudogap in the ZnO inverse opal.

Figure 5.3: Angular dependence of (a) photonic stop-band FWHM and (b) relative stop-gap shift for PS-opal and ZnO inverse opal.

To further illustrate the enhanced photonic behavior in the ZnO inverse opal, Fig. 5.4 compares the stop-band dispersion diagram near the L point of the fcc BZ. The dispersion diagrams were plotted based on the data in Fig. 5.3. The stop-band in the inverse opal is wider due to the increase in RIC. The angular dependence, i.e., stop-band dispersion becomes much smoother as well. These observations are consistent with, if not better than, the results published by other workers [42, 103, 104]. We deduce this to be a consequence of, firstly, the large area, single crystal colloidal template used in this study, which was prepared by vertical deposition, compared with the colloidal templates prepared by gravitational sedimentation used in most previous studies, which consists of

numerous polycrystalline domains. Secondly and more importantly, our results suggest that it is the feature of complete infiltration, specific for electrodeposition, which results in the *full* transformation of the interconnecting network of interstices from a low dielectric (air) in the opal to a high dielectric one in the inverse opal and thus a change in the scattering potential of light in a more complicated unit cell of an inverse structure, that gives rise to an isotropic photonic pseudogap. We further discuss this claim in the following sections.

Figure 5.4: Photonic stop-band diagram from 0° to 45° in the vicinity of the L point of the FCC Brillouin zone.

5.2.3 Role of Infiltration Mode

Inverse opals have been realized by various forms of chemical or physical infiltration methods. Most infiltration techniques have assumed a homogeneous infiltration model, where the infiltrated materials grow increasingly thicker following the geometry of the spheres. This yields a conformal “shell”-like coating around the spheres, leaving well-defined air-pockets in the interstitials as shown in Fig. 5.5(a). In practice, conformal

infiltration can only fill up to ~86% of the air volume of the interstices with dielectric material because the tetrahedral interstices are completely filled before the octahedral interstices.[100] On the other hand, the electrochemical infiltration approach employed in our work gives rise to complete infilling of the interstices by “flooding” the interstices between spheres [Fig. 5.5(b)] as the infiltrated materials grow upward and around the spheres from the bottom of the opal template.

Figure 5.5: Schematic description of the mode of infiltration: (a) “shell”; (b) “flood”.

To support the above argument on the effect of infiltration mode on dispersion of photonic pseudogap, we calculated reduced photonic bands of inverse opals with infiltrations of 85% (equivalent to shell-mode infiltration) and 100% (equivalent to flood-mode infiltration) along the LW direction, which corresponds to the angular range explored experimentally. The infiltration percentage is related to the shell thickness, which is expressed as the ratio of the radius of the coated spheres (R_{shell}) to the fcc lattice constant (a), with $R_{shell}/a = 0.4063$ for 85% infilled. As shown in Fig. 5.6, the good match of the experimental stop-band dispersion with the reduced photonic band structure of

100% filled inverse opal up to a wavevector value of 0.4 (corresponds to an incident angle of 35° experimentally) verifies that the air interstitials in the electrodeposited ZnO inverse opal must have been completely filled. The left panel of Fig. 5.6 shows the reflectance peak at normal incidence (0°), i.e., the (111) Bragg's peak, corresponding to the pseudogap at the L point in the BZ. The spectral position of the pseudogap is centered around $a/\lambda = 0.68$.

Figure 5.6: Comparison of calculated bands (lines) along the LW direction and experimental reflectance peaks (dots) for electrodeposited ZnO inverse opal.

In order to examine the dependence on topology of the dielectric/air network of the dispersion of the low energy pseudogap, consider a hypothetical situation where the RIC for both an opal and an inverse opal is kept constant at 1.625. Figure 5.7(a) compares the variation of the gap-to-midgap ratio ($\Delta\omega/\omega_g$) of the primary pseudogap along the LW direction between dielectric spheres (opal) and air spheres (inverse opal, 86% and 100% filled) on an fcc lattice. In all cases, the pseudogap becomes narrower from L point and eventually closes up at W point. Although the RIC was kept constant in all cases, the

pseudogaps in the inverse opal are wider ($\Delta\omega/\omega_g \approx 0.05 - 0.10$) than that of the opal ($\Delta\omega/\omega_g \approx 0.01 - 0.06$) from L point towards the W point (within the wavevector range of 0 to 0.55). This clearly demonstrates the impact on the dispersion of pseudogap by the basis of the unit cell, which changes from an interconnecting network of low dielectric (air) interstices in the opal to a high dielectric one in the inverse opal. The more complicated unit cell of an inverse structure with an inversion in refractive index ($n_{\text{backbone}}/n_{\text{sphere}}$) could result in a change in the scattering potential of light. The wider pseudogap in the completely filled inverse opal compared to that in the partially filled inverse opal further underlines the role of the geometry of dielectric backbone on dispersion of primary pseudogaps.

Figure 5.7: (a) $\Delta\omega/\omega_g$ and (b) $\omega_{\text{shift}}/\Delta\omega$ of opal and inverse opal with the same RIC of 1.625.

In addition, the fraction of space forbidden of light propagation can be quantified by the relative shift of the pseudogap along high symmetry directions ($\omega_{\text{shift}}/\Delta\omega$), which characterizes the rate of approaching complete PBG (for complete PBG, $\omega_{\text{shift}}/\Delta\omega < 1$ in all directions).[52] For different points along the LW direction, ω_{shift} corresponds to the shift in the midgap frequency at each point with respect to the midgap frequency at the L

point, while $\Delta\omega$ corresponds to the width of the gap at the same point. This forbidden space is larger in the inverse opal than the opal, as can be seen from the large extent of the overlap of the pseudogaps along the LW directions [see Fig. 5.7(b)]. Experimentally, this manifests as a pseudogap with unchanged central frequency upon varying the incident angles, in deviation to modified Bragg's Law. When compared to the opal, the relative shift for the inverse opal is less than 1 in the vicinity of the L point up to a wavevector of 0.4. This indicates clearly a less-dispersive pseudogap characteristic in the inverse opal.

We have also performed a study of the dispersion of the pseudogap as a function of RIC for the 100% infill inverse opal (equivalent to flood-mode infiltration). The RIC of 1.94 corresponds to the case of a ZnO inverse opal while a RIC of 3.0 is necessary to open up a complete PBG between higher-order bands in a 100% infill inverse opal. As expected, Fig.5.8(a) shows that the width of the pseudogap at the L point increases with the RIC and saturates to a value of $\Delta\omega/\omega_g \approx 0.22$ above the threshold RIC. [3] Similarly, increasing the RIC extends the range of non-dispersive pseudogap up to a wavevector of value 0.5, which amounts to about 75% of the total light propagating path along the LW direction and cannot be further improved once the threshold RIC has been reached.

Figure 5.8: (a) $\Delta\omega/\omega_g$ and (b) $\omega_{\text{shift}}/\Delta\omega$ of inverse opals with different RIC.

5.3 Suppression of Spontaneous Emission

The emission behavior of light sources embedded into PhCs has been studied with great interest recently. One of the driving forces is the possibility of inhibition of spontaneous emission to achieve low threshold lasers. In the case of a complete PBG, the emission inhibition can be achieved if the PBG overlaps the electronic band gap due to the associated reduction in the density of photon states (DOS) [1]. Three-dimensional PhCs are required to achieve the full PBG control upon the emission dynamics, which is hard to realize though in the visible regime. The alternative focus being actively pursued is on the emission modification by directional pseudogaps in PhCs, which are, in principle, also accompanied by a redistribution of DOS. Several groups have investigated the emission of light emitting components (e.g. semiconductors quantum dots [38], dye molecules [76], rare earth ions [77], etc.) incorporated in the body of the opal or decorated over a small fraction of the opal surface. In most previous studies, however, the inhibition of emission was limited by the small RIC and/or low quantum efficiency light source [108]. Furthermore, studies of emission decay rate by time-resolved experiments of weak PhCs so far have yielded controversial results [109, 110] due to the strong effects of the emitter distribution on the decay kinetics [111]. Nevertheless, inhibition of spontaneous emission from ZnSe-coated CdSe quantum dots has recently been demonstrated in strongly photonic titania inverse opal [78].

On the other hand, there have only been a few reports on the luminescence behavior of an emissive PhC, i.e., the emission of the dielectric that constitutes the opal body [79, 112]. Since there is a significant dependence of emission spectrum on the emitter positions in the PhCs [113], this architecture has the advantage of minimizing the spatial uncertainty in the emitter positions. Interestingly, a recent report on emission from fcc emissive PhCs composed of Ruthenium-based dye [112] shows that strong intensity suppressions only occur for (111) diffraction. Diffraction from the remaining $\{111\}$ and

the {200} planes are instead associated with mode enhancements. This emission is naturally anisotropic and is believed to be arising from (i) modes coupling confined directions into leaky directions, and (ii) maxima in optical mode density adjacent to pseudogaps.

It is also worth mentioning that while the light emission in directional gaps has been widely studied, the emission in a hetero PhC with an effective photonic pseudogap remains unclear. Since photonic multilayers fabricated from colloids with different sizes exhibit additive PBG properties [92], we believe that the PBG effect on emission from an emissive hetero-opal is simply additive as well. Hence, this section attempts to provide an insight into this emission behavior through experimental evidence. The study is confined to the suppression of emission overlapping with the pseudogap in the [111] direction.

5.3.1 Experimental

For this study, the ZnO-PS hetero-opal fabricated by electrodeposition infiltration of PS opal templates with sphere diameter of 200 nm was used. The fabrication and reflectance measured at normal incidence in the [111] direction has been described in Chapter 4. Non-photonic disordered samples were also prepared as reference samples for photoluminescence (PL) measurements. The disordered PS film was prepared by depositing a few drops of PS colloids added with ionic salt (100mM KCl) [114], while a homogeneous ZnO film was deposited under the same conditions.

The PL spectra were acquired at room temperature under excitation by the 325 nm line of a continuous wave 30 mW He-Cd laser, a 0.55 m spectrometer, a PMT detector, and a lock-in amplifier. The collection was performed in the normal direction from the sample surface.

5.3.2 Effective Photonic Pseudogap for Suppression of Spontaneous Emission

Figure 5.9 shows the PL spectra comparing the emission behavior of unstructured/disordered film with ordered opaline PhC. The PL spectrum of the disordered PS film was collected from the non-photonic reference sample while the PL spectrum of the disordered ZnO-PS film was calculated by superimposing the PL spectra of the ZnO reference sample and PS opal. As shown in Fig. 5.9(a), the disordered PS film emits visible emission related to the $S_2 \rightarrow S_0$ transitions upon UV excitation that yields broadband emission from 475 to 550 nm with a long emission tail from 400 nm [115]. The PS opal, on the other hand, exhibits a pronounced peak at 512 nm. The PL emission is modified by the photonic structure with the emission ‘squeezed’ to an energy lower (longer wavelength) than the photonic stop gap.

Figure 5.9: PL spectra of (a) the disordered PS film vs. PS opal; (b) the disordered ZnO-PS film vs. ZnO-PS opal. The arrows indicate the positions of the photonic stop gap.

The PL spectra of ZnO are generally dependent on the growth characteristics. In this work, the electrodeposited ZnO film exhibits a broad visible band at around 510 nm (green). This could be due to deep-level defect-related emission which has been

associated with oxygen vacancy defects and interstitial Zn ions [96, 97]. The absence of UV excitonic emission of ZnO at 375 nm could be attributed to the presence of high concentration of non-radiative recombination centers. Figure 5.9(b) shows that the intensity of the green emission is significantly lower in the ZnO-PS hetero-opal, which indicates the partial suppression of the green emission with the use of the ZnO-PS hetero-opal.

The suppression of emission by PBG effect becomes more obvious in the relative PL intensity spectrum, which is obtained by normalization of the PL spectrum of opaline PhC with respect to that of the unstructured disordered sample. This method provides an approximate indication of the DOSP at the angle of detection [97]. As shown in Fig. 5.10(a), the minimum of DOSP determined from the PL relative intensity spectrum coincides with the photonic stop gap of the PS opal determined from the Bragg peak.

Figure 5.10: Relative PL spectra superimposed with reflection spectra for (a) PS opal, (b) ZnO-PS composite opal. The vertical dotted line represents the anchor point discerning the pseudogap effect from PS opal and ZnO-PS opal. The shaded regions represent the error for the relative PL spectra from 3 sets of data.

It is interesting to note that there is only a single dip in DOSP for the PS opal while there are two dips for the ZnO-PS hetero-opal with an anchor point at a wavelength of 510 nm. The fact that the first and second minimum observed in the hetero-opal corresponds well with the minimum in the PS opal and ZnO-infiltrated PS opal, respectively, demonstrates that the overall pseudogap effect on emission in a hetero-opal is a superposition of the individual effects from its component opals. In order to distinguish between the individual pseudogap effects from the PS component and the ZnO-PS component, the reflection spectrum was fitted by an asymmetric F-variance peak function (goodness of fit, $r^2 \sim 0.995$) and decomposed into two separate peaks, representing the photonic stop gaps of PS opal and ZnO-PS opal [Fig. 5.10(b)]. This confirms that the stop gap in PS opal is responsible for the first dip in DOSP that spans between 486 to 510 nm while the ZnO-PS opal is responsible for the second dip that begins from 510 nm. The anchor point at 510 nm corresponds to the stop band edge of the ZnO-PS opal. It is thus the combined pseudogap effects from both the PS opal and the ZnO-PS opal that suppress the green emission of the ZnO-PS composite opal due to overlapping of the effective photonic pseudogap with the emission spectrum. The presence of the clear anchor point shows that there is no observable interaction effect between the two stop gaps.

It is worth noting that the PL dip is weaker as compared to the height of the Bragg peak of the same sample. The reasons could be:

1. The defect modes within the stop gap originated from the inherent imperfections of the opal could provide leakage paths for the emission to escape unaffected by the stop-band [116].
2. Emission from the near-surface region, which is unaffected by the internal photonic structure.

5.4 Chapter Summary

In summary, we have demonstrated an improvement in the photonic pseudogap characteristics in the optically active ZnO PhCs fabricated by electrodeposition via colloidal templating.

ZnO inverse opal with a pseudogap approaching omnidirectionality near the L point in the fcc BZ was obtained. The width of the first pseudogap increases by $\sim 25\%$ and its angular dispersion is much smoother compared to its parent bare opal for θ from 0° to 45° . Since the dielectric/air network topology is one key factor that determines the opening of a complete PBG, we have verified that electrodeposition achieved the flood-mode infiltration which enables complete infiltration and results in a non-dispersive, low-order pseudogap in inverse opals upon the inversion in refractive index. The range of the non-dispersive pseudogap is dependent on the RIC in the low refractive index region. It stretches over 75% of the total light propagating path along the LW direction when the critical RIC has been reached. It follows that, in addition to the high-order flat bands and band edge, the non-dispersive pseudogap displays reduced group velocity as well which, we infer, could be exploited to enhance optical processes including stimulated emission and absorption [117].

In addition, we have correlated the suppression of the green band in the optically active, lattice-matched ZnO-PS hetero-opal with an effective photonic pseudogap effect. The effective pseudogap influence on emission in a composite was found to be approximately the superposition of individual effects from its component opals. We believe that this observation is also applicable for other active hetero-opals, with different phase distributions. This linear additive property of the effective pseudogap of hetero-opals could help in engineering interesting photonic behavior of heterogeneous PhCs.

Chapter 6:

LASING IN ELECTRODEPOSITED ZNO INVERSE OPAL

6.1 Introduction

The amplification of light emitted in a photonic crystal (PhC) can be enhanced by (1) localization of light over a defect within the photonic bandgap (PBG) whereby it serves as an ultra-small high-quality microcavity [2] or (2) reduction in the group velocity of light at a photonic band edge and flat-band region which increases the interaction time between light and gain medium for enhanced distributed feedback (DFB) [23]. Infrared (IR) PhC lasers have been demonstrated in two-dimensional (2D) PhCs, with either defect [59] or DFB modes [58]. Enhanced emission in the blue/green wavelengths has also been reported in a 2D PhC based on III-nitride materials [118] while ultraviolet (UV) lasing has been achieved in a 2D ZnO PhC [119]. A three-dimensional (3D) PhC with an omnidirectional PBG is essential for complete confinement of light. While modification of emission from semiconductor nanocrystals (NCs) by PBG engineering [38, 78, 79] has been demonstrated in NCs-infiltrated 3D opaline PhCs in the visible wavelengths, reports on 3D semiconductor PhC UV lasers have been scarce. The short wavelength implies a nanometer-scale periodicity which imposes great fabrication challenges. Recently, room-temperature UV lasing has been demonstrated in the flat, high-order bands of 3D ZnO inverse opals fabricated by atomic layer deposition [120]. This scheme allows fabrication of PhCs with relatively large lattice constants, which leads to a relaxation of the stringent fabrication requirements. Structural defects inevitably present in these structures introduce disorder that leads to strong scattering and random lasing; hence these devices

are labeled as partially ordered random lasers. Later, it has been reported that tuning the first Γ - L pseudogap to gain spectrum can lead to a five-fold reduction in lasing threshold due to enhanced light confinement [121]. However, the lasing threshold remains high (>100 MW/cm²).

In this chapter we report room-temperature UV lasing in electrodeposited ZnO inverse opal. We have further examined the reduction of the lasing threshold through PBG engineering. Since random lasing [122] can also be observed from ZnO polycrystalline thin films, we also compare the lasing spectra between the inverse opal and the unstructured polycrystalline film. We then discuss the role of the periodic structure in improving the lasing characteristics.

6.2 Experiment

To obtain ZnO inverse opal, ZnO material was electrochemically infiltrated into a polystyrene (PS) opaline template, which was subsequently removed by heat treatment. The lattice constant of the inverse opal is a function of the PS sphere diameter for the opaline template. Details of the fabrication have been described in Chapter 4. To overlap the position of the primary pseudogap of the inverse opal with the ZnO gain spectrum, the lattice constant was altered from $a = 283$ nm to 344 nm. The position of the pseudogap was determined by performing optical reflection measurements at normal incidence. A top-view field emission scanning electron micrograph (FESEM) of the ZnO inverse opal is shown in Fig. 6.1(a) ($a = 283$ nm). The inverse opal displays iridescent colors corresponding to its primary pseudogap [see Fig. 6.1(b)].

Figure 6.1: (a) Top-view FESEM of a ZnO inverse opal with lattice constant $a = 283$ nm. The blue circle illustrates the possible shape of whispering gallery mode (WGM) resonator that can be formed within the ZnO dielectric backbone. (b) Optical microscope images (magnification 5x) of ZnO inverse opals with lattice constant $a = 283$ nm (violet) and $a = 344$ nm (green).

To measure the emission, the sample was excited at room temperature by a frequency tripled (355 nm) Nd:YAG laser at pulsed operation (6 ns full width at half maximum (FWHM), 10Hz). The pump stripe of length ~ 1 mm and width ~ 60 μm was focused on to the ZnO inverse opal by a cylindrical lens and light was illuminated normal to the surface of the sample.

6.3 Lasing Spectra

In this study, the ZnO inverse opal exhibits both excitonic (ex-ex) and electron-hole plasma (EHP) laser emissions. Figure 6.2(a) shows the evolution of the emission spectra with pump intensity. At low excitation intensity, the emission spectrum consists of a single broad spontaneous emission peak at ~ 387 nm with FWHM of ~ 15 nm. As the pump intensity increases above a threshold (~ 0.38 MW/cm^2), sharp lasing peaks with

linewidth < 0.1 nm centered at ~ 387 nm (ex-ex collision) emerge. As the pump stripe is moved across the sample, at pump intensity just above the threshold, these lasing modes appear periodic and well-separated in some cases. These lasing modes are tentatively identified as whispering gallery modes (WGMs), which will be further discussed in the following section. Further increase in pump power increases the number of lasing modes without shifting the center frequency. From the light-light (L-L) curve given in Fig. 6.2(b), the presence of a “kink” [point “iii” in the inset of Fig. 6.2(b)] clearly marks the onset of lasing action at a pump threshold above which the output intensity increases rapidly with excitation intensity.

Figure 6.2: (a) Emission spectra as a function of pump intensity and (b) *L-L* curve of ZnO inverse opal with $a = 283$ nm for increasing pump intensity. Inset: Enlarged view of the *L-L* curve for low pump intensity region (< 1 MW/cm²). The first and second threshold occurs at 0.38 MW/cm² and 2.7 MW/cm², respectively.

The suppression of the broad spontaneous emission background further confirms that high quality lasing modes have occurred in the sample. The quality factor (Q-factor) for these lasing modes can be calculated using $Q = \lambda/\delta\lambda$, where $\delta\lambda$ is the width of the emission mode at wavelength λ . A Q-factor of ~ 6500 was obtained with essentially zero spontaneous emission background, suggesting efficient light trapping. The quality of the lasing modes in our work is comparable to [123-126] or better than [127, 128] the previously reported data for epitaxial ZnO films, albeit with a higher threshold. In addition, when the pump intensity exceeds a second threshold ($\sim 2.7 \text{ MWcm}^{-2}$), the intensity of the ex-ex emission saturates while another group of lasing modes centered at $\sim 392 \text{ nm}$ (EHP recombination) is excited. The FWHM of the entire spectrum is reduced to $\sim 5 \text{ nm}$. In this case, the emission intensity increases with the excitation intensity at a rate slower than the ex-ex emission mentioned earlier and its center frequency shifts towards lower energy, characteristics of an EHP emission [129]. The distinct thresholds and dependence of center frequency on pump intensity makes differentiation of the different recombination mechanisms unambiguous.

6.3.1 Reduced Lasing Threshold by Tuning the Primary Photonic Pseudogap

We have also observed enhanced light confinement for the ZnO inverse opal when its primary pseudogap approaches the ZnO gain maximum ($\sim 387 \text{ nm}$). As shown in Fig. 6.3(a), for the inverse structure with $a = 283 \text{ nm}$, the Bragg's reflection peak which corresponds to the opening of the primary pseudogap is shifted towards the ZnO gain maximum. It is clear that the ex-ex and EHP laser emissions are well-resolved under high optical pumping. The single mode EHP emission does not coincide with the gain maximum and lies within the wavelength range of the pseudogap. For the inverse structure with $a = 344 \text{ nm}$, when the primary pseudogap is far away from the gain maximum, the lasing spectrum is dominated by the ex-ex emission, where multiple EHP

emission lines coexist and merged with it. The entire lasing spectrum is centered at the gain maximum.

Figure 6.3: (a) Lasing (pump intensity $\sim 6 \text{ MW}/\text{cm}^2$) and reflection spectra and (b) L - L curves of ZnO inverse opals with different lattice constants. The areas enclosed by dotted lines indicate the position of the primary photonic pseudogap obtained by photonic band structures computed using a freely available software package [106].

Figure 6.3(b) compares the light-light curves for the ZnO inverse opals of different lattice constant. It is evident that the lasing threshold for the EHP emission in ZnO inverse opal has been reduced by half with a higher gain and conversion efficiency (i.e., slope efficiency) after overlapping the primary pseudogap with the gain spectrum. We attributed the lasing EHP emission for the inverse opal with $a = 283$ nm and $a = 344$ nm to be photonic lasing and random lasing respectively. With this, we verified that photonic lasing has a lower threshold than random lasing. It is worth mentioning that the photonic lasing mode changes in frequency with the illumination region on the inverse opal. This suggests that the photonic lasing mode originates from the localized defect mode within the primary pseudogap.

6.3.2 Role of Periodic Structure

To further evaluate the role of periodic structure on the lasing characteristics, a homogeneous polycrystalline ZnO thin film was deposited and heat treated under the same conditions as a reference sample. The unstructured ZnO thin film displays ex-ex laser emission lines centered at ~ 390 nm while the ZnO inverse opal shows laser emission lines shifted to ~ 387 nm (see Fig. 6.4). Comparison of the lasing spectra between the inverse opal and the unstructured ZnO thin film reveals a blue-shift in lasing energy (~ 20 meV) and a narrower band-width in the former (5 nm vs 6 nm).

Figure 6.4: Lasing spectra under a pump intensity of 6 MW/cm^2 for the electrodeposited ZnO inverse opal and the unstructured ZnO thin film.

We postulate this to be a consequence of strain-induced shift in the excitonic energy. We obtained the lattice parameters of ZnO crystal from X-ray diffraction measurements. From the (101) diffraction peak, the c-axis lattice parameter for the reference film and inverse opal was determined to be approximately 5.196 nm and 5.202 nm, respectively. The strain along the c-axis of the films perpendicular to the substrate is

defined by $\varepsilon_{zz} = (c - c_0)/c_0$, where c_0 (~ 0.5205 nm) is the lattice parameter in the unstrained crystal. ε_{zz} for the reference film and inverse opal are estimated to be -0.17% and -0.06% , respectively. Both samples are under compressive strain, the inverse opal being less compressive. It has been reported that the excitonic energy of strained ZnO shifts to higher energy as ε_{zz} increases, from compressive to tensile [130]. This is consistent with our results and the magnitude of the change in the excitonic energy is comparable.

6.3.3 Whispering Gallery Mode Lasing in ZnO Inverse Opals

Interestingly, as the pump power increases just above the first threshold (~ 0.38 MW/cm²), distinct, spectrally well-separated lasing peaks superimposed on the spontaneous emission peak emerge in the emission spectra [Fig. 6.5(a)]. About 4 laser modes can be resolved. These peaks are centered at ~ 385 nm and the linewidth of these peaks is < 0.1 nm, which is 100 times smaller than the linewidth of the spontaneous emission peak below the threshold. To explore the suppression of spontaneous emission for enhancing light confinement, we tailored the wavelength range of the primary pseudogap (i.e., the Bragg's reflection peak) to overlap with the ZnO gain spectrum by using ZnO inverse opal with $a = 283$ nm and 297 nm. As shown in Fig. 6.5(b) and 6.5(c), very sharp lasing peaks with essentially zero spontaneous emission background are realized in these ZnO inverse opals. A Q-factor of ~ 6500 was obtained, for all the ZnO inverse opals investigated, independent of their lattice constants.

Figure 6.5: Room temperature lasing emission spectra of ZnO inverse opals for different lattice constants. The corresponding reflection spectra are also inserted.

The cavity length, L of the laser emission lines was determined by performing power Fourier transform (FT) to the lasing spectra [131]. The FT spectrum consists of several peaks of harmonics related to the fundamental resonator length. Figure 6.6 shows the FT distribution of the lasing spectra of ZnO inverse opals with $a = 283$ nm, 297 nm and 344 nm. The fundamental resonator length for the ZnO inverse opals was found to be 7.95 μm , 14.89 μm , and 13.03 μm , respectively.

Figure 6.6: Fourier transform of lasing spectra of ZnO inverse opals for different lattice constants showing the existence of resonators and their harmonics. The arrows indicate the cavity length of the dominant resonator.

We attribute the observed sharp peaks to Mie resonance or WGM of a sphere or dielectric cavity [132]. WGM of a sphere occurs when light undergoes total internal reflection (TIR) at the curved surface of the sphere and becomes trapped within the sphere. The circle in Fig. 6.1(a) illustrates the WGM resonator possibly formed by the highly reflecting air-sphere with ZnO dielectric shell, analogous to the NCs-doped hollow microspheres in [133]. With the light emitters constituting the air-sphere itself, their positions are fixed to the surface of the air-spheres, allowing enhanced light confinement close to the rim of the air-spheres. We further discuss this postulation in the following paragraphs.

The cavity length, L of the laser emission lines can be determined by the equations formulated for Fabry-Perot (FP) cavities, with the substitution of the linear cavity length, L by the circular geometry, $\pi D/2$, since these optical modes form closed circular beams supported by TIRs. Thus, according to the FP condition for interference maximum,

$$m\lambda = 2L = \pi D$$

where m is the order of interference, which has been determined to be $m \approx 2$, and λ is the wavelength of emission line. Similarly, the mode spacing, $\Delta\lambda$ is given by

$$\Delta\lambda = \frac{\lambda^2}{2nL}$$

with a refractive index of $n \sim 2.5$ for ZnO. Table 6.1 summarizes the estimated characteristics of the resonators formed by the air-spheres of the ZnO inverse opals.

Table 6.1: Cavity length (L) and mode spacing ($\Delta\lambda$) of air-spheres in ZnO inverse opals with different lattice constants (a).

$a = \sqrt{2}D$ (nm)	L (nm)	$\Delta\lambda_{calc.}$ (nm)
283	314	95
297	330	90
344	382	78

On the other hand, assuming negligible optical absorption and scattering, the Q-factor of a FP resonator can be related to the reflectivity of the resonator by

$$Q = \frac{2\pi L}{\lambda} \frac{\sqrt{r}}{\sqrt{1-r}}$$

where r is the reflectivity of the two facets in a FP resonator. Accordingly, it was found that to obtain a Q-factor of 6500, the reflectivity needs to be $\sim 99\%$, which can only be accomplished by TIRs for WGM. In addition, the intrinsic optical waveguiding effect in the air-spheres could possibly reduce the loss in the cavity as well such that high reflectivity for TIRs can be achieved to obtain a high Q-factor. The sharp emission with zero background observed in Fig. 6.5(b) and 6.5(c) also suggests that the inverse opal PhC offers inherent characteristics essential for enhancing light confinement, such as its

high refractive index contrast and high reflectivity at the Bragg's maximum (i.e., pseudogap). This supports our hypothesis that the lasing characteristics can be assigned to WGM resonances.

The low-order WGMs of an isolated sphere are typically very leaky and have a short lifetime. They cause dull resonances with large frequency width. As a periodic lattice of such spheres is formed, the WGMs leaked from one sphere can be transferred to the neighboring spheres through "hopping" of photons from sphere to sphere. Thus, as the number of spheres increases, a coherent motion or band motion of photons results and the lifetime of photons becomes longer [134]. The narrow width of the emission mode observed in our experiments further substantiates our postulation. In fact, the origin of the photonic bands can be discussed in the context of the WGM coupling model.

Experimentally, however, the spacing between neighboring modes was found to be far larger than that calculated based on the FP theory (*cf.* Table 6.1). As an example given in Fig. 6.7, $\Delta\lambda_{\text{expt}} = 1.9$ nm for ZnO inverse opals with $a = 344$ nm, in contrast to the calculated $\Delta\lambda_{\text{calc}} = 78$ nm. Moreover, due to the fact that these structures may also be regarded as partially ordered random lasers, it is believed that the WGM lasing modes are superimposed on the random lasing modes, as can be seen in Fig. 6.5. A proposal to distinguish the WGM from random lasing modes is presented in the future work.

Figure 6.7: Typical emission spectrum of a ZnO inverse opal WGM laser.

6.4 Chapter Summary

In summary, we have achieved room-temperature UV lasing in a 3D ZnO inverse opal fabricated by electrodeposition. Lasing modes associated with radiative recombinations of ex-ex and EHP were discerned. There is a blue-shift in the stimulated emission with reduced bandwidth in comparison with an unstructured ZnO thin film. The optical gain is enhanced when the gain spectrum overlaps the primary photonic pseudogap, which leads to a two-fold reduction in the threshold for EHP lasing. Therefore, we infer that periodic structures facilitate strain-induced change in lasing energy and provide modulation in refractive index for enhanced light confinement as well as optical feedback.

We have also demonstrated the use of ZnO inverse opals for generating WGM lasing. Lasing in WGM has previously been reported at room temperature in hybrid ZnO/SiO₂ microdisks [135] and ZnO nanonails with hexagonal head [136]. In our work, the WGM lasing occurs above an excitation threshold of $\sim 0.38 \text{ MW/cm}^2$, which, to our knowledge, is one of the lowest thresholds ever attained for WGM lasing in ZnO [135, 136]. The ZnO air-spheres form high Q-factor resonators ($Q \sim 6500$). By tuning the

primary photonic pseudogap of the inverse opal to the gain spectrum, discrete lasing modes with an emission linewidth less than 0.1 nm and a zero background can be obtained due to the suppression of spontaneous emission. Our results imply the possibility of using inverse opal structures for laser-beam shaping applications.

Chapter 7:

OPTICALLY ACTIVE PLANAR DEFECTS IN OPALINE COLLOIDAL CRYSTALS BY SELF-ASSEMBLY OF NANOCRYSTALS

7.1 Introduction

The development of photonic crystals (PhCs) into useful optical devices involves the controlled introduction of functional defects within the periodic nanostructures. This enables the localization of defect states within the photonic band gap (PBG), and allows complete manipulation of light in much the same way as a semiconductor manipulates electrons [6, 137]. Defects of various architectures (point, line and bend, or planar) have been incorporated into 2D and 3D PhCs by both top-down and bottom-up micro-fabrication approaches [138, 139]. Recently, Braun *et al.* [140] has demonstrated a two-photon polymerization technique for the introduction of complex, multidimensional features within 3D PhCs. Considerable effort has also been made to insert planar defects within opals, which are ordered face-centered cubic (fcc) photonic lattices of monodispersed colloidal spheres with 3D periodicity on an optical length scale. Dielectric defect slabs have been embedded within opals by layer-by-layer (LbL) deposition strategies, such as spin coating [141] and Langmuir-Blodgett technique [142, 143], as well as a combination of self-assembly with chemical vapor deposition [144, 145]. Chemically active polymeric defects have also been incorporated into opals by microcontact transfer printing of a doped polyelectrolyte multilayer [146]. This technique, however, requires a transfer printing step for preventing the functionalized polymers from penetrating into the underlying opal voids. So far, there have been limited reports of the

direct introduction of optically active defects into opals except for a technique based on laser dye doping in gels [147] or polymers dissolved in hydrophobic organic solvents and sacrificial material infiltration [148]. The need for the sacrificial material highlights the challenging problem of growing suspended layers on top of porous structures. While the dye-embedded polymer approach is potentially universal for the creation of active planar defects, it comprises multiple steps and is limited to polymers or particles that are soluble in hydrophobic solvents. The use of organic solvents also limits the opal material to inorganic colloidal spheres like silica (SiO_2). Table 7.1 provides an evaluation of the various published reports on the insertion of planar defects within opals.

Table 7.1: Previous reports on building planar defects into opals.

Methods	Demonstrated on fluorescent materials?	Complexity	Limitations
Langmuir-Blodgett	No (Possible)	Medium	Laser dyes may be washed away during the growth of top-PhC
Chemical Vapor Deposition	No	Low	Emissive PhC, no localized defect planar cavity
Microcontact Transfer Printing	No (Proposed)	High	Laser dyes may be washed away during LbL rinsing or the self-assembly of top-PhC
Spin-coating of nanoparticles	No (Possible)	Low	Aggregate size exceeding the size of the opaline PhC interstices is necessary
Spin-coating of doped polymers	Yes (Laser dyes)	High	Compatibility with hydrophobic solvent is necessary

In this chapter, we demonstrate a simple and fast “anti-infiltration” approach combining fluid motion in porous media and self-assembly of nanocrystals (NCs) for creating optically active planar defects in opals. Our “anti-infiltration” approach offers an edge over standard techniques as it involves simple solution-based deposition processes. By simple deposition of a sessile drop of nanocolloids of controlled volume onto the bottom-opal and fine-tuning the evaporation of the solvent, a freestanding film of NCs could be obtained through self-assembly of the NCs at the water-opal interface, without penetrating into the opal voids below. The NCs themselves serve both as the defect layer as well as the optically-active species. Using uniform aqueous nanocolloids, this approach is applicable for both organic and inorganic colloidal crystals. We demonstrate this technique with CdSe nanocrystals on SiO₂ and polystyrene (PS) opals, and provide the analytical guidelines for its generalization to other NC/PhC combinations.

7.2 Rationale

We first discuss the critical conditions for the wetting of porous surfaces. The idea is rooted in the kinetic energy considerations of a liquid droplet impinging on a porous surface[149, 150]. The evolution of the shape of the droplet is governed by three main mechanisms: (i) initial momentum of the droplet, (ii) resistance imposed by the porous substrate, which tends to hinder liquid penetration into the substrate, and (iii) capillary force to draw the liquid into the substrate. This can be described in two stages as shown in Fig. 7.1(a). When a droplet of initial radius R_0 settles on a porous medium, there is an immediate enlargement of the droplet size to R_c to dissipate the impact momentum (stage I droplet impact). Subsequently, the droplet is further enlarged to R_c to dissipate the impact momentum completely by capillary spreading upon the surface coupled with sorption into the pores (stage II spreading and sorption) at a certain spread ratio. The liquid penetration slows down gradually as the droplet radius increases, for reasons of

conservation of mass and momentum. The magnitude of the fluid velocity is a balance between momentum dissipation due to viscous drag of the porous substrate and capillary penetration [149].

Figure 7.1: Evolution of the shape of a droplet of (a) pure liquid and (b) colloidal suspension striking on a porous surface. R_0 is the initial radius of the droplet, R_e is the radius of the droplet immediately after impact, and R_c is the final radius of the droplet when the kinetic energy is completely consumed. In general, $R_0 < R_e < R_c$. $R_e = R_c$ in the case of droplet immobilization with zero capillary spreading and sorption.

In some cases, when the resistance of the substrate is large enough to rapidly reduce the initial droplet momentum, the droplet is prevented from penetrating into the substrate and is thus suspended as a liquid film on top of the porous surface at stage I. This is dependent largely on fluid flow parameters such as the Reynolds number (Re) and Darcy number (Da), which indicate, respectively, the strength and rate of the momentum

dissipation by viscous drag of the solid matrix of the substrate. At stage II, Re determines the degree of lateral spreading and liquid penetration, while the liquid continues to spread laterally as it would on a solid flat surface for extremely small Da . We postulate that when the viscous drag is sufficiently strong to dissipate most of the initial droplet momentum, the droplet is immobilized, limiting the lateral spreading on top of the porous surface such that the droplet size remains as R_e at stage II with negligible capillary penetration and sorption inside the substrate [see Fig. 7.1(b) for an example]. This forms the basis for anti-infiltration. Besides droplet impingement and spreading, another crucial aspect of the anti-infiltration method relies on the self-organizational ability of the nanocrystals in suspension.

The self-organization of highly uniform NCs has been extensively studied recently [151]. NCs superlattices of dots can be obtained by gentle evaporation of the NCs dispersion. It was found that 3D faceted colloidal crystals are formed in the bulk of solution by homogeneous nucleation driven by interparticle interactions. Thin, ordered superlattice of dots can be produced by heterogeneous nucleation at a solid or liquid interface which acts as a template for providing dimensional restriction [152]. Recently, free-floating nanocrystallite sheets of monolayer and bilayers have also been generated in solution with the combination of anisotropic electrostatic interaction and directional hydrophobic attraction [153].

In essence, the anti-wetting of nanocolloids sitting on the opal surfaces allows the pinning of the nanocolloid droplet along its perimeters such that a suspended sheet of NCs can be deposited upon evaporation.

7.3 Fabrication Scheme

(1) Fabrication of Opaline Photonic Crystals

Colloidal PS and SiO₂ spheres with diameter ~280 nm were synthesized following the emulsion polymerization [154] and Stöber-Fink-Bohn method [155], respectively. The opaline PhCs were then deposited on a 10 × 22 × 0.30 mm³ glass substrates (microscope glass slides, Marienfeld, Germany) at 55°C by the vertical convective self-assembly technique [11]. Colloids with volume fraction of ~0.1% were employed.

(2) Deposition of Nanocrystals

We have used commercial CdSe/ZnS coated Evidots stabilized in water (EviTags, Evident Technologies product) stabilized in water as the optically active defect material. The nanocolloids were used as received. Two different EviTags NCs that fluoresce at birch yellow and lake placid blue colors were used. The concentration of the nanocolloids is 4.5 (11) nmol/ml and the average size of the dots is 3.2 (1.9) nm (approximate hydrodynamic diameter is 25 nm), which gives an emission at 574 (491) nm.

In our scheme (Fig. 7.2), the insertion of the active planar defect was accomplished simply by spreading the nanocolloids on the surface of the bottom-opal at which the evaporation induced self-assembly of NCs takes place at raised temperature. The uniformity of the defect layer can be controlled by the solvent evaporation rate. This was done by pre-heating the substrate on which the opal had been deposited on a hot-plate at temperatures 50°C to 105°C for 5 min. Then, 30 µl of the nanocolloids was drip coated onto the surface of the opal. The droplet dried up within 10 min, leaving behind a ring pattern. The dimensions of the dryout stain pattern can be managed by controlling the size and concentration of the nanocolloids as well as the evaporation condition.

Figure 7.2: Schematic illustration of the introduction of nanocrystalline planar defects into opaline colloidal crystals.

One very significant observation was that the as-deposited nanocrystallite layer was able to float on the liquid surface when the sample was placed vertically into a vial of water or a colloidal suspension of microspheres. This implies that the self-assembled NCs free-floating film is mechanically robust. Before the deposition of a second opal, the sample was annealed at 105°C for 15 min to improve the adhesion of the nanocrystallite layer with the bottom-opal.

(3) Growth of the Top-Opal

A second opal was grown on top of the NCs layer using the same convective self-assembly technique described above to form the top-opal. Thus an opaline PhC with its periodicity disrupted by an optically active planar defect was obtained.

(4) Characterization

The quality of the structure was examined by a field-emission scanning electron microscopy (FESEM, JEOL JSM-6340F). The reflection measurements were performed using a home-made microscope-spectroscopy (Fig. 7.3) to determine the optical Bragg

diffraction peak from the colloidal crystal planes arising due to the existence of photonic pseudogap. The light source is focused on the sample on the microscope stage via an objective lens. A miniature fiber optic spectrometer (Ocean Optics, USB2000) was connected to the TV port of a light microscope (Leica, DMLS) via an optical fiber (200 μm diameter) for collecting the reflected/transmitted light. The PL spectra were acquired using a spectrofluorophotometer (Shimadzu, RF-5301PC) with a solid/powder sample holder.

Figure 7.3: The home-built microscope-spectroscopy setup.

7.4 Key Findings

The final structure with a NCs planar defect is shown in Fig. 7.4. The FESEM images in Figs. 7.4(b) and (c) show the close-up of NCs-opal interface for opals made of two different materials: SiO_2 (hydrophilic) and PS (hydrophobic). For NCs deposited on SiO_2 -opal, the nanocrystallite layer follows the contour of the bottom-opal, and thus the bottom surface of the defect layer appears undulated. In contrast, the self-assembled layer of NCs lies flat on top of the PS-opal. This suggests that the PS-opal surface is so hydrophobic

that aqueous nanocolloid tends to bridge the highest points of the spheres, suspending across the surface of undulating bottom-opal.

Figure 7.4: (a) SEM images of the cross-section of a 280 nm SiO_2 -opal with embedded planar defect composed of NCs. Self-assembly of nanocolloids on bottom-opals with different wettability: (b) hydrophilic SiO_2 -opal, (c) hydrophobic PS-opal. Anti-infiltration prevents the penetration of NCs into the bottom-opal, evident by the distinct NCs-opal interface.

In our experiments, the crystal diameter (d) of the NCs used was 3.2 nm (approximate hydrodynamic diameter is 25 nm) while the average size (D) of the microspheres was 280 nm. By simple geometric calculations, the diameter of the largest sphere that could pass through the interstices between three touching spheres in the close-packed plane corresponds to $d = 0.155D$, in our case, $d \approx 43$ nm. It is noteworthy that despite its minute crystal diameter, there is no sign of NCs infiltrating into the bottom-opal voids. The same observation was also found for opal formed using larger SiO_2 microspheres of $D = 500$ nm, where $d \approx 78$ nm, 24 times larger than the NC size. In the spin-coating method [141], NCs are prevented from infiltrating the void space by forming

nanocrystalline aggregates that are larger than the size of the interstices. So far, such aggregates have not been detected in our samples.

7.3.1 Anti-Infiltration

We further evaluated the role of anti-infiltration for the formation of a suspended layer on close-packed sphere arrays. Figure 7.5 shows the cross-section of a suspended layer of NCs on a SiO₂-opal made of 300 nm spheres deposited at 55°C. The as-deposited nanocrystallite layer has sufficient structural continuity to float off as a sheet onto a liquid surface when the sample was placed vertically into a vial of water. Despite the hydrophilicity of the SiO₂-opal and the minute NC size, there is no sign of NCs infiltrating into the porous opal voids. This implies that the resistance to penetration is strong enough to rapidly reduce most of the initial droplet momentum, such that the nanocolloid droplet lies suspended as a NC sheet on top of the SiO₂-opal after complete drying [see Fig. 7.1(b)]. However, a small enough Da for zero capillary penetration and sorption into the SiO₂-opal of submicron spheres has not been attained based on the droplet configuration in our experiments.

Figure 7.5: Suspended layer of NCs on a 300nm SiO₂-opal. The NCs were deposited by dripping 30 µl of CdSe/ZnS nanocolloids onto the surface of the opal at 55 °C.

We attribute the strong resistance to fluid penetration to be a consequence of meniscus pinning of the nanocolloid droplet along its perimeter during drying of the nanocolloid. This is the well-known static nature of the contact line of a drop of colloidal suspension accompanied with a decreasing contact angle during drying, in contrast to the moving contact line of a pure liquid to reach the equilibrium contact angle. As shown in Fig. 7.6, the solvent loss (highest evaporation rate at the drop edge) leads to convective mass transport of NCs to the meniscus of the droplet where self-assembly takes place, driven by the natural interaction forces in charge-stabilized colloids and the capillary forces built into the equilibrium shape of the sessile drop [156-158]. As such, the capillary forces for spreading, had the fluid been a pure liquid, now serve as the driving force for self-assembly of colloids and counteracts the capillary sorption into the substrate. Consequently, the NCs accumulate and induce viscous drag to dissipate most of the initial droplet momentum. This immobilizes the nanocolloid droplet and limits the lateral spreading as well as the infiltration into the substrate.

Figure 7.6: Schematic of the evaporation process of the nanocolloid droplet.

While the growth continues with meniscus deformation at the droplet edge on top of the substrate, nanocolloid in the middle of the droplet infiltrates into the substrate due to the radial projection of liquid, albeit at a much slower rate (fluid flow inside porous substrate is reduced by as much as 2 orders of magnitude in terms of unit velocity [149]). Our observations reveal that a water droplet penetrates into the substrate considerably

faster than a nanocolloid droplet. This is consistent with the numerical results obtained in [149] whereby the complete sorption into the substrate for a system with viscous effects strong enough to halt the lateral spreading is nearly 1000 times slower than a system with small viscous effects that the liquid spreads and absorbs freely. In this work, capillary penetration and sorption are also constantly competing with the rapid solvent loss by evaporation at raised temperatures throughout the process. As the droplet evaporates and the meniscus shrinks, it leaves behind a typical ring pattern [68, 159, 160] consisting of self-assembled NCs on the opal surface. The size of the NC layers is larger than the interstices preventing further infiltration into the pores. This generates a filter cake that serves to impede the infiltration.

To verify the immobilization of the nanocolloid droplet to hinder capillary spreading and sorption, we repeated the same experiment with a sessile drop of water. The diameter of the water droplet was found to be larger than that of the nanocolloid droplet (~12 mm vs ~8 mm). This is believed to be a result of lateral capillary spreading and sorption that has occurred in the case of water droplet due to the absence of meniscus pinning.

Following the concept of effective density of assembled particles introduced in a previous report [161], the effective density of the assembled NCs is $(\pi/3\sqrt{3}) \rho_{\text{NCs}} \sim 0.6$ (specific gravity of the NCs is ~1.0), which is lower than the density of water. Hence, it is reasonable to assume that the assembled NCs will float on the water surface as observed experimentally.

7.3.2 Optical Characteristics

To confirm the light modulation by the introduction of the NCs defect layer, we examined the optical characteristics of the opaline PhCs with NCs planar defect. The reflectance spectrum in Fig. 7.7 shows a dip within the spectral range of the photonic pseudogap of

the defect-free opal. The dip corresponds to a defect state at which transmission is allowed, which is coupled through the planar defect. The corresponding transmission spectrum is also included to provide complementary evidence for the presence of a planar defect, showing that a peak appears at almost the same position (615 nm) as the transmission dip.

Figure 7.7: (a) Optical reflection and transmission spectra of a 280 nm SiO₂-opal containing a NCs plane. The arrow indicates the peak and dip position. (b) Reflection spectra of a PS-opal containing NCs planar defect collected at different locations across the sample. The reflection spectrum of PS host opal (dashed line) is also included for the purpose of comparison.

As the probing beam was moved across the sample, the symmetry of the dips varied while their position remained almost unchanged within the resolution of the spectrometer [see Fig. 7.7(b)]. The stability of the dip position reflects the uniformity of the thickness of the defect layer in the sample [141-145]. On the other hand, the origin of the variation in the symmetry of the dip is relatively unclear now. Such behavior may be a function of the finite thickness of the top and bottom opals at both sides of the defect layer as well as the difference in the corrugation between the top and bottom surfaces of the defect layer.

The frequency range of the pseudogap has been tailored to overlap with the photoluminescence (PL) of the NCs such that the emission of the NCs can be modified or manipulated [1]. Figure 7.8 shows the PL spectra comparing the emission behavior of non-photonic NCs film with NCs embedded within opals as active planar defect. The non-photonic NCs reference samples were prepared by depositing the same amount of nanocolloids on the surface of bottom-opal and annealed under the same condition. As shown in Figs. 7.8(a) and 7.8(b), the non-photonic NCs films emit visible emission at 574 nm and 491 nm respectively, which is tuned by the size of the NCs. This reveals that the NCs retained their size-quantized characteristic emission after annealing. The emissions for NCs embedded within opals, on the other hand, change in spectral shape as well as intensity. The PL spectra for NCs defect exhibit a reduction in emission in the frequency range corresponding to the reflectance maxima of the pseudogaps. The modification of emission becomes more obvious in the relative PL intensity spectrum, which is obtained by normalization of the PL spectrum of NCs defect with respect to that of the NCs reference sample. As shown in the example given in Fig. 7.8(c), the minimum in the plot of the PL ratio coincides with the frequency range of the pseudogap of the opal.

Figure 7.8: Comparison between the PL emission of the non-photonic NCs (dashed lines) and the PL of the NCs in the opals (solid lines): (a) PS 280 nm opal, (b) PS 240 nm opal. (c) Relative PL spectrum superimposed with reflection spectrum for PS 240 nm opal embedded with a NCs planar defect. The arrow indicates the position of the transmission band introduced by the NCs defect.

7.5 Chapter Summary

In summary, we have presented a novel “anti-infiltration” approach for introducing optically active planar defects into opaline PhCs which are either hydrophobic or hydrophilic. It is derived from the dynamic balance between capillary penetration and convective self-assembly of nanoparticles to form suspended NC layers on porous opal surfaces. Our method, based on a sessile drop configuration, is simple and fast, although the thickness control is not yet perfect. It can cover an array of pores in a one-step process without the need of removing sacrificial sublayers. It is applicable for colloidal arrays with different pore shapes, sizes, and arrangements. The NCs planar defect induces a defect state within the photonic pseudogap. This method should be applicable for any uniform nanocolloids and opens up an opportunity for introducing a wide variety of

planar defects with new functionalities derived from the collective properties of self-assembled NCs.

Chapter 8:

CONCLUSIONS & FUTURE WORK

This thesis made strides toward the development of optically active three-dimensional (3D) photonic crystals (PhCs) through colloidal self-assembly (CSA) for manipulating light at ultraviolet (UV) and visible wavelengths, and demonstrated their potential applications in low-threshold PhC lasers. This entails the innovation of two optically active 3D PhCs that differ in the manner of light emitter incorporation: (a) inherently optically active and (b) optically active planar defect. The key findings and major contributions of this work are summarized as follows:

1. Demonstrated an effort to reduce macroscopic growth defects in 3D colloidal self-assembly

In this study, we have identified three distinct growth zones with varying crystalline quality in colloidal crystals produced from vertical convective self-assembly. The relative extent of the growth zones is a function of colloidal concentration. This growth pattern can be explained by a “stick-slip” motion of the meniscus growth front, a direct consequence of the competition between surface tension forces due to the change in the contact angle and the convective transport of colloidal spheres. Within these zones, the crystalline quality of the colloidal crystals is dependent on the wetting characteristics of the meniscus. These colloidal crystals also exhibit cracks of different morphologies within the different growth zones as a result of the drying process. Based on this understanding and corroborating optical data, optimum growth conditions for achieving

high quality colloidal crystals over areas as large as $\sim 2 \times 1 \text{ cm}^2$ has been obtained as colloidal templates for the subsequent research work.

2. Fabricated inherently optically active 3D ZnO PhCs via colloidal templating with electrodeposition

Two inherently optically active 3D ZnO PhCs, namely ZnO inverse opal and lattice-matched ZnO-polystyrene (PS) hetero-opal, have been prepared. The electrodeposition infiltration process has been systematically investigated and successfully employed in the fabrication of the ZnO PhCs. The resulting structures are polycrystalline and exhibit strong photoluminescence. The photonic nature of the ZnO PhCs was also successfully established based on optical measurements. Specifically, the preparation of a hetero-opal leads to an effective photonic pseudogap.

3. Achieved a non-dispersive photonic pseudogap in electrodeposited ZnO inverse opal

An improvement in the photonic pseudogap characteristics was achieved in electrodeposited ZnO inverse opal. Compared to its parent PS opal, the photonic stop-band in the inverse structure is ‘blue’-shifted, widened and remained fixed at its central frequency along different directions. The extensive spectral overlap of the stop-bands indicates a smooth angular dispersion approaching omnidirectionality within a specific range of directions.

This behavior is a consequence of the change in the dielectric/air network topology: the interconnecting network of interstices changes from a low dielectric (air) in the opal to a high dielectric one in the inverse opal. With the results from calculated photonic bands, we have verified that electrodeposition qualifies as flood-mode infiltration, which enables complete infiltration and results in a non-dispersive, low-order

pseudogap in inverse opals upon the inversion in refractive index. Further increase of the refractive index contrast above the threshold necessary to open up a complete photonic bandgap between the 8th and 9th bands does not have significant effects on improving the non-dispersive characteristic in the pseudogap. The results could be extended to make other inverse photonic structures of different symmetry with non-dispersive bands suitable for the study of optical processes involving low group velocity.

4. Investigated the effective photonic pseudogap effect on spontaneous emission of lattice-matched ZnO-PS hetero-opal

We report the observation of suppression of the green photoluminescence from the optically active, lattice-matched ZnO-PS hetero-opal. This is interpreted to be the consequence of an effective photonic pseudogap formed by the hetero photonic crystal. The effective pseudogap's effect on emission of the optically active hetero-opal is simply the addition of the effect of each component opal, with no noticeable interaction effect, thus suggesting a simple route for engineering the photonic behavior of heterogeneous photonic crystals.

5. Demonstrated lasing in electrodeposited ZnO inverse opal

We have achieved room-temperature UV lasing in a 3D ZnO inverse opal fabricated by electrodeposition. This occurs under optical pumping above an excitation threshold of $\sim 0.38 \text{ MW/cm}^2$. There is a blue-shift in the stimulated emission with reduced bandwidth in comparison with an unstructured ZnO thin film. The optical gain is further enhanced by tuning the primary photonic pseudogap to gain maximum, which reduces the lasing threshold by half. Hence, we deduce that the periodic photonic structure plays a dual role: (1) to induce strain and a change in lasing energy, and (2) to provide modulation in refractive index for enhanced light confinement as well as optical feedback.

We have also proposed the use of ZnO inverse opals for generating whispering gallery mode (WGM) lasing. A high Q-factor cavity for coherent amplification of light is realized by the interconnecting air-spheres within the dielectric framework for total internal reflections accompanied by the suppression of spontaneous emission by the photonic band gap effect. Hence, room temperature UV lasing in WGM with a Q-factor as high as 6500 was observed. This implies the possibility of using inverse opal structures for laser-beam shaping applications.

6. Developed an anti-infiltration approach for introducing optically active planar defects into opaline photonic crystals

A novel “anti-infiltration” approach for introducing CdSe nanocrystals (NCs) as optically active planar defects into opaline PhCs which are either hydrophobic or hydrophilic is presented. The method relies on the resistance of an aqueous suspension droplet to infiltrate a porous network; hence the method is named anti-infiltration. The process works by combining fluid dynamics of a liquid droplet during impact/absorption onto a porous surface with convective self-assembly of NCs. The immobilization of the liquid droplet edge due to self-assembly of NCs at the meniscus is harnessed to halt the lateral spreading of the droplet and consequently, the capillary penetration of the liquid immediately after droplet impact. Further capillary penetration of the liquid is drastically reduced due to the competition between capillary forces and convective losses as well as the rapid occlusion of the pores as soon as a continuous NC film has formed upon evaporation of the suspension. This method should be applicable for any uniform nanocolloids and opens up an opportunity for introducing a wide variety of planar defects with new functionalities derived from the collective properties of self-assembled NCs.

Recommendations for future work include further study on the following areas:

1. Theoretical calculation of electromagnetic field distribution and cavity modes confined in hollow microspheres arrays

The eigenmodes of a 3D microcavity are characterized by the angular momentum number l and radial quantum number n for the transverse electric (TE_l^n) and transverse magnetic (TM_l^n) field modes. As such, to complement our prediction of WGM in ZnO inverse opals, it would be worthwhile to perform a detailed calculation of the electromagnetic field distribution of such a periodic sphere system with arrays of submicron air-spheres of light-emitting dielectric shells. Subsequently, the experimentally obtained cavity modes can be assigned to their quantum numbers TE/TM, l and n , using Mie Theory.

2. Temperature dependence of photonic crystal lasers

One of the key issues for ultimate control of light emission by PhCs is the suppression of non-radiative processes in light emitters at high temperature – the non-radiative processes involved should be identified in order to eliminate them for the implementation of efficient temperature-insensitive PhC lasers and other PhC devices. While the temperature dependence of semiconductor lasers in threshold, wavelength, and efficiency has been widely investigated, it remains poorly understood for PhC lasers. Recently, the thermal behavior of 2D semiconductor PhC membrane lasers [162] and PhC cavity lasers with semiconductor quantum dots [163] has been reported. The red-shift in the lasing wavelengths as well as the increasing threshold power with temperature have been explained by the temperature dependence of refractive index and surface recombination rate. Paradoxically, this unique feature observed in ZnO epilayers has been proposed for the development of novel ZnO UV lasers, which allow “temperature-tuning” of the lasing wavelength over a wide range. [164] Therefore, a thermal study is necessary in order to determine the characteristic temperature and have a better assessment of the performance

of the electrodeposited ZnO PhCs developed in this work. In addition, the mechanism governing the periodic lasing modes discussed in Chapter 6 remains controversial. It remains unclear on how to distinguish the WGM from random lasing modes. In this respect, the same experiments on temperature dependence could help unravel the true origin of this phenomenon.

3. Electroluminescence from ZnO photonic crystals for development of photonic crystal light emitting devices

To be truly useful, photonic crystal devices should be electrically pumped. To date, almost all of the 3D opaline PhCs incorporated with light emitters, including the optically active 3D PhCs developed in this work, are optically driven. The demonstration on electrically pumped light emitting devices in opaline PhCs has been scarce, except for a report on electroluminescence (EL) composites opal- $\text{Zn}_2\text{SiO}_4\text{:Mn}$ and opal- GaInZnS:Mn prepared by chemical bath deposition [165]. On the contrary, motivated by its attractive optoelectronic properties as an UV light emitting material, recent research has realized ZnO-based EL devices from ZnO nanowires [166-169], nanorods [170, 171], nanoparticles [172, 173], and epitaxial films [174, 175]. Nevertheless, electrically pumped ZnO lasers have yet to be demonstrated. As such, the first evidence of a high performance ZnO PhC laser is both relevant and appealing.

4. Lasing in photonic crystal planar defect laser with semiconductor nanocrystals

For the past two decades, quantum dot (QD) lasing has been realized in relatively large (~10 nm) CdSe nanoparticles fabricated via high-temperature precipitation in glass matrices [176], epitaxially grown nanoislands (epitaxial or self-assembled QDs) [177, 178], and close-packed films of chemically synthesized CdSe nanocrystal QDs [179]. It is envisioned that the newly developed PhC defect laser with nanocrystals could be

successfully applied to reduce the lasing threshold for nanocrystals. Tuning the photonic stop-band to the gain spectrum of the nanocrystals can suppress spontaneous emission, while the photonic crystals at both sides of the planar defect could act as a perfect mirror exhibiting a stop-band capable of reflecting a significant portion of emission back into the gain medium (active defect) to promote lasing.

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Appendix I:

OPTICAL REFLECTANCE SPECTRA & IMAGES

Polystyrene opals of different sphere diameters

Figure A.1: Optical reflectance spectra and images (magnifications of 5x) in the [111] direction of the PS opals (0.10 vol.%, 50°C) made of different sphere sizes.

ZnO inverse opals of different sphere diameters

Figure A.2: Optical reflectance spectra and images (magnifications of 5x) in the [111] direction of the ZnO inverse opals using PS templates made of different sphere sizes.

Comparison of reflectance peak positions with theory

Figure A.3: Reflectance peak positions predicted theoretically [modified Bragg's Law (circles) and photonic band diagram (triangles)] for PS opals (open shapes) and ZnO inverse opals (solid shapes) of different sphere diameters (D). The values determined experimentally (squares) agree reasonably well with the theory. Relatively larger deviation observed in the ZnO inverse opals is believed to be a consequence of difficulties in the determination of the sphere size and effective refractive index. For the

modified Bragg's Law, $\lambda = 2\sqrt{\frac{2}{3}}Dn_{\text{eff}}$, where $n_{\text{eff}} \approx 1.46$ for PS opal and $n_{\text{eff}} \approx 1.27$ for

ZnO inverse opal. According to the photonic band diagram, $\lambda = \frac{a}{0.6}$ for PS opal and

$\lambda = \frac{a}{0.68}$ for ZnO inverse opal, where the lattice parameter, $a = \sqrt{2}D$.

Cross-sectional view of electrodeposited ZnO inverse opal

Figure A.4: Cross-section of electrodeposited ZnO inverse opal fabricated using a PS template with $D = 400$ nm and a thickness of ~ 15 layers. Here, thinner colloidal template of larger spheres was employed such that the entire cross-sectional view of the sample could be captured by the scanning electron microscope (SEM) to show simultaneously the glass substrate, the spheres, and top surface of the inverse opal. It can be seen that the ZnO inverse opal is a faithful replica of the original PS template with its intrinsic line defects (indicated by the arrow) retained and a smooth top surface. It proves that the infiltration process was well-controlled without introducing further disorder. The detachment of the film from the substrate was introduced during the sample preparation for SEM investigation.

Appendix II:

LIST OF AUTHOR'S PUBLICATIONS

Journal Publications

1. **L. K. Teh**, Q. Yan, C. C. Wong, "Fabrication of suspended nanoparticle layer on porous close-packed colloidal arrays", *ACS Applied Materials & Interfaces*, (2008) *accepted*.
2. **L. K. Teh**, C. C. Wong, H. Y. Yang, S. P. Lau, S. F. Yu, "Lasing in electrodeposited ZnO inverse opal", *Applied Physics Letters*, Vol. 91 (16), p. 161116 (2007); also in *Virtual Journal of Nanoscale Science & Technology*, Vol. 16, Iss. 18, 2007. Times cited: 4
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