Abstract

The discovery of photonic crystals made over two decades ago sparked great excitement in the scientific community as this breakthrough brought with it the promise of novel and highly advanced photonic devices for a broad range of new technologies. Surprisingly, for a myriad of reasons, a few of which will be discussed in this thesis, little headway has been made in the development of commercial devices based on photonic crystals. Indeed, a disproportionate amount of research has been devoted to more fundamental studies and thus confined to the academic arena. In this thesis, we demonstrate the fabrication of novel bottom-up or combined bottom-up and top-down photonic crystals and demonstrate their integration into viable optoelectronic technologies. In particular, we highlight the fabrication of colloidal one-dimensional and three-dimensional photonic crystals with color reflectivity that is electrically tunable throughout the entire visible spectrum. In our methodology, a requisite material for the preparation of an electrically tunable one-dimensional photonic crystal, was a porous one-dimensional photonic crystal fabricated entirely from nanoparticles. We thus fabricated and highlight here the preparation of one-dimensional photonic crystals from various combinations of SiO₂, TiO₂, SnO₂, and Sb:SnO₂ (ATO) nanoparticles. We also demonstrate that these nanoparticle one-dimensional photonic crystals are also capable of serving as the resonator structure in organic dye and polymer based distributed feedback lasers. Finally, we also describe
the fabrication of the first example of electrically conductive one-dimensional photonic crystals for optical wavelengths based entirely on conducting and optically transparent metal oxides. Owing to the conductivity and optical transparency of such materials, they are particularly well suited for serving simultaneously as the anode and mirror of a Light Emitting Diode microcavity for enhanced color purity.
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Chapter 1
Introduction

1.1 Photonic Crystals

Major technological breakthroughs in electronics ensued with the advent of the engineering capacity to manipulate the electrical properties of semiconductor materials in such a manner as to make them perform in a prescribed way. It is based on such a capability that semiconductor devices such as diodes and transistors, which have had revolutionary impact, were developed.

It is predicted that similar technological breakthroughs are possible if a comparable degree of control of the optical properties of materials can be attained. Such breakthroughs should allow for the control over the guiding, bending and localization of light in a material. Optical fibers which are able to guide light through the phenomenon of total internal reflection over significant distances represented the first accomplishment toward such a goal. Indeed, fiber optic cables have had a major and lasting impact on the telecommunications industry by simultaneously reducing attenuation and boosting data transmission rates over previously employed technologies.

In 1987, E. Yablonovitch\textsuperscript{[1]} and S. John\textsuperscript{[2]} independently put forth the concept that an arrangement of metallic or dielectric objects that is periodic on various length scales can produce many of the same phenomena for photons as for electrons at the atomic scale in crystals. Namely, the series of reflections and refractions within such a periodic lattice could produce the property of a \textit{photonic bandgap} (PBG, analogous to the electronic bandgap of an atomic crystal), which represents the range of photon frequencies that cannot propagate within the material.\textsuperscript{[3]} The structure was therefore appropriately referred to as a \textit{photonic crystal} (PC), a material capable of controlling the flow of light by prohibiting the propagation of light over a certain band of frequencies or wavelengths, while allowing others to propagate freely. The particular building blocks employed in the fabrication of a PC depends on the frequency range of interest, ideally a material of sufficiently high dielectric constant and low absorption at the appropriate frequency range are sought and thus, metallic and dielectric species are well suited for the microwave and
optical regime, respectively. An example of a PC which can exhibit the property of a photonic bandgap is shown in Figure 1.1.

Once a photonic crystal has been designed, its properties can be engineered in a manner similar to that which is done for an electronic crystal, through the process of doping. In a photonic crystal, as will be highlighted below, doping is achieved by either adding or removing dielectric material to a certain area of the crystal.\cite{4} The region bearing more or less dielectric material then acts as a defect region subsequently creating allowed states in the PBG that in turn can be used to localize light. Doping a photonic crystal offers a broad range of possibilities for optical device development through light localization.

Photonic crystals are classified mainly into three categories: one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) according to the dimensionality of the periodicity within the photonic lattice (see Figure 1.2).\cite{5} Accordingly, the bandgaps are direction dependent, meaning that light propagation can only be modulated in the directions of periodically varying dielectric constant. Thus, only 3D PCs can modulate light in all spatial directions and it is for that reason that \textit{complete photonic bandgaps} are only possible in such materials. Materials with complete PBG prohibit the propagation of light over a certain frequency range in all three spatial directions. Direction dependent photonic bandgaps (which occur in each of the materials of interest in this thesis) are often referred to as photonic stopbands.

1D photonic crystals (see Figure 1.2a) represent the simplest class of PCs as they are multilayer structures consisting of alternating layers of high and low refractive index materials.
Figure 1.2. Schematic (top) and SEM micrographs (bottom) of a 1D PC (grating), a), a 2D PC (fiber), b), and a 3D PC (woodpile), c). The schematics and SEM images of b) and c) were reprinted with permission from reference [13]. The SEM image of a) was reprinted with permission from ref. [14]).

Such photonic structures have been fabricated by a variety of methods. For example, 1D PCs consisting of alternating layers of dense SiO$_2$ and TiO$_2$ have been prepared by both bottom up sol-gel methods$^{[6-8]}$ or top-down magnetron sputtering$^{[9]}$ or a combination of both. In addition, high quality 1D PCs consisting of dense SiO$_2$ as the low index material and dense SiN$_x$ as the high index material can easily be obtained by plasma enhanced chemical vapor deposition.$^{[10]}$ For electrically pumped vertical cavity surface emitting lasers (VCSELs), where high mobility defect free semiconductor (ie. GaAs and AlGaAs) 1D PCs are required, molecular beam epitaxy is the method of choice.$^{[11]}$ Cholesteric liquid crystals, similar to opals, are often treated as 1D PCs since such systems exhibit a periodicity in dielectric constant commensurate with optical wavelengths along the direction parallel to the pitch of it’s helical structure.$^{[12]}$ In addition, pure silicon 1D multilayer PCs can be readily obtained via the electrochemical etching of crystalline silicon.$^{[15]}$ Within these Si photonic structures, a periodicity in dielectric constant is generated by the modulation of the porosity of the individual layers which can be easily manipulated via the
control of the current density passed during the electrochemical etching process. Such materials have found use as mirrors in all Si based optical microcavities\cite{16} as well as biosensors\cite{17}.

As illustrated in Figure 1.2b, a 2D PC is periodic along two orthogonal geometric axes and homogenous along the third. Photonic bandgaps appear in the plane of periodicity and again inside the bandgap, no photonic states can exist and therefore, any light incident on the plane is reflected. In contrast to 1D PCs, 2D PCs are capable of controlling the light flow in any direction within it’s plane of periodicity. Surprisingly, over a century passed\cite{18} for scientists to realize that extending the PC effect from 1D to 2D and 3D would be an area of technological relevance. Of the PC systems known, 2D PCs have experienced the greatest development since they are most commonly fabricated by very mature lithographic techniques developed over decades in the microelectronics industry. As a result of their method of fabrication, 2D PCs are ideally suited to be married with well developed electronic integrated circuitry allowing for the development of hybrid systems bearing tandem optical and electronic function.\cite{19}

The common architecture for 2D PCs are ordered arrays of rods or air cylinders in a material of interest. The latter has been demonstrated in GaAs-AlGaAs where a periodic array of holes was generated by reactive ion etching though an electron beam lithographically defined mask.\cite{20} This has also been demonstrated by Gruning et al. in n-type Si again via anodic etching of lithographically patterned Si under back side light illumination. By this method, the authors obtained for the first time a material exhibiting a complete 2D band gap in the near-infrared at a wavelength of 4.9 µm.

2D PC glass fibers, due to their strong resemblance to glass fiber optic architectures have also been at the center of a great deal of interest within the scientific and industrial community. Cregan et al., as shown in Figure 1.3, developed a fiber in which light can be strictly guided without leakage through a hollow central core (ie. a defect).\cite{22} Within this structure, light is confined to the defect core by a 2D PBG in the fiber cladding. Macroscale lengths of PC fiber can be obtained by stacking, in a close-packed architecture, silica glass fibers which have been drawn on a fiber-drawing tower down to the requisite dimensions.

2D PCs have also been prepared by soft lithographic techniques such as micro-contact printing,\cite{23} replica molding,\cite{24} and nanoimprinting\cite{25}. In the latter, a pattern with periodicity on the scale of light is transferred through pressure contact and heating of a lithographically generated master to a thermoplastic. Heeger et al. used nanoimprinting to fabricate 1D and 2D photonic crystals of Super Yellow, an emissive and conjugated polymer, which demonstrated
Figure 1.3. a) and b) are low and high magnification SEM images, respectively of the cleaved end-face of a typical 2D PC fiber. The external diameter of the fiber is 105 μm. Image c) is an optical micrograph of the field intensity pattern observed at the end of the tube. Taken with permission from ref. [22]. Copyright Science Magazine.

low-threshold distributed feedback (DFB) lasing at second-order photonic bandedge wavelengths.[26]

Lastly, we consider 3D PCs (see Figure 1.2c), which are materials with dielectric periodicity in all three spatial directions. As noted above, a great deal of interest in 3D PCs exists due to the possibility of achieving complete photonic bandgaps with such materials.[4] The first realization of a complete PBG crystal operating at microwave frequencies, as confirmed by angle-resolved reflectivity and transmissivity measurements, was reported by Yablonovitch (the structure generated is thus appropriately referred to as a *Yablonovite*). The Yablonovite was obtained via controlled drilling into a dielectric material and most closely resembled the diamond lattice.[27] Below we survey some other methods that have been employed to fabricate 3D PCs.

Two related techniques that will be mentioned together here for the fabrication of 3D PCs include interference lithography (IL)[28] and direct laser writing (DLW).[29] IL at present certainly stands as the preferred method for preparing periodic and quasi-periodic patterns over large areas. In IL, the interference of four coherent laser beams creates a standing wave pattern in three dimensions, which in turn can be recorded in a photoresist. The spatial-period of the grating can be as low as half the wavelength of the interfering light, allowing for structures of the order of 100 nm from UV wavelengths; features as small as 30-40 nm are also possible if a deep ultraviolet ArF laser.[41] The latter method, DLW, makes use of multiphoton polymerization in a photoresist that is transparent to the wavelength of the laser employed and has emerged as a
technique for the rapid, cheap and versatile fabrication of photonic nanostructures. By scanning and properly modulating the laser, polymerization occurs at the focal spot of the laser and can be controlled to create an arbitrary three-dimensional periodic pattern. Interesting 3D PC structures fabricated to date with such methods include diamond\cite{30}, gyroid\cite{30}, and woodpile\cite{31}. A drawback of both techniques however is that they must be performed in photoresists, which inherently possess relatively low refractive indices (RI), which in turn inhibits PCs with complete PBGs from being obtained. Nevertheless, high refractive index 3D PCs with PBGs have been fabricated from these methods by employing recently developed high refractive index (RI) photoresists (ie. silica acrylate\cite{32}, arsenic sesquisulfide composites\cite{33}) or by replicating the structure of a patterned photoresist with a high RI inorganic through processes referred to as a *single inversion* or *double inversion*. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) have been used for infiltration of such patterned 3D PCs with Si,\cite{34} Ge,\cite{35} and TiO$_2$.\cite{36} Metals or metal oxides can be infiltrated into polymer 3D PCs by making use of electrodeposition.\cite{37}

In addition to the above, 3D PCs have also been generated by deep X-ray lithography, as well as robotic manipulation. The first method has been successful at replicating the *Yablonovite* structure\cite{38, 39} and the latter has allowed for the first demonstration of the highly sought after diamond structure opals (see Figure 1.4)\cite{40}.

**Figure 1.4.** A diamond opal lattice grown in the (100) direction fabricated by robotic manipulation. Taken with permission from reference [41]. Copyright Wiley-VCH.
1.1.1 Colloidal Crystals

Virtually all of the PCs considered to this point were fabricated by top-down fabrication methods. In contrast, colloidal crystals, which are fabricated by bottom-up methodologies, represent a unique class of photonic crystal obtained from colloidal building blocks. Recall that colloids in general are dispersions of small particles (on the nanometer or micrometer scale) in a liquid or gas medium. Colloidal crystal materials occur in nature and are well-known for their brilliant iridescence and structural color as exemplified by the opal gemstone. This colorful iridescence is a direct manifestation of the photonic stopband of the opal. In this thesis we will consider two types of colloidal photonic crystals, the first being opals\(^{[42]}\) made of monodisperse microspheres and the second, colloidal 1D PCs made of nanoparticles.\(^{[43-45]}\) As highlighted below, colloidal 1D PCs not only display brilliant colors originating from stopband reflectivity but also possess an intrinsic mesoporosity which can be exploited for a number of interesting applications. Such 1D PCs are expected to generate similar interest in the materials community as opals did over a decade ago.

1.1.1.1 Opals – Colloidal 3D PCs

Opals are natural occurring gemstones that consist of nearly close-packed and silica-fused silica microspheres. Such materials are imparted with photonic crystal properties owing to a periodicity in dielectric constant that is commensurate with optical wavelengths. Although crystalline arrays of colloidal spheres are not expected to exhibit complete PBGs (stemming from the low dielectric constant of the colloidal building blocks), scientists have still nevertheless attempted to replicate the opal structure from synthetic organic or inorganic microspheres in the laboratory. Owing primarily to the simplicity of the fabrication process, such colloidal 3D PCs have served as prime candidates for fundamental studies of photonic band structure. In addition, as we highlight below, the intense color reflectivity exhibited by opaline PC materials renders them interesting for a range of possible applications likes reflective displays, optical filters and chemical sensors.

To date, the preferred spherical building blocks for opals have been made of silica or polystyrene primarily as such materials can be readily prepared as monodisperse colloidal dispersions. Although opal formation is somewhat defect tolerant, highly monodisperse particles are desired for this application as they are able to close-pack into well-ordered photonic lattices,
Figure 1.5. a) Photographs of three different silica opals prepared from silica spheres with three different sizes. b) includes transmission spectra, which clearly illustrate the Bragg reflectivity of such structures prepared from polystyrene spheres of three different sizes. Images a) and b) reprinted with permission from ref. [55] and ref. [53], respectively. Copyright American Chemical Society and Wiley-VCH.

which subsequently affords well-defined Bragg scattering. Monodisperse silica microspheres can be prepared via a modified Stöber-Fink-Bohn method,\(^\text{[46]}\) which is described further in Chapter 2, and polystyrene microspheres by emulsion polymerization\(^\text{[47]}\). Lopez,\(^\text{[48]}\) Vlasov,\(^\text{[49]}\) Zhang,\(^\text{[50]}\) and Colvin\(^\text{[51]}\) and their respective co-workers have extensively investigated the photonic properties of artificial opals fabricated from monodispersed silica colloids and the group of Xia has focused more on the photonic properties of opaline structures assembled from polystyrene beads.\(^\text{[52,53]}\) The photograph of Figure 1.5a is a testament to the brilliant structural color displayed by silica opals. Figure 1.5b corresponds to the typical transmission spectra of opals fabricated from polystyrene beads of a specific size: 270 nm for the red color, 220 nm for the green color, and 206 nm for the blue color. The peaks observed in these spectra are appropriately referred to as Bragg peaks as they arise from Bragg interference which correlate with the photonic stopband (and thus the reflected color) of the opal PCs. The central wavelength of the Bragg peak of an opal structure (and thus its reflected color) can be mathematically described by the Bragg-Snell equation:\(^\text{[54]}\).

\[
m\lambda = \frac{2d}{\sqrt{n_{eff}^2 - \sin^2 \theta}}
\]

eqn.1.1
Figure 1.6. a) Powdered samples of ZrO$_2$ inverse opals of various periodicities obtained from opals prepared by the method of sedimentation. b) (left) A schematic depicting the method of vertical evaporation induced self-assembly. b) (middle) includes a cross-sectional SEM image depicting the ordered face-centered cubic structure where the [111] direction is normal to the substrate. c) includes a photograph of an opal prepared by evaporation induced self-assembly. The black arrows indicate the direction of the growth of the films. (image a) reprinted with permission from ref. [77]). Copyright American Chemical Society.

where $m$ is 1 (for fundamental stop band), $d$ is the (111) interplanar distance, $\theta$ the angle between the incident beam and the normal of the film, and $n_{eff}$ is the effective refractive index given by:

$$n_{eff} = fn_{sphere} + (1-f)n_{void}$$  \hspace{1cm} eqn. 1.2

The most widely used opal assembly method, vertical evaporation induced self assembly,$^{55}$ consists of submersion of a flat substrate (e.g. glass or silicon) in a dilute colloidal suspension. As solvent is allowed to evaporate (see left image of Figure 1.6b), sphere deposition proceeds in a crystalline arrangement at the meniscus. In this method, the number of sphere layers deposited can be easily controlled by manipulation of the original colloid concentration. In addition, spin-coating can be applied for rapid preparation of opal films.$^{56}$ In this method, the
concentration and spin speed allow for control over the thickness of the resulting opaline film. Other noteworthy methods of opal fabrication reported to date include sedimentation,\(^{[57]}\) electrophoresis,\(^{[58]}\) confinement in special cells,\(^{[59]}\) or some minor modifications of these methods.\(^{[60, 61]}\)

The artificial opals prepared in the previously mentioned studies (and many others which have followed) consist of face-centered cubic close-packed spherical colloids (middle image of Figure 1.6b) as this structure is the thermodynamically favored. Within such a structure, the colloids occupy 74 \% of the crystal volume and the remaining 26 \% percent is occupied by air (ie. void volume). What immediately became clear from the aforementioned pioneering investigations was that the porosity of the synthetic opal structure offered unique opportunities for host-guest inclusion chemistry with a wide range of active guest materials thereby providing a simple methodology for making active 3D PCs. Active implies here that the bandgap position or reflectivity (ie. the Bragg peak represented by \(\lambda\) of eqn. 1.1 for the case of the opal) of the 3D PC can be dynamically altered in response to an external stimulus, the particular stimulus being dependent on the properties of the material from which the 3D PC is fabricated.

The fabrication of active color tunable photonic crystals, the subject of part of this thesis, currently represents an active area of research. Again due to the relative ease of preparation, most tunable 3D PC systems reported to date, have been opaline-based and thus we explore the topic further mainly within such a context. Eqn. 1.1 represents a good starting point for a discussion pertaining to tunable opaline PCs. From eqn. 1.1, it is evident that in order to vary \(\lambda\), a given stimulus must induce an event which results in a change in lattice spacing, \(d\), or the effective refractive index of the opal, \(n_{\text{eff}}\). Toward this end, Asher, Braun, Foulger, and other groups developed opals that were responsive to pH changes,\(^{[62, 63]}\) temperature changes,\(^{[64-66]}\) solvent composition,\(^{[67]}\) chemical and biomolecule binding,\(^{[68-71]}\) mechanical stresses,\(^{[72]}\) magnetic fields,\(^{[73]}\) and electric fields\(^{[74, 75]}\) primarily for applications in sensing and displays. In Chapter 2, we describe our group’s distinctive contribution to the area of tunable PCs through our demonstration of how the porosity of bare opals can be exploited to fabricate an electrically tunable PC over a broad wavelength range (~300 nm) by infiltrating the opal void volume with an electroactive polymer.

The composite resulting from infiltration of opal void volume with a given material (as described in the list above) can be further processed into a new material with combined macroporosity and mesoporosity as well as an increased Bragg reflectivity over the parent
structure. In particular, the initial opal template can be removed via dissolution or etching, leading to materials appropriately referred to as inverse opals,\textsuperscript{[76]} examples of which are depicted in Figure 1.6a (ZrO\textsubscript{2})\textsuperscript{[77]} and Figure 1.7 (Si)\textsuperscript{[78]}. Inverse opals are particularly interesting because they exhibit a large enough porosity, provided of course that the material making up the walls of the PC possess a suitably large dielectric constant, to exhibit a complete PBG. Most notably, Blanco and \textit{et al.}\textsuperscript{[78]} reported on the preparation of an inverse silicon opal (Figure 1.7) which possessed a full PBG at a wavelength of 1.5 µm which is particularly relevant for potential applications in telecommunications. Although highly sought after, inverse opals with complete PBGs in the visible range of the EM spectrum have yet to be fabricated owing to the lack of materials available with both low absorption and sufficiently large dielectric constant at visible wavelengths. Nevertheless, inverse opals with intense reflectivity have been fabricated from a broad range of materials including inorganic metals\textsuperscript{[79-81]} and semiconductors\textsuperscript{[82-84]} to organic dielectrics\textsuperscript{[85-87]} and semiconductors\textsuperscript{[88-90]}. The requirements for inverse opal fabrication include that a processable form (ie. from the gas phase or solution) of the target inverse opal material exists such that the inverse opal structure possess sufficient mechanical stability to survive the opal template removal. In Chapter 2, we describe the fabrication of an electroactive inverse polymer opal and demonstrate its potential use as a reflective display technology.
1.1.1.2 Nanoparticle 1D PCs

As mentioned in section 1.1, 1D PCs, consisting of dense alternating layers of high and low refractive index materials have been known and exploited in optical devices for many decades. However, such dense photonic structures ultimately suffer from low functionality. Very recently, in an attempt to impart added functionality to 1D PCs, variations in the conventional 1D PC structure have been investigated. In particular, Rubner et al. reported the observation of structural color as well as vapor sensing from stacked polyelectrolyte (consisting of polymer and nanoparticles) multilayer heterostructures with alternating fully dense and controlled porosity regions.\[^91\] The same group reported structural color from TiO\(_2\)/SiO\(_2\) nanoparticle-based 1D PCs.\[^40\] The nanoparticle 1D PCs were assembled by polyelectrolyte-assisted layer-by-layer deposition with subsequent calcination of the films to remove the polymer components. Choi et al.\[^92\] and Fuertes et al.\[^93\] reported the template-based synthesis of 1D PCs consisting of alternating layers of periodic mesoporous TiO\(_2\) and SiO\(_2\) materials. The authors demonstrated reversible sensitivity of the structural color of such mesoporous PCs to the adsorption-desorption of gaseous analytes in their internal network of voids. Colodrero et al.\[^41\] developed SiO\(_2\)/TiO\(_2\) nanoparticle-based 1D PCs by spin-coating from TiO\(_2\) and SiO\(_2\) nanoparticle dispersions and subsequently studied their optical properties at different ambient vapor pressures for different film architectures.\[^94\] Another interesting 1D PC made from only TiO\(_2\) nanoparticles with periodically alternating layers bearing different porosities was published recently.\[^95\] This same group has also recently fabricated enhanced efficiency dye sensitized Gratzel type solar cells by incorporating SiO\(_2\)/TiO\(_2\) nanoparticle 1D PC as an overlayer on the absorbing dye-loaded nanocrystalline titania layer.\[^96\]

In Chapter 3, we describe our attempts to expand and enrich upon the foundational work of our group and others described above in the area of mesoporous and functional 1D PCs as we report on a generalization of the nanoparticle spin-coating approach to 1D PCs by preparing such photonic structures from various combinations of SiO\(_2\), TiO\(_2\), SnO\(_2\), and Sb:SnO\(_2\) (ATO) nanoparticles. As will be shown, these materials, similar to their 3D colloidal counterparts, opals, exhibit brilliant structural color, intense reflectivity, and mesoporosity, key properties that we seek to exploit for display and lasing applications.
1.2 Organic Lasers

In Chapter 4 of this thesis, we report on the use of nanoparticle 1D PCs (see section 1.1.1.2) as the resonator structure in organic distributed feedback lasers. To appropriately set the stage for the work described in Chapter 4, an introductory discussion pertaining to the area of organic lasers is provided here.

The development of lasers represented one of the most important scientific and technological breakthroughs of the last century as such devices have found use in a plethora of highly relevant applications. The gain and resonator materials in lasers can be made from either inorganic or organic materials, with the former being capable of electrically driven lasing owing to inherently high charge carrier mobilities. Of particular interest to our research however, is the later, which are commonly referred to as organic lasers. Lasing from organic dyes was demonstrated over 40 years ago [97,98] and currently dye lasers find widespread use in laser technology. In contrast, the development of lasers based on conjugated polymers (ie. semiconducting polymers) has been comparatively slow as it was only in 1992 that lasing was demonstrated from solutions containing conjugated polymers [99] and not until 1996 that laser-like emission in a solid conjugated polymer was demonstrated [100]. Perhaps in order to make up for lost time, research into conjugated polymer lasers is currently a very active and highly competitive field. Nevertheless, emissive organic materials, be it dyes or conjugated polymers, exhibit properties which render them particularly well-suited for lasing. For example, such materials; i) are inherently four-level electronic systems (a condition particularly favorable for achieving a population inversion) owing to the existence of vibronically coupled electronic levels; ii) can be dissolved in a range of solvents which allows for direct optical pumping of solutions or for easy and convenient solution processing amenable to printing or coating techniques for making a diverse range of resonator architectures; iii) can exhibit large gain (ie. optical amplification); and finally iv) possess high photoluminescence quantum yields [101]. Laser light is unique in that it simultaneously is coherent (both temporally and spatially), polarized, intense, and nearly monochromatic [102]. However, in order to achieve light emission of such nature, a laser must consist of at least two components, i) an optical gain medium that amplifies light via stimulated emission (i.e. a process whereby an incident lightwave stimulates a transition to radiate more light as depicted in Figure 1.8a), and ii) an optical feedback structure that
The optical feedback system is conventionally called the optical resonator and numerous designs have been explored and demonstrated to date particularly following the development of electron-beam lithography. We will here only consider two types of resonators, schematics of which are provided in Figures 1.8c and 1.8d, that of a planar microcavity and a 1D PC (see sections 1.1 and 1.1.1.2).

The planar microcavity (Figure 1.8c) is a Fabry-Perot type resonator as it consists of only two mirrors, either metallic or dielectric or both combined, sandwiching a gain medium with a thickness comparable to optical or infrared wavelengths. As will be highlighted in detail below, the effect of such a mirror configuration is a reorganization of the photon density of states (DOS) of the electromagnetic (EM) field, $D(\omega)$, in the cavity region which in turn significantly

Figure 1.8. Schematic of a laser gain medium and resonator. a) The process of stimulated emission. b) The most commonly employed resonator consists of two mirrors that pass light backwards and forwards through the gain medium. c) The planar microcavity, which consists of a thin layer of gain material sandwiched between two mirrors. d) Another alternative is the 1D PC resonator, in which the gain medium is corrugated. Reprinted with permission from ref [102]. Copyright Macmillan Publishers Ltd.
modifies the emission properties of gain materials present within the cavity. At certain frequencies, this structure supports a standing-wave EM field and thus the photonic DOS is particularly high at such frequencies.

The effects associated with radiation in cavities (as well as within 1D PCs as will be mentioned below) are best quantified using Fermi’s golden rule.\[^{[104]}\] Fermi’s golden rule states that the radiative transition rate of an emitting species, \(W_{i \rightarrow f}\), can be expressed as:

\[
W_{i \rightarrow f} = \frac{2\pi}{\hbar^2} \langle f | H' | i \rangle^2 D(\omega)
\]

*eqn. 1.3*

where \(\langle f | H' | i \rangle\) is the atom-vacuum matrix element between electronic wavefunctions \(\psi_f\) and \(\psi_i\), and \(D(\omega)\) is the effective photon DOS of the electromagnetic field. Note that \(W_{i \rightarrow f}\) is identical to Einstein’s \(A\) coefficient.

The parameter relevant to a theoretical discussion of resonator structures in lasers is of course \(D(\omega)\) as the basic effect of introducing a cavity (or any resonator for that matter) is to rearrange the photon DOS of the electromagnetic field in the cavity region. In a microcavity, as shown in Figure 1.9, \(D(\omega)\) will be given by a series of delta functions, referred to as resonant cavity modes. Thus \(W_{i \rightarrow f}\) is zero everywhere except at the resonant cavity modes which in 1D are separated by:

\[
\Delta \omega = \frac{\pi c}{L}
\]

*eqn. 1.4*

where \(L\) is the length of the cavity. The situation is illustrated in Figure 1.9. On resonance (\(\omega = \omega_o\)), the photonic DOS is maximized corresponding to \(g_c(\omega_o)\). Also shown is the free space photonic DOS, \(g_f(\omega)\), and in 1D the following relation is true:

\[
g_c(\omega_o) \delta \omega = g_f(\omega) \Delta \omega
\]

*eqn. 1.5*

where \(\delta \omega\) is the width of the cavity mode and \(\Delta \omega\) is the separation between modes. Thus, the DOS are conserved and simply reorganized upon introduction of a cavity. Upon consideration of Figure 1.9, it becomes evident that if a gain material with a transition frequency of \(\omega_o\) is introduced into the cavity, then by Fermi’s golden rule, we know that its transition rate is increased by:

\[
F = \frac{g_c(\omega_o)}{g_f(\omega_o)}
\]

*eqn. 1.6*
Herein lies the origin of the spontaneous emission enhancement and in a combined resonator/gain material system, if spontaneous emission is enhanced then so too is the process of stimulated emission and thus, at a particular pump energy density (ie. excitation energy), optical gain can exceed optical loss (ie. deleterious scattering or absorption) inside the cavity (the particular pump energy at which this is achieved is referred to as the laser threshold) and lasing can ensue. Optical gain refers to the amplification of the optical field originating from stimulated emission and the wavelength dependent gain coefficient is simply the product of the stimulated emission cross section, $\sigma^{[105]}$, and the population inversion density, $N$, that is:

$$g = \sigma N$$

We are at present actively pursuing the fabrication of microcavity lasers consisting of novel types of nanoparticle 1D PCs serving as one or both of the mirrors of the optical cavity. The progress of this work though will only be very briefly discussed in the final chapter of this thesis. In Chapter 5, we not only describe the fabrication of a novel class of conductive and transparent 1D PC but also the integration of such into an organic light emitting diode (OLED) microcavity. The fabrication of an OLED in a microcavity architecture however is not for lasing purposes, since the mobility of organics is not sufficiently large to support electrical pumping (however note that an electrically pumped organic laser truly represents a holy grail in the area of organic
lasers), but rather solely for the modification of the color purity of the emission properties of the OLED (see below). Although not a lasing system, the formalism developed above is still perfectly applicable for rationalizing the observed optical effects.

An almost identical rational, as developed above, can also be used to explain the resonator effect of 1D PCs as seen and exploited in distributed feedback lasers (DFB lasers).\cite{106} In DFB lasers, gain material is uniformly distributed throughout the resonator structure and the feedback in such systems is a result of Bragg scattering from a periodic index or gain variation, schematically depicted in Figure 1.8. It can be easily shown that a 1D PC of periodicity \( a \) induces coupling between forward and backward propagating waves at Bragg frequencies\cite{107}:

\[
\omega_B = \frac{N\pi c}{a} \quad (N \text{ an integer})
\]

which in turn opens up bandgaps around \( \omega_B \). A typical transmission spectrum of a 1D PC is shown in Figure 1.10a with the most notable feature being a range of frequencies with zero transmission. This frequency range of course corresponds to the photonic stopband of the PC. Therefore, as a result of Bragg diffraction, and again analogous to the microcavity effect explained above, the presence of the 1D PC, as illustrated in Figure 1.10b, causes a reorganization of the photonic DOS of the EM field within the PC. In a 1D PC, a sharp peak in

\[\text{Figure 1.10. Typical simulated transmission spectrum of a 1D PC obtained by solving the transfer matrix; and b) the calculated photonic DOS of the 1D PC.}\]
Figure 1.11. Laser characteristics. a) Below threshold, the emission from the gain material (blue plot) is broad and above threshold, the emission is significantly narrowed (red plot) and. b) The output power has a nonlinear dependence on the input power, with a kink at the lasing threshold. c) The laser output above threshold consists of a beam (the image includes is from a two-dimensional polymer DFB laser pumped well above threshold). Reproduced with permission from reference [102]. Copyright Macmillan Publishers Ltd.

The DOS exists at the bandedges (see Figure 1.10b) of the photonic stopband and thus, in accordance with Fermi’s golden rule (eqn. 1.2) spontaneous emission of the gain material can be significantly enhanced at bandedge frequencies. This in turn increases optical gain for modes at such frequencies and induces lasing if again optical gain exceeds loss. In a finite 1D structure, $D(\omega)$ is directly related to the group velocity, $v_g$, as follows\[107\]:

$$D(\omega) \propto \int dk \delta(\omega - \omega(k)) = \left| \frac{d\omega}{d\varepsilon(\omega)} \right|^{-1} = \frac{1}{v_g(\omega)}$$

eqn. 1.9

The above equation implies that modes near the bandedge where the bands are flat have small group velocities. Physically, what does this mean however? Consider the electronic analogue again where at bandedge energies in a semiconductor, the electron de Broglie wave is nearly standing, and the effective mass of the electron becomes very large.\[108\] Here, in the photonic case, an accepted way to visualize the effect is to consider that near the bandedge the photon is undergoing many multiple reflections in the lattice, and it only slowly percolates through the structure with a mean velocity given by $v_g$. Immediately, we can see that if gain material were present, the large increase in optical path length would enhance the effective optical gain on a single pass through the laser plane. With the rudiments of the theory more or less considered, let
us now ask (to paraphrase I. D. W. Samuel\textsuperscript{[102]}) how, then, can we recognize lasing in a gain/resonator system? As described above, laser light is both spectrally and temporally coherent and thus appropriate measurements to support a claim of lasing should demonstrate the following properties (Figure 1.11); (i) the laser should have an emission with a very narrow FWHM (Figure 1.11a); (ii) the light output should consist of a beam with small divergence, (Figure 1.11c); (iii) there should be an obvious threshold in both the laser output power (as shown in Figure 1.11b, this involves simply a plot of emission intensity at the lasing wavelength vs. excitation pump power) and line-width and; (iv) the frequency at which light amplification occurs should correlate strongly with the properties of the resonator (ie. the frequencies at which cavity modes occur in a microcavity vs. bandedges in a photonic crystal).\textsuperscript{[102]}

1.3 Organic Light Emitting Diodes, OLEDs

The original demonstrations of electroluminescence in organic small-molecule and conjugated polymer thin films\textsuperscript{[109,110]} propelled the area of organic electronics to the forefront of materials research.\textsuperscript{[111]} Indeed, immense advancement has been made to such an extent now that flat-panel displays based on OLEDs are commercially available worldwide.\textsuperscript{[112]} However, further research in the field is necessary if OLEDs are going to rival the popularity of LCD and plasma displays.

OLEDs usually consist of multiple organic and metallic layers deposited on an ITO-covered glass plate. These layers may be deposited by various methods, such as: plasma deposition, thermal evaporation, Langmuir–Blodgett deposition or spin-coating from solutions.\textsuperscript{[113]} Each of the organic layers present in the device should be chemically stable and highly transparent to the emitted radiation to prevent light loss. As shown in Figure 1.12a, except for the anode and cathode, electroluminescent devices may contain single or multiple organic layers. The energy-level diagrams in Figure 1.12 illustrate the electronic structure parameters pertinent to the engineering of OLEDs.\textsuperscript{[114]} The single-layer device is the simplest as it consists of a single organic emitting layer sandwiched between the anode, comprised usually of a high-work-function (labeled $\phi_a$) materials, such as ITO and a cathode, which is made from low-work-function ($\phi_c$) metals such as calcium, magnesium, aluminum or alloys, such as Mg:Ag. In such a configuration, holes and electrons, driven into the emitting layer from the respective electrodes by the applied electric field, undergo recombination in the emitter to form singlet and triplet
Figure 1.12. a) Common OLED architectures with or without a hole-transport material (HTM), an electron-transport material (ETM) or both. b) Photograph of a flexible OLED device. c) Energy level diagrams of a single-layer (left) and two-layer (right) OLED. a) and c) were reprinted with permission from ref. [114] and b) from ref [115]. Copyright American Chemical Society.

Excitons. In the single-layer device, electron transport will occur through the lowest unoccupied molecular orbital (LUMO), which lies at an energy equal to the electron affinity (EA) of the active organic material, and holes are transported through the highest occupied molecular orbital (HOMO), which lies at an energy level equal to the ionization potential (IP) of the active organic material. The LUMO and HOMO levels relative to the cathode work function and the anode work function, respectively, determine how effectively charge can be injected into the diode. Large mismatches in the aforementioned energy levels create large barriers for hole injection at the anode ($\Delta E_h = \phi_a - \text{IP}$) and electron injection at the cathode ($\Delta E_e = \phi_c - \text{EA}$) which culminates in poor device performance. The ideal organic material for a single-layer OLED would be both emissive and ambipolar, that is, able to transport holes and electrons with equal efficiency (ie. mobility). However, in reality, the majority of emissive organic materials have a relatively small $\Delta E_h$ and a relatively large $\Delta E_e$, that is they preferentially transport holes. The arylene vinylene polymers 1 and the polyfluorenes 2 are classic examples of organic emitters exhibiting such characteristics. Note that poly($p$-phenylenevinylene) (PPV, Figure 1.13), with an IP of 5.1 eV
Figure 1.13. Molecular structure of poly(phenylene vinylene) 1, and poly(9,9-dinonlyfluorene), 2.

and an EA of 2.7 eV, was employed to fabricate the first polymer LEDs with a device structure, ITO/PPV/Al. As a result of the energy mismatches, the PPV based LED exhibited very low external quantum efficiencies (EQEs = 10^{-4} to 10^{-3} \%).\cite{109}

The aforementioned energy level misalignment which greatly hinders the performance of single-layer OLEDs requires that an alternative approach to the development of OLEDs be adopted. This involves using a multilayer device structure instead of a single-layer structure. In such a device, as shown in Figure 1.12a, additional layers, conventionally referred to as an electron transport layer (ETL) and a hole transport layer (HTL) are introduced above and (or) below, respectively, the emitter material in order to balance charge injection and transport. Transport and injection are balanced in ETL and HTL containing OLEDs because the LUMO of the ETL matches well the work function of the cathode (which serves to lower $\Delta E_e$) and the HOMO of the HTL matches well the work function of the anode (which serves to lower $\Delta E_h$).

1.3.1 OLED Microcavities

Development of organic light-emitting diodes (OLEDs) for display applications represents a very active area of academic and industrial research. However, in digital displays, typically each pixel is sub-divided into three sub-pixels, serving as red, green, and blue color sources. For a given display, it is desired that as broad a color gamut be spanned, which can only be realized if each of the sub-pixel sources provide pure and saturated colors. Unfortunately, organic emitters exhibit poor color purity as they emit light with very broad spectral bandwidth due both to their vibronic sidebands and strong inhomogeneous broadening of their electronic
transitions. One route to overcome the problem of the poor color purity associated with such characteristic broad emission is by making use of an optical microcavity as describe earlier in section 1.2. By incorporating the OLED inside a microcavity (Figure 1.14a), and coupling the device emission to a cavity mode, the spectral line width of the device emission can be narrowed, and the directionality of the emission as well as the emission light intensity can be improved effectively leading to purer color generation.\textsuperscript{116-122}

Recall from section 1.2 that planar microcavities consist of solely two mirrors (either metallic or dielectric as in the case of a 1D PC, see section 1.1.1.2) sandwiching a medium that is hundreds of nanometers in thickness. Because our studies deal solely with microcavities consisting of a dielectric mirror and a metal mirror, only devices bearing such an architecture will be considered herein. Thus, for the microcavity devices consisting of a dielectric mirror and a metal mirror, the total optical thickness of the cavity, $L(\lambda)$, is given by\textsuperscript{123}:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{a) The device structure of a typical OLED microcavity, b) molecular structure of OLED layers.}
\end{figure}
where $\Delta n$ is the refractive index difference between the layers that constitute the 1D PC, $n$ is the average refractive index, $n_j$ and $L_j$ are the refractive index and thickness of the $j$th layer of the OLED, $\phi_m$ is the phase shift at the metal reflector, and $\theta$ is the internal angle of incidence.

The first term in Eq. 1.10 represents the penetration depth of the electromagnetic field into the dielectric stack, the second term is the sum of optical thickness of the layers between the two mirrors, and the last term represents the effective penetration depth into the top metal mirror. The resonant wavelength of the cavity mode can then expressed as:

$$m\lambda = 2L(\lambda) = \frac{n}{\Delta n} + \frac{\sum n_j L_j \cos \theta + \left| \frac{2\pi \phi_m}{2\pi} \right|}{\lambda}$$

where $m$ is the mode number. Within such a cavity architecture, it is evident that the mode positions and spacing can be modulated by varying the reflectivity maximum of the 1D PC or by varying the optical thickness of the cavity, $\Sigma n_j L_j$. In general, if the Bragg peak of the 1D PC is red-shifted or if the thickness of the cavity region is increased, the cavity mode and thus the emission peak wavelength of the OLED is red-shifted and vice versa. The resonant emission enhancement factor $G_{cav}$ (in the direction normal to the cavity) of the cavity OLED vs. the noncavity OLED is given by:

$$G_{cav} = \frac{\xi}{2} \left[ \frac{1 + \sqrt{R_1}}{1 - \sqrt{R_1}} \right]^2 \frac{\tau_{cav}}{\tau}$$

where $R_1$ is the reflectivity of the metal mirror, $R_2$ is the reflectivity of the dielectric mirror, $\xi$ is the antinode enhancement factor, $\tau_{cav}/\tau$ is the ratio of exciton lifetimes in the cavity and the noncavity device. In general, $\xi$ has a maximum value of 2 when the exciton recombination zone is located exactly at the antinode of the standing wave, and experimentally measured $\tau_{cav}/\tau$ is less than 1.

The spectrally integrated enhancement $G_{int}$ of a cavity to noncavity device is then given by integrating the enhancement factor $G$ over the spectral width of the cavity and noncavity device emission:

$$G_{int} = \frac{G_{cav} \Delta \lambda_{cav}}{G_{noncav} \Delta \lambda_{em}}$$
where $\Delta \lambda_{\text{cav}}$ and $\Delta \lambda_{\text{em}}$ are the widths of cavity mode and molecular emission spectrum. It can be seen that $G_{\text{int}}$ is a function of $R_1$ and $R_2$. This indicates that rationally designing $R_1$ and $R_2$ may lead to the desired microcavity effect which can be simply summarized as $G_{\text{int}} > 1$.

In Chapter 5 of this thesis, we describe the fabrication of a novel class of conductive and transparent 1D PC and their subsequent integration into an organic light emitting diode (OLED) microcavity with the same structure shown in Figure 1.14a and demonstrate enhanced OLED color purity.

1.4 References

[18] Lord Rayleigh, Phil. Mag. 1897, 43, 259,


Chapter 2
Electrically Tuneable Opals and Inverse Opals


2.1 Introduction

Owing to the complexity of the fabrication process, there have been only a few early attempts at achieving photonic crystal devices capable of exhibiting dynamically tuneable transmissivity or reflectivity. With regards to three-dimensional PC systems, the majority tuneable PC systems reported to date have been opaline based. Toward this end, Asher, Braun, Foulger, and other groups developed opals with reflectivity that was responsive to pH changes,[1,2] temperature changes,[3-5] solvent composition,[3] chemical and biomolecule binding,[6-9] mechanical stresses,[10] magnetic fields,[11] and electric fields[12,13]. Materials with capabilities are expected to be suitable for a range of applications in sensing and displays.

Herein, we describe the development of a novel reflective flat-panel display technology based on the electrical actuation of opaline three-dimensional photonic crystals. Our tunable PC displays, dubbed Photonic Ink (P-Ink), and Inverse Photonic Ink (IP-Ink) employ a crosslinked network of polyferrocenylsilane (PFS), an iron-based metallopolymer, as a component which actively mediates the lattice spacing of an opal or inverse opal PC through an electrochemically-driven swelling and shrinking process. The active material in P-Ink is a two component composite consisting of PFS infiltrated into the void spaces of a silica opal and in IP-Ink, the active material is purely a PFS inverse opal. As will be discussed in sections 2.3 and 2.4, the seemingly minor difference between the two active materials of these two technologies, accounts for major differences in overall device performance. Nevertheless, both of these materials display non-bleachable structural color, reflecting narrow bands of wavelengths which can be tuned throughout the entire visible spectrum by expansion and contraction of their photonic crystal lattices. The active materials are inherently bright in well-lit environments, exhibit electrical bistability, low operational voltage, can be actuated on flexible substrates, and are
unique amongst all display technologies in that a continuous range of colors can be acquired from a single active material negating the use of deleterious color filters.

2.2 Experimental Details

Materials and Instrumentation: Ferrocene, tetraethylorthosilicate, tetramethylethlenediamine (TMEDA) and n-butyllithium were obtained from Aldrich. Methylvinylidichlorosilane and divinylidichlorosilane were purchased from Gelest. Dilithioferrocene (FcLi2·2/3TMEDA) was prepared according to a previously published method. All manipulations were performed under inert conditions in either an N2 filled glovebox or using conventional schlenk techniques. NMR spectra were acquired on a Varian Mercury 400 spectrometer using CDCl3 or C6D6 as the solvents. Gel Permeation Chromatography (GPC) data was acquired relative to polystyrene standards in THF on a Viscotek GPCmax. Cyclic voltammograms were obtained with a BAS epsilon potentiostat from a three-electrode configuration with the composite PFS infiltrated silica opal or PFS inverse opal on ITO, a platinum wire, and a silver/silver chloride electrode serving as the working, counter, and reference electrodes, respectively. The solvent/electrolyte for cyclic voltammetry was acetonitrile / tetrabutylammonium hexafluorophosphate (0.3 M). Optical spectra were acquired with an Ocean Optics SD2000 fibre optic spectrophotometer coupled to an optical microscope. SEM micrographs were acquired on a Hitachi S5200 in scanning mode at 1.0-2.0kV using Analysis settings.

Synthesis of methylvinylsilaferrrocenophane: FcLi2·2/3TMEDA (20 g, 70 mmol) was dissolved in 300 mL of dry ether and cooled to -78°C. Then methylvinyldichlorosilane (9.89 mL, 75.7 mmol) was added dropwise to the solution and stirred for a further 10 min. The cooling bath was then removed and the reaction was allowed to warm to room temperature and left to stir overnight. The solvent was then evaporated and the remaining precipitate was redissolved in ~150 mL of hexane. The resulting solution was then filtered through celite in order to remove LiCl byproduct. The filtrate was then reduced to half of it’s original volume and then placed at -60°C to induce crystallization of the desired product. Crude product was recrystallized another two times and the supernatant was collected at each recrystallization and further concentrated and cooled to collect more product. Prior to polymerization, crystals were sublimed at least three times under vacuum and moderate heating (~40°C). Yield: 65 %, 1H-NMR (see Appendix A),
(C₆D₆, 400MHz, ppm): δ0.44 (s, 3H); δ3.97 (m, 2H); δ4.09 (m, 2H); δ4.39 (m, 4H); δ6.24 (m, 3H).

Synthesis of polyferrocenylmethylvinylsilane (PFMVS): Polymerizations were performed under standard anionic polymerization conditions. In an N₂ filled glove box, 300 mg of methylvinylsilaferrrocenophane was dissolved in 3 mL of dry THF. To this solution was added via a microsyringe, 7 μL of 1.6 M n-butyllithium. The reaction was then septum capped, allowed to proceed for 45 min. and then finally quenched via addition of two drops of degassed methanol. The desired polymer was then precipitated from methanol (yield: 80 %, PDI: 1.34, Mₙ: 24 kg/mol). ¹H-NMR (C₆D₆, 400 MHz, δ in ppm): δ0.59 (s, 3H); δ4.12 (m, 4H); δ4.29 (m, 4H); δ5.83 (dd, 1H); δ6.05 (dd, 1H); δ6.52 (m, 1H).

Synthesis of Silica spheres: Silica spheres in the size range of 165-270 nm were prepared via a seeded-growth Stöber method with an apparatus similar to that depicted in Figure 2.2. For particles in this size range, the synthesis proceeds in three (for 165 nm spheres) or four steps (270 nm spheres). The first step involves preparation of small silica particles (average diameter = ~17.5 nm) by the rapid injection of the silica source, tetraethylorthosilicate (Si(OEt)₄), into 0.2 M NH₄OH, 10 M H₂O in ethanol under vigorous stirring at 60°C. The amount of Si(OEt)₄ was added such that the concentration of Si(OEt)₄ was 0.1 M. Following injection, the mixture was permitted to stir for an additional minute at which point the stirring was stopped and the mixture allowed to stand at 60°C overnight leading to particles with a mean diameter of 17.5 nm. The generated dispersion was then used as the seeds for the second step of this synthesis which involves the re-growth of the 17.5 nm silica particles to a size of ~55 nm (~3x the original size). For the re-growth to ~55 nm size particles, the reaction temperature was first lowered to 40°C, the ammonia content adjusted to 0.6 M, and the seeds diluted to a [SiO₂] of 0.2 M. Two sets of reagents, one of which consists of the silica source, Si(OEt)₄, in ethanol (1 : 2 volume ratio) and the other a mixture of NH₄OH and H₂O in ethanol, were then added to the seed solution in a controlled manner using peristaltic pumps. The reagent amounts and their rates of addition were such that the concentrations of H₂O and NH₄OH in the reaction solution were always maintained at 8 M and 0.6 M, respectively, and the final [SiO₂] was 1 M. The amount of Si(OEt)₄ added depended of course on the desired final particle size and was computed from the following equation:
where $\Phi_{\text{seed}}$ and $\Phi_{\text{new}}$ are the diameter of the seeds and the final particles, respectively, and $M_{\text{TEOS,seed}}$ and $M_{\text{TEOS,total}}$ are the concentrations of Si(OEt)$_4$ in the seeds and final dispersion, respectively. The addition rate of Si(OEt)$_4$ was 0.025 mol/hr. To further grow the $\sim$55 nm particles to $\sim$165 nm, the aforementioned process used to acquire $\sim$55 nm particles from the 17.5 nm seeds was simply repeated. 270 nm particles were subsequently obtained via the re-growth of the 165 nm particles.

Preparation of PFS infiltrated silica opal: Firstly, opal film made of monodisperse silica spheres are deposited on glass by the well-known method of evaporation induced self-assembly (EISA).\[19\] To acquire an initial reflectance of blue, films are grown from 160 nm silica spheres prepared at a concentration of 1 vol%. The void volume of the prepared silica opal is then infiltrated with a concentrated solution (1 mg of polymer/4 μL of toluene) containing either one of the two polymers bearing terminal C=C bonds, 5-10 mol% of 1,8-octanedithiol and 1 mol% Igracure 819 in toluene. The composite is subsequently exposed to ultraviolet light for 10 hours in order to crosslink the polymer chains to afford a composite PFS infiltrated silica opal.

Preparation of inverse PFS opal: The first step involves the preparation PFS infiltrated silica opal which is described in the previous paragraph. After crosslinking, the silica spheres of the PFS infiltrated silica opal composites are etched out by immersing in 1-2% aqueous hydrofluoric acid for 10 min. The resulting free standing inverse polymer gel opals are then subsequently collected onto ITO coated glass for electrical analysis and actuation.

Cell Design: The cell employed is a simple two-electrode electrochemical cell\[20,21\] with the composite PFS infiltrated silica opal or PFS inverse opal on ITO serving as the working electrode and bare ITO coated glass serving as the counter electrode. The two electrodes are fused together with a 4mil. Surlyn hot-melt spacer (Dupont\textsuperscript{®}) which is cut in the form of a frame for the inverse opal material with a small opening made to allow for introduction of solvent/electrolyte. The solvent/electrolyte, which consists of butyrolactone/lithium triflate (0.3 M), is introduced into the cell by N$_2$ back-filling.
2.3 Results and Discussion - Three-Dimensional Photonic Ink (P-Ink)

Scheme 1 includes the synthetic methodology employed for the preparation of the polyferrocenylsilane polymers employed in this study. The synthesis begins with the dilithiation of ferrocene in the presence of tetramethylethylenediamine to afford dilithioferrocene (1). Dilithioferrocene is then treated with methylvinylidichlorosilane (2) to yield the strained methylvinylsilaferrrocenophane (to obtain divinylsilaferrrocenophane, we simply employ divinylidichlorosilane instead of methylvinylidichlorosilane at this stage). The desired polymer (3), is then obtained under anionic polymerization conditions, by treatment of methylvinylsilaferrrocenophane with n-butyllithium. Under anionic conditions, the acquisition of purely linear polymers from such monomers is unexpected owing to the presence of vinyl groups within each monomer unit. Rather branched systems stemming from propagation through addition at the vinyl moiety as well as through ring-opening of the strained silaferrocenophane were anticipated and indeed observed at long polymerization times. Nevertheless, ring-opening of the silaferrocenophane is expected to be favored over addition to the carbon-carbon double bonds due to the appreciable ring strain present in the silaferrocenophane (80-90 KJ/mol) as well as the steric bulk of the attacking nucleophilic cyclopentadienyl anion (with ring-opening being sterically favored). The preceding argument is supported by the $^1$H-NMR and GPC provided in

**Scheme 2.1**: Synthesis of poly(methylvinylferrocenylsilane), 3.
Figure 2.1. a) $^1$H-NMR (CDCl$_3$, 400 MHz) and b) GPC of PFMVS ($M_n = 24$ kg/mol).

Figure 2.1 of poly(methylvinylferrocenylsilane) obtained under anionic polymerization conditions. The former displays the presence of vinyl protons with chemical shifts in the range of 5.8-6.2 ppm and the latter displays essentially a bimodal distribution with relatively narrow PDI~1.34. For the application described herein, it is necessary that pendant carbon-carbon double bonds be present along the polymer backbone to enable subsequent crosslinking through the well-known thiol-ene process$^{[22]}$.

The monodisperse silica spheres employed for this application are obtained via a modified seeded-growth Stöber-Fink-Bohn method which involves the controlled base-catalyzed hydrolysis of tetraethylorthosilicate$^{[17,18]}$ (described at detail in section 2.2). Opal film quality hinges on the monodispersity of its colloidal building blocks with higher quality films being obtained from more monodisperse colloidal systems. Thus, to ensure monodispersity, a LaMer
Figure 2.2. Synthesis of silica spheres used in the preparation of silica opals. a) includes the apparatus employed in the synthesis which invokes a seeded-growth process whereby the addition of two sets of reagents, one of which consists of the silica source, Si(OEt)$_4$, in ethanol and the other a mixture of NH$_4$OH and H$_2$O in ethanol, are strictly controlled using peristaltic pumps. b) SEM image of monodisperse 165 nm SiO$_2$ spheres prepared by the aforementioned method. c) Concentration of silica source vs. time plot highlighting the LaMer model used for the preparation of monodisperse particles. d) Particle distribution analysis for the particles shown in b).

model (Figure 2.2c)$^{[23]}$ for the synthesis of the silica colloids is followed. According to the model, the nucleation stage of the synthesis should proceed rapidly (so that each of the nuclei are
Figure 2.3. Fabrication of thin film electroactive photonic crystals. a) Fabrication scheme. b) Cross-sectional SEM images of a silica opal (left) prior to infiltration and following infiltration (right) with PFS gel components. c) Molecular structures of the components of the electroactive gel in P-Ink.

generated at essentially the same instant) as well as proceed separately from the growth stage. The latter condition can effectively be realized by ensuring that the concentration of monomer does not exceed the critical supersaturation levels necessary for nucleation during the designated growth period. Figures 2.2a and 2.2b include an illustration of the experimental apparatus employed for the synthesis of the silica colloids as well as an SEM of the synthesized particles,
respectively. A particle distribution analysis is also provided in Figure 2.2d, the results of which indicate a mean particle diameter of 165 nm and a polydispersity of 5.3 %. These values are indeed suitable for fabrication of opals diffracting at optical wavelengths.

To prepare P-Ink, thin films of monodisperse silica colloids are first deposited on tin doped indium oxide (ITO) coated glass plates by evaporation induced self-assembly. The voids between the silica spheres are then infiltrated with PFS gel components which consist of either PFMVS or PFDVS, a multifunctional thiol (ie. 1,8-octanedithiol) and a radical photoinitiator (ie. phenyl bis(phenyloxy) phospine oxide also known as Igracure 819), the molecular structures of which are provided in Figure 2.3c. The infiltration process is highlighted in Figures 2.3a and 2.3b which include cross-sectional SEMs of the opal prior to and following infiltration with the PFS gel, respectively. Following infiltration, the composite is exposed to UV irradiation to generate chemical crosslinks between the polymer chains through a thiol-ene reaction[22].

As would be expected from a polymer network-based PC composite[11-13], P-Ink films display color changes based on solvent swelling. Solvent influx into the network causes the periodicity in refractive index in the composite material to increase causing a red-shift of the Bragg diffraction peak. The increase in lattice constant upon swelling is shown schematically in Figure 2.4a and can be directly visualized by the SEM images shown in Figure 2.4b. The degree of swelling is influenced both by the swelling solvent as well as the degree of crosslinking, this latter parameter determining the ultimate range of tunability[24]. The effect of crosslinker content can be clearly seen when the composites are swollen with toluene, Figure 2.4c.

Electrical actuation of a P-Ink film was performed by its incorporation into a sealed two-electrode electrochemical cell. A schematic diagram of the cell is provided in Figure 2.5a, and consists of the P-Ink composite supported on ITO-glass as the working electrode, a hot-melt ionomer spacer (Dupont®), and an ITO coated glass slide as the counter electrode. The cell is filled with an electrolyte by vacuum filling, and sealed with epoxy. It is known that PFS polymers in solution as well as in supported films display reversible electrochemical oxidation and reduction, with the partial electronic delocalization along the polymer backbone leading to a continuously tunable degree of oxidation[25]. The cyclic voltammogram of PFS infiltrated silica opal (measured in a three-electrode configuration), Figure 2.5b, displays a profile characteristic of main-chain ferrocene based polymers, with two wide oxidation-reduction couples. The first couple corresponds to oxidation of every other iron atom along the chain, the second to full oxidation.
Figure 2.4. Mechanochromic behavior of thin film electroactive photonic crystals. a) Schematic of tuning mechanism. b) SEM images of an as-infiltrated (left) and swollen (right) sample. c) Photographs showing areas of thin-film PFS-silica composites and their crosslinker dependant solvent swelling and color tuning behavior.

When a suitable positive potential is applied to the electrode bearing the P-Ink composite in the two-electrode cell, the ferrocene moieties in the PFS backbone are oxidized with concomitant anion infiltration from the electrolyte (surrounded by a solvent shell) into the polymer to neutralize the generated positive charge. The influx of both ions and solvent into the polymer causes it to swell and push apart the layers of spheres, red-shifting the reflected optical Bragg diffraction peak. Applying a reducing potential drives the system in reverse, by reducing the PFS backbone and the anions being ejected from the polymer film into the electrolyte. The expansion in the PC lattice occurs mainly perpendicular to the substrate due to covalent
Figure 2.5. a) Schematic of the two-electrode electrochemical cell with relevant components. The P-Ink film is approximately 3-5 micrometers in thickness, while the cell gap can range from 10’s to 100’s of micrometers. b) A cyclic voltammogram of the silica-PFS composite using a Ag/AgCl reference electrode. c) Picture of an assembled multipixel electrochemical cell with attached electrode leads, and d) the same cell after oxidizing the middle pixel with 1.5 V, and e) 2.6 V. The reflected colors are due to Bragg diffraction from the composite PC. f) and g) include pictures of a larger area pixel under 2.6 V actuation.

By virtue of their continuously tunable state of oxidation, P-Ink films display voltage-dependent continuous shifts in reflected colors. The plot in Figure 2.6a spectroscopically anchoring of the composite thereto. Figures 2.5f and 2.5g include a demonstration of the above concept as it includes photographs of the device in operation. Initially, a single pixel is shown here to be reflecting green and following a 2.6 V bias for ~1 min., the reflectance of the material is shifted to red owing to the phenomena described above. Again, the process can be reversed simply by applying a reverse bias of -2.6 V.

By virtue of their continuously tunable state of oxidation, P-Ink films display voltage-dependent continuous shifts in reflected colors. The plot in Figure 2.6a spectroscopically...
**Figure 2.6.** Electro-mechanochromic behavior of P-Ink thin films. a) Reflection spectra taken at a series of increasing voltage applications clearly showing a continuum of accessible colors. b) Spectra of a sample showing reflection of all three primary colors upon incremental oxidation. c) The Bragg peak maximum vs. number of cycles for a series of 100 oxidation-reduction cycles. The voltage was cycled between 2.5 V and −2.5 V d) Electrical bistability measurement. The sample was oxidized at 2.5 V, after which the leads were disconnected and the peak position monitored as a function of time. e) Dependence of the maximum tuning range on the crosslinker content of the composite.
illustrates how the Bragg peak gradually shifts through a given wavelength range when the applied voltage is incrementally varied. The position and magnitude of the tuning range depends both on the starting sphere size, as well as on the degree of crosslinking (Figure 2.6e). By appropriately choosing the starting sphere size and crosslinker content, a single sample can be tuned to all 3 primary colors as displayed spectroscopically in Figure 2.6b. Once a particular voltage was applied, the peak shift was complete within 1-2 min. It is important to note that the reflected wavelength can also be switched into the near-infrared region, rendering the materials transparent and providing a black or white state depending on the color of the background.

The cycling stability of the materials was found to be excellent, with a series of 100 oxidation-reduction (or equivalently, green-to-red reflectance) cycles shown in Figure 2.6c. As can be clearly seen, the peak maximum shifts reversibly, with its position returning to within nanometers after each voltage application. The electrical bistability (ie. the ability of the device to retain a voltage generated color change in the absence of the applied voltage) of this material was investigated by applying an initial voltage pulse to red-shift the diffraction peak, then disconnecting the electrical leads and measuring the position of the Bragg peak with time. As shown in Figure 2.6d, the P-Ink material displays bistability as the peak position remains stable over an approximately 2 hour period.

The inherent flexibility of our polymer-silica composite PCs makes it possible to integrate them into flexible displays. In addition to rigid devices, we also constructed flexible devices by using ITO-coated poly(ethylene terephthalate) sheets as both the working and counter-electrodes. While these devices are less developed, we were able to obtain similar color shifts as with devices assembled from ITO-glass substrates.

2.4 Results and Discussion - Three-Dimensional Inverse Photonic Ink (IP-Ink)

The previously described 3D Photonic Ink indeed represents a significant contribution to the development of tuneable photonic crystal devices. However, although impressive and elegant, overall the device suffered from a number of drawbacks which effectively hindered the further development of such a technology for end display applications. In particular, the device exhibited relatively low reflectivity (ie. low color contrast), a relatively slow response time, poor color homogeneity upon electrical actuation, and insufficient tuning ranges for full-color
tunability from a single material. Thus, a number of efforts were subsequently put forth in order to ameliorate the performance of the P-Ink device, one of which involved the inclusion of high refractive index nanoparticles within the PFS gel to increase the reflectivity of the active material. Although this modification did increase the reflectivity of the active material, it simultaneously decreased the filling fraction of the polymer which amplified the other already existing problems noted above. However, the most dramatic improvement in device performance was observed when an inverse polyferrocenylsilane opal (instead of a PFS infiltrated silica opal as in the original P-Ink device) was employed as the active component in the display technology.

This subsection of Chapter 2 describes the performance of such a device, dubbed Inverse Photonic Ink (IP-Ink), and highlights its dramatic improvements in performance over the original P-Ink system. It should be emphasized here that it was the observation of such notable improvements which eventually lead to the use of an inverse PFS opal as the active material in the Photonic Ink display technology, the further development of which is being pursued by Opalux Inc.

The methodology used to prepare the inverse PFS opals is illustrated in Figure 2.7a. Note that the precursor to the PFS opal is simply the original P-Ink material which recall consists of a PFS gel infiltrated silica opal. Thus, to arrive at the inverse PFS opal, the composite is first prepared according to the methods outlined in 2.2 and 2.3. Following the crosslinking step and removal of polymer overlayer, the silica spheres of the polymer/silica opal composites were removed upon treatment with 1-2% aqueous hydrofluoric acid. Because the composites are mounted on glass, HF etching yields free standing inverse PFS opals which can be subsequently collected onto ITO coated glass for electrical analysis and actuation. Figure 2.7d includes a top-down SEM image of the opal prior to PFS infiltration which confirms face-centered cubic close packing of the silica spheres of 270 nm diameter. Figure 1e includes an SEM image of the resulting inverse PFS gel opal revealing a 3D periodic structure consisting of a network of ordered macropores connected to one another via ordered mesopores corresponding to the silica microspheres where they touched, respectively. The fabricated inverse opal is a material of periodically varying refractive index with periodicity commensurate with visible wavelengths and thus the material is diffractive.

Figure 2.7c consists of reflectance spectra taken at various stages throughout the inverse opal fabrication process. The red curve centered at 603 nm corresponds to the reflectance
Figure 2.7. a) Schematic representation of the preparation of PFS-based inverse opals. b) Molecular structure of the electroactive polymers employed in active opals. c) Evolution of the Bragg peak throughout the opal, opal composite and inverse opal fabrication process with the green curve corresponding to the inverse PFS opal, the red curve to the silica opal, and the black curve to the PFS/silica opal composite. d) SEM image of a silica opal prepared with 270 nm diameter silica spheres. e) SEM image of an inverse polymer gel opal templated by 270 nm silica spheres. The scale bars of both d) and e) represent 3 μm.
spectrum of the bare opal prepared from silica spheres with a diameter of 270 nm. Following infiltration of the opal with the PFS polymer gel, the reflectance of the resulting composite (black curve with a stopband maximum at 686 nm) is red-shifted by 84 nm and the stopband intensity decreased by 30% relative to the bare silica opal. Finally, the desired polymer inverse opal exhibited a Bragg reflectance peak centered at 538 nm which was blue-shifted by 65 nm and 150 nm relative to the bare silica opal and polymer gel infiltrated silica opal composite, respectively. The aforementioned observed changes in the reflectance spectra from one material to another in the series are attributed entirely to differences in refractive index contrast between the opaline lattice and the material (or lack thereof) in the interstitial void volume. The reflectance spectra agree well with the theoretical prediction of the Bragg-Snell equation, eqn. 1.1.

Figure 2.8 includes cyclic voltammagrams of equal area (1 cm x 1 cm) and thickness (~5.2 microns) inverse polymer gel opal (IP-Ink) and a polymer gel infiltrated silica opal film (P-Ink) on ITO coated glass acquired in a three-electrode configuration and overlayed for comparative purposes. Both the inverse polymer gel opal and the polymer gel/silica opal films display electrochemical features characteristic of main chain ferrocene-based polymers, exhibiting two broad and overlapping redox waves.[25] The obvious difference however, is the larger peak current measured from the inverse polymer gel opal (dark plot) compared to the polymer gel opal composite (lighter plot). This indicates that a greater volume of material is sampled over the timescale of the CV measurement in the inverse polymer gel opal which most likely can be attributed to significantly enhanced electron and ion transport compared to the polymer gel infiltrated silica opal composite. As will be emphasized below, these enhanced transport properties are desirable for a range of active opal applications and are particularly responsible for the superior performance of IP-Ink.

Electrical color tuning of IP-Ink is again achieved within a two-electrode electrochemical cell consisting of the inverse polymer gel opal supported on ITO–glass serving as the working electrode separated from an ITO–glass or FTO-glass counterelectrode by a hot-melt ionomer spacer (Dupont®). The electrolyte consists of lithium triflate in butyrolactone and again potentials are applied to the cell by connecting the top face of each electrode to the leads of a potentiostat or another suitable power supply.

As expected, the inverse polymer gel opal (IP-Ink) exhibited similar voltage dependent diffraction characteristics as the polymer gel opal composite (P-Ink). For example, when an
oxidative potential is applied to the electrode bearing the inverse polymer gel opal, the color reflected is red-shifted owing to electrolyte influx into the polymer gel, which recall is necessary

Figure 2.8. Cyclic voltammagrams of equal area (1 cm x 1 cm) and thickness (5.2 microns) films on ITO coated glass of a inverse polymer gel opal and a polymer gel/silica opal composite acquired in a three-electrode configuration and overlayed for comparative purposes. Each voltammagram was acquired at a scan rate of 10 mV/s with the black curve corresponding to the inverse opal and the red curve to the polymer infiltrated silica opal composite.

to maintain charge neutrality. Applying a reducing potential drives the reverse process, with electrons being injected back into the polymer and the anions being expelled out into the electrolyte. This mechanism is operative in both opal systems described herein hence the similar optical response to the electrical stimulus. The plot of Figure 2.9b illustrates the ability of inverse polymer gel opal film to display voltage-dependent continuous shifts in reflected color as the Bragg peak is swept throughout the entire visible spectrum with voltages in the range 1.2 V - 2.8 V applied in 0.1 V increments.

While IP-Ink and P-Ink both display voltage tunable structural color, the former is notably superior in all aspects of device performance. First, the range over which the stopband of the inverse PFS opal with a crosslinker content of 5 mol% and under an applied bias of 2.8 V was observed to be approximately 300 nm (see Figure 2.9b). In contrast, a tuning range of only
Figure 2.9. a) Schematic representation of the electrochemical cell fabricated for the electrical actuation of the inverse PFS opal. c) Photographic and b) spectroscopic representation of full color tuning achieved via manipulation of applied voltages, with larger color shifts accompanying larger voltage biases. The crosslinker concentration in this sample was 10 mol%.

210 nm at a significantly lower crosslinker content of 0.5 mol% and a larger bias of 3.2 V was observed with the PFS gel silica opal composite. Second, a significantly larger color tuning range was accessible at significantly lower potentials for the inverse PFS opal compared to the PFS silica opal composite. For example, at 10 mol% crosslinker concentration and under an applied voltage of 2.4 V, the former displayed a peak to peak shift of 240 nm whereas the latter, at a crosslink concentration of 0.5 mol% and under a 2.4 V bias, a shift of 100 nm was obtained. Third, these results are scientifically important and technologically significant not only because a 300 nm tuning range affords the possibility of being able to fabricate a single PC device capable of spanning the entire visible spectrum, namely a single material for all colors (Figure 2.9a and
2.9b), but also because the stability (mechanical, thermal, electrochemical) of the polymer gel in such devices has been observed to improve with increasing crosslinker content. Samples with low crosslink densities suffer stability issues and so use of lightly crosslinked samples is impractical from a commercial perspective. It is much more desirable to fabricate a device consisting of a suitably crosslinked polymer gel in the 5-10 mol% range to ensure stability which is simultaneously capable of swelling to extents necessary for full color tuning.

The impressive performance of the inverse polymer gel opal is attributed primarily to its highly porous structure which increases the specific surface area of the film in contact with electrolyte. In the composite PFS silica opal composite in contrast to the inverse system, the electrolyte is only in contact with the top surface of the film prior to electrical actuation. Therefore, in order for the polymer gel to swell completely and homogeneously, on applying a positive potential to the film, ions are forced to diffuse all the way through an effectively non-porous matrix of polymer and silica opal to find the electrode surface, a distance which can fall anywhere in the range of 5-10 microns. However, for the inverse polymer gel opal the ordered interconnected macropores and mesopores extend throughout the entire electroactive material and thereby decrease the diffusion lengths of electrons and ions into and out of the polymer gel necessary for maximal swelling of the inverse opal lattice. The overall effect of such enhanced diffusion capacity is a decrease in the cell resistance as is evident by the lower potentials necessary to drive the device (as described above).

The kinetics of the color tuning of a 5 mol% crosslinked inverse PFS opal have been investigated and the results displayed in Figure 2.10. The first plot provided is the chronoamperometric response of the two electrode device, which essentially includes the monitoring of the current running through the device upon application of two potential steps. In this experiment, the current was first measured following application of a potential step of 2.6 V over a 10 s interval (corresponding to the forward scan) followed by an instantaneous polarity switch with an application of -2.8 V for 20 s (corresponding to the reverse scan) potential step. The rapid decay of the current from an initial value (observed with both the forward and reverse biasing) and acquisition of diffusion control almost immediately following biasing is testament to the good electronic conduction and ionic mobility present in the inverse polymer gel. In addition to the current, the Bragg peak shift was also monitored over the same time range of the applied voltage pulses, Figure 2.10b. Initially, upon application of the 2.6 V forward bias, swelling of the polymer gel with concomitant red-shifting of the stopband is relatively minute,
Figure 2.10. a) Chronoamperometric response of the two electrode inverse polymer gel opal device upon application of two potential steps, the first at 2.6 V for 10 s and the second at -2.8 V for 20 s. b) Evolution of the Bragg peak maximum with time over the same time intervals as shown in a). The crosslinker concentration for this sample was 5 mol%.

with a shift of only 41 nm occurring after 4 s of biasing. At the 4 s instant however, a dramatic red-shift of 194 nm is observed over a 1s interval followed by a tapering of the stopband response with the remainder of the forward biasing. The large stopband shift at 4 s is believed to occur as a result of a significant increase in the hole-conductivity of the polymer gel originating from a p-doping effect. At the 10 s mark, the polarity is switched in order to reverse the swelling process and monitor the kinetics of the contraction of the polymer gel to its original state. The most significant blue-shift is observed initially as soon as the polarity is reversed. As the negative bias is continually applied, blue-shifting persists relatively slowly with a lesser shift occurring with each passing second. The more sluggish behavior of the reverse scan is attributed primarily to the p-type character of the polymer (which is believed to be a poor conductor of electrons) as well as a “de-doping effect”[26]. For other voltages, similar stopband shift versus time profiles were obtained, the only difference being that larger shifts were observed with larger applied voltages for the same time intervals in accordance with the data displayed in Figure 2.9b.

The work described herein provides the first example of an electroactive inverse opal that offers full color at very low drive voltages with unprecedented wavelength shifts traversing the ultraviolet, visible and near infrared spectral ranges. Technological hurdles to be overcome
include reflectivity enhancement, boosting the speed of the reverse scan and cycle lifetime. Adding nanoparticles to the polymer gel can enhance color contrast and provide control over viewing angle while tailoring the device components can reduce cell resistance enabling full color tuning with applied voltages below 2 V.

2.5 Summary

We have successfully prepared for the time broadband electrically tunable PCs based on opal and inverse opal structures. PCs can clearly provide electronic displays with unique and attractive characteristics. In contrast to any other display technology, these materials can reflect color whose wavelength is voltage tunable throughout the visible range without the need for expensive color filters or sub-pixellation of red-green-blue elements, thereby wasting much less of the accessible light output. The aforementioned coupled with an inherent bistability and low operating voltage offer power requirements compatible with a number of applications such as outdoor and indoor signage, portable electronics, architectural panels, active camouflage and full-color electronic paper. Since PC theory is scalable throughout the whole electromagnetic range, P-Ink and IP-Ink coatings can also be readily integrated into devices modulating UV, visible, or infrared light reflectivity and transmissivity.

2.6 References


Chapter 3
Passive and Active Nanoparticle One-Dimensional Photonic Crystals


3.1 Introduction

Although a subject of great scientific merit, relatively little has been reported in the literature pertaining to the development of tuneable one-dimensional PCs. As mentioned in the introductory section, cholesteric liquid crystals (CLCs) are viewed as 1D PCs and Kent Displays[1] and MagInk[2] are two companies that have developed reflective electronic displays based on such materials in a solid and flexible form. In CLC systems, each pixel can be electrically tuned between two states, colored, with the particular color reflected being dependent on the pitch length of the cholesteric material, and noncolored corresponding to completely randomly oriented LCs. Certainly a holy grail in the CLC field is the development of a single CLC system capable of full color tuneability (analogous to IP-Ink of Chapter 2), that is the development of a CLC system with a dynamically tuneable pitch length. So far, a patent[3] filed claims such a capability however no report in literature supporting this claim has surfaced. In addition to the aforementioned CLC systems, Thomas et al. also just recently reported on the electrochemical tuning of all-polymer one-dimensional PCs prepared by block copolymer self-assembly.[4]

Although the original Photonic Ink technologies displayed impressive performances, either form described in the previous chapter still suffered from low reflectivities and an unacceptable color contrast for commercial applications. To address this problem, we turned our focus to one-dimensional photonic crystals (section 1.1 and 1.1.1.2) and asked the question of whether Photonic Ink could instead be prepared using a colloidal one-dimensional photonic crystal rather than a colloidal three-dimensional system. The advantages associated with employing a 1D PC for the P-Ink application include; (i) higher reflectivities (ie. better color contrast) as in 1D PCs, one can make use of higher refractive index materials affording higher reflectivity coefficients at each interface; (ii) the use of thinner active layers (ie. usually below 1
µm which should be compared with the 5-10 µm thickness of the active materials of 3D P-Ink) which would inevitably improve color switching rates and electromechanical properties; and (iii) a broader range of materials can be employed in this system since the nanoparticle dispersions need not be monodisperse for this application. However, as mentioned above, in order to prepare a 1D P-Ink, one must begin from a colloidal 1D PC. It must be colloidal because our method of fabrication involves infiltration of the PC with an electroactive polymer gel and thus the 1D PC must be porous. To satisfy this requirement, we propose that the entire PC be fabricated from nanoparticles (NPs) spin-coated or dip-coated from the appropriate dispersions. Once the nanoparticle 1D PC is obtained, we are then able to employ the same methodology as that used for 3D P-Ink in order to effectively arrive at an electrically tunable 1D PC. Prior to discussing the details of the fabrication of nanoparticle 1D PCs, a brief theoretical description of 1D PCs is provided. It is relevant to provide this point at this stage of the discussion because the remainder of the work described in this thesis focuses primarily on devices bearing 1D PCs in various forms.

When white-light impinges on a 1D PC, as shown in Figure 3.1, each layer boundary causes a partial reflection of an optical wave with many boundaries giving rise to multiple reflections. Provided that the variation in refractive index or dielectric constant is periodic,

![Figure 3.1. Schematic of a quarter-wave 1D PC where \( n \) refers to the refractive index of the materials (both high and low \( n \)) and substrate employed.](image)
encountered when each alternating layer of equal refractive index is deposited with the same geometric thickness, the many reflected waves can constructively interfere effectively creating a high-quality reflector.[5] A special class of 1D PC, referred to as a quarter-wave stack, is formed if the optical thickness of each layer (i.e. \( n_{\text{eff}}d \) where \( n_{\text{eff}} \) is the refractive index of the layer with thickness \( d \)) is equal to \( \lambda/4 \), where \( \lambda \) corresponds to the central bandgap wavelength. For such a multilayer architecture, all layers have a common phase thickness causing the same two-way travel-time delay for light which physically ensures that every reflected ray from every interface undergoes constructive interference. Provided that the refractive index contrast is sufficiently high, a material with intense and broadband reflectivity (or equivalently, a bandgap) centered at \( \lambda \) is subsequently formed. The reflectance of a quarter-wave stack centered at \( \lambda \) in air is given by eqn. 1[6]:

\[
R = \left( \frac{(1 - Y)}{(1 + Y)} \right)^2 \times 100\%
\]

with

\[
Y = \left( \frac{n_2}{n_1} \right)^N \left( \frac{n_2}{n_s} \right)^2
\]

where \( n_1, n_2 \) and \( n_s \) are the refractive indices of the low-index material, the high-index material, and the substrate, respectively in the multilayer film. From eqn. 3.1, it is evident that the reflectance increases with increasing the number of bilayers, \( N \), as well as by increasing the refractive index contrast \( (\Delta n = n_2 - n_1) \) of the layers. The width of the reflectance band and thus of the bandgap of a quarter-wave PC is given in eqn. 3.3[7]:

\[
\Delta \omega = \frac{4\omega_{\text{MAX}}}{\pi} \sin^{-1} \left( \frac{n_1 - n_2}{n_1 + n_2} \right)
\]

From such, it is evident that the bandwidth is also dependent on the refractive index contrast between the two materials in the multilayer structure. Owing to the fact that the reflectance and bandwidth is maximized in the quarter-wave configuration, 1D PCs with either a large number of bilayers or a large refractive index contrast are capable of serving as very efficient mirrors (more efficient than metallic mirrors) for light over a given frequency range and thus, such structures commonly find use as optical filters or as mirrors in optical cavities.
It should be mentioned however, particularly for the purposes of this thesis and this chapter, that 1D PCs need not satisfy the quarter-wave configuration to be reflective. The major difference here being that not all reflected rays from every boundary surface are in phase to undergo perfect constructive interference. Nevertheless, brilliant “structural color” (originating purely of course from the reflectivity of the material), as will be demonstrated below, which is comparable or even sometimes superior to that of opals, can be displayed from such nonquarter-wave 1D PCs. In fact, for applications such as displays and sensors, high color purity is often desired and this can only be obtained from a 1D PC by adhering to a nonquarter-wave configuration. The first-order central wavelength $\lambda$, of a 1D PC under nonquarter-wave conditions can be expressed mathematically by the Bragg equation:

$$\lambda_B = 2(n_1d_1 + n_2d_2)$$

where $n_1$ and $d_1$, and $n_2$ and $d_2$ are the refractive indices and thicknesses of the low-index and the high-index material, respectively, in the multilayer film. Particularly interesting for the application described in this chapter is that the Bragg equation indicates that the band of wavelengths reflected by a 1D PC is dependent on the optical thicknesses, $n_1d_1$ and $n_2d_2$. Thus, by simply manipulating the optical thicknesses of each layer by either a change in geometric thickness or effective refractive indices, the color of the thin film heterostructure can be tuned across a range of wavelengths of the optical spectrum. Note here that the formalism is quite analogous to that already used for opals.

In the first subsection of this chapter, we describe our attempts at expanding upon the foundational work of our group and others in the area of 1D PCs as we report on a generalization of the nanoparticle spin-coating approach to 1D PCs by preparing nonquarter-wave 1D PCs from various combinations of SiO$_2$, TiO$_2$, SnO$_2$, and Sb:SnO$_2$ (ATO) nanoparticles. As will be shown, to prepare a nanoparticle 1D PC, a pair of two different metal oxide nanoparticle compositions was sequentially spin-coated from carefully engineered colloidally stable dispersions to create a PC with the desired number of layers. The appeal of the methodology lies not only in the scope of the materials composition field that can be employed but also in the ease and speed by which high structural and optical quality nanoparticle 1D PCs can be prepared over large areas. As this thesis will attest, it is expected that this genre of nanoparticle 1D PC will be suitable for a range of applications in optics and optoelectronics. In the second subsection of this chapter, we explore one such optoelectronic application, namely the development of 1D Photonic Ink, an electrically
tuneable 1D PC. In addition, in Chapter 4, we demonstrate how such materials can be employed as resonators in distributed feedback lasers.

### 3.2 Experimental Details

*Materials and Instrumentation:* SiO$_2$, SnO$_2$, and ATO nanoparticles were purchased from Aldrich (Ludox CL-X, 30 wt.%), Nyacol Inc. (15 wt.%), and Alfa Aesar (Nanotek, 50 wt.%), respectively. TiO$_2$ nanoparticles were prepared according to literature protocol.\[9,10\] Briefly, titanium ethoxide was added dropwise to 0.1M HNO$_3$ at room temperature under vigorous stirring. The suspension was then peptized by stirring at 80°C for 8 hrs. The resulting dispersion was filtered to remove any agglomerates and subsequently diluted to the desired concentration. The spin-coater used was a Laurell WS-400A-6NPP/LITE. Reflectance spectra in the range 350 to 850 nm were collected using an Ocean Optics SD2000 fiber–optic diode–array dual–channel spectrometer interfaced with an ocular tube of an Olympus BX41 binocular microscope by fibre optics, using the microscope’s light source (Olympus TH4–100) and a 20x working distance objective (Olympus 20X/0.40 BD LMPlan FI). SEM images were obtained on a Hitachi S-5200 model operated with an accelerating voltage of 1.5 kV. High-resolution scanning transmission electron microscopy (STEM) images were obtained using Hitachi HD-2000 in the Z-contrast mode at an accelerating voltage of 200 kV and emission current of 50 μA. AFM imaging was performed on a Digital Instruments / Veeco Bioscope scanning probe microscope using a Dimension scanner interfaced with a Digital Instruments Nanoscope IIIA controller. Images were acquired in contact mode using V-shaped 150 micron long pyramidal DNP-S tips at a scan rate of 1Hz as 512 x 512 pixel data sets. All images were captured in the downward scan direction at a scan angle of 90 degrees. Roughness analysis was performed on a 10 micron square field of view using the Nanoscope software version 5.30R3sr3. Spectroscopic ellipsometry analyses were performed with a Sopra GES-5E ellipsometric porosimeter at a fixed incidence angle of 70.15° in the range 1.5–3.0 eV. The modeling and regression of the ellipsometric spectra were performed using the software Winelli II© provided by the ellipsometer manufacturer. Optical spectra were simulated by scalar-wave approximation transfer-matrix calculations in a non-commercial software package developed by our group. The crystal phase and particle size of the films were analyzed by X-ray diffraction (XRD) using a Siemens D5000.
diffractometer and Cu-kα line as the X-ray source. The Rietveld refinement was carried out with Bruker AXS general profile fitting software Topas™.

**Preparation of Nanoparticle 1D PCs:** Piranha and air-plasma treated glass slides, fluorine-doped tin oxide (FTO), or silicon wafers were used as the substrates for the nanoparticle 1D PCs. In general, to prepare a single nanoparticle 1D PC, a pair of two different metal oxide nanoparticle compositions was spin-coated from modified dispersions iteratively until the desired number of layers was deposited. Prior to spin-coating each dispersion was stirred thoroughly, sonicated for 10 mins., and filtered through a 0.20 µm pore syringe filter to remove any aggregates. Following each bilayer deposition, for the SiO₂/TiO₂, SiO₂/SnO₂ and SiO₂/ATO nanoparticle 1D PCs, thermal treatment involving bathing at 450°C for 20 mins. was incorporated into the methodology. For the SnO₂/TiO₂ and ATO/TiO₂ 1D PCs, thermal treatment under the same conditions as mentioned above was required following each layer deposition.

**Preparation of 1D P-Ink:** See the Experimental Section of Chapter 2, Section 2.2. The method of fabrication of 1D P-Ink is identical to that of 3D Inverse P-Ink, the only difference being that a nanoparticle 1D PC was employed in replace of a 3D PC (ie. SiO₂ opal). Following PFS infiltration and crosslinking, the composite PFS infiltrated 1D PC is immersed in aqueous 1 vol.% HF for 1 min. in order to etch the SiO₂ nanoparticles which leaves behind an active material consisting of alternating layers of porous PFS polymer and PFS infiltrated TiO₂ nanoparticles.

### 3.3 Results and discussion - Nanoparticle One-Dimensional Photonic Crystals

Of the nanoparticles employed for the preparation of nanoparticle 1D PCs, only the TiO₂ particles were synthesized and the remainder purchased as aqueous dispersions and diluted to the concentrations (Table 3.1) required for PC fabrication. Wide angle X-ray diffraction (Figure 3.2) confirms that the prepared TiO₂ particles crystallized in the anatase form. Invoking the Scherer equation to the (101) peak of the acquired diffractogram yields an average TiO₂ particle diameter of 10 nm, a value that is consistent with particle sizes determined by STEM (Figure 3.1b) and SEM where particles in the range of 6 to 12 nm were observed. The TiO₂ dispersion was
Figure 3.2. Wide angle X-ray diffractogram and a high resolution STEM image of the TiO$_2$ particles used in the preparation of TiO$_2$ containing 1D PCs are shown in a) and b), respectively.

therefore quite polydisperse. However, as will be highlighted below, what is key to the realization of the application described herein is that the particles of the dispersions employed be small (to reduce light scattering by individual particles) rather than monodisperse.

Figure 3.3 includes cross-sectional SEM images of SiO$_2$/TiO$_2$, SiO$_2$/SnO$_2$, TiO$_2$/SnO$_2$, TiO$_2$/ATO, and SiO$_2$/ATO nanoparticle 1D PC structures prepared by iteratively spin-coating from the appropriate aqueous nanoparticle dispersions. As diffraction requires, each 1D PC displays a periodic multilayer structure corresponding to equal thicknesses of alternating layers of two materials bearing a difference in refractive index along the direction normal to the sample substrate. With the exception of the ATO based PCs, the interfaces between the materials selected for each are also well defined and uniform with minimal roughness, a necessity for fabricating nanoparticle 1D PCs with “good optical quality” as poor interfaces serve as sources of deleterious incoherent scattering.

We here define a “good quality” nanoparticle 1D PC as an optical structure exhibiting uniform color over relatively large areas (ie. 2 cm x 2 cm) which also exhibits a minimal density of comets and striations (both such being the more common defects encountered with the spin-coating process). Comets usually occur when large particles (particle aggregates and impurities such as dust) present in the dispersion or on the film prior to solution dispensing inhibit the normal flow patterns of the solution on the substrate. The comets present as significant incoherent scattering centers with color gradients extending radially from their respective center. In our experiences, comet formation can be almost entirely prevented by working in meticulously clean environments (ie. a clean room) as well as by filtering dispersions at the
dispensing stage of the spin-coating process through 0.20 µm pore Nylon syringe filters. In addition to comets, striations are radial lines of thickness variability which form as a result of evaporation driven surface tension effects. If a given 1D PC is simultaneously striation ridden as well as diffracting at optical wavelengths, the striations often appear as a different color than the underlying film. Based on our experiences, striations are primarily caused by solvent evaporation being too rapid (resulting from the use of too volatile a solvent) or by using too fast a rotation and acceleration speed during the spin-coating process. To address the former drawback, it was found that applying spin-rates in the range of 2000-5000 rpm applied for 20 seconds yielded the best quality films. If spin-rates of >5000 rpm were employed, striations always developed regardless of the dispersion composition. With regards to rapid solvent evaporation, all dispersions employed in our study were aqueous which inhibited the prevalence of Marangoni effects which inevitably lead to striation formation. The rapid evaporation of volatile solvents can cause an increase in the concentration of water and/or other less volatile species in the surface forming layer. If the surface tension of this layer is greater than that of the initial solution then an instability is created where the higher surface tension actually draws material in at...
Figure 3.4 a) and c) are the AFM and optical microscopy image of a SiO₂/TiO₂ 1D PC prepared from an aqueous SiO₂ dispersion and 1:1 (v:v) water:methanol TiO₂ dispersion. b) and d) are the AFM and optical microscopy image of SiO₂/TiO₂ 1D PC prepared from an aqueous SiO₂ dispersion and aqueous TiO₂ dispersion.

regular intervals and the spaces in-between are more able to evaporate, and surface relief develops."^{11} This particular effect occurs most commonly when methanolic or ethanolic dispersions are employed and so can be almost prevented altogether if aqueous dispersions are used for the process. Figure 3.4 compares the surface profile as well as optical properties, using AFM and optical microscopy of two SiO₂/TiO₂ nanoparticle 1D PCs whereby the first was prepared from purely aqueous dispersions of SiO₂ and TiO₂ and the second prepared from an aqueous dispersion of SiO₂ and a 1:1 by volume water:methanol, TiO₂ dispersion. The 1D PC
fabricated from just aqueous dispersions is evidently superior as it is virtually striation free and exhibits a lower surface roughness (2.25 nm versus 2.68 nm).

In addition to the aforementioned, other important measures were taken in order to build such “high quality” PCs. Firstly, with every spin-coating step, it was necessary to ensure that the dispersion to be coated, exhibited good wettability of the surface of the underlying layer onto which it was being deposited. Good wettability is an absolute necessity for ensuring film homogeneity and uniformity upon spin-coating. It is for this reason that, in addition to alleviating Marangoni effects, each of the dispersions used were aqueous and each of the nanoparticles employed were metal oxides as the latter with their abundance of surface hydroxyl groups are hydrophilic. Secondly, the dispersions employed had to exhibit good film forming properties and it is well known that polymers inherently possess this property. In our study, for the TiO\textsubscript{2} and ATO nanoparticle dispersions, it was necessary that high molecular weight polymer additives were introduced to their respective dispersions in order to enhance the film forming properties of the dispersions. In the absence of such polymer additives, the resulting TiO\textsubscript{2} and ATO films suffered from a higher density of defects, particularly striations. High molecular weight poly(ethylene glycol) (PEG) was the polymer of choice due it’s high solubility in water and inertness toward the particles and other additives present in the dispersions. Use of polymers that strongly interact with the particles, such as poly(acrylic acid) often led to immediate or delayed flocculation of the nanoparticles. To this same end, we have also had marginal success using poly(vinyl pyrrolidone) at similar concentrations as PEG. No additives other than water for the purpose of dilution to the desired concentration were introduced into the SiO\textsubscript{2} (Ludox) and SnO\textsubscript{2} (Nyacol) dispersions as such were observed to form films of high quality (at spin rates of 2000-5000 rpm). Both such dispersions were purchased from commercial sources and so their exact contents were not known however, it is suspected that it is the organic content of the dispersion that is primarily responsible for their respective film forming properties. A complete summary of the polymer additives employed along with their respective concentrations in the various dispersions are listed in Table 3.1.

In order to continue with subsequent layer depositions to build the desired 1D PC, it was necessary to remove the organics added to the dispersions following the spin-coating step. It is for this reason that the SiO\textsubscript{2}/TiO\textsubscript{2}, SiO\textsubscript{2}/SnO\textsubscript{2}, and SiO\textsubscript{2}/ATO 1D PCs were thermally treated at 450\textdegree{}C for 20 mins. following every bilayer deposition. For the SnO\textsubscript{2}/TiO\textsubscript{2} and ATO/TiO\textsubscript{2} 1D
Figure 3.5. a) Reflectance spectra of representative nanoparticle 1D PCs. Note in particular the quality of the 14-bilayer SnO$_2$/TiO$_2$ 1D PC. b) Photographs of different compositions of 4-bilayer nanoparticle 1D PCs on glass substrates.

PCs, heat treatment under the same conditions as the other SiO$_2$ based reflectors was employed following every single layer deposition. If not heat treated at the stages described above,
subsequent layer deposition resulted in the dissolution of the organics of the underlying layers which in turn caused interparticle penetration eradicating the necessary well defined interfaces.

Lastly, another parameter of control in the preparation of such nanoparticle 1D PCs concerns the size of the nanoparticles. In all circumstances, better results were attained with smaller particles and preferably, the two different nanoparticle compositions should possess as similar particle sizes as possible in order to ensure minimal nanoparticle interlayer interpenetration upon deposition. For the reflectors described herein, nanoparticles in the size range 5 – 30 nm were used.

Table 3.1. Dispersion compositions and spectroscopic ellipsometry analysis of nanoparticle film

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (wt. %)</th>
<th>Additive (wt.%)</th>
<th>n_{eff} (633nm)</th>
<th>Porosity (%)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO_{2}</td>
<td>5.8</td>
<td>-</td>
<td>1.33</td>
<td>38</td>
<td>125</td>
</tr>
<tr>
<td>TiO_{2}</td>
<td>5.0</td>
<td>1.25-2.5</td>
<td>1.75</td>
<td>34</td>
<td>80</td>
</tr>
<tr>
<td>PEG*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO_{2}</td>
<td>13.9</td>
<td>-</td>
<td>1.45</td>
<td>33</td>
<td>105</td>
</tr>
<tr>
<td>Sb:SnO_{2}</td>
<td>10.1</td>
<td>0.5-1.0</td>
<td>1.24</td>
<td>51</td>
<td>62</td>
</tr>
<tr>
<td>PEG</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*PEG: poly(ethylene glycol), 125 kDa (Aldrich)

Figure 3.5a displays representative optical spectra of the aforementioned series of nanoparticle 1D PCs. For most compositions, spectra for different layer thicknesses or number of bilayers are provided to effectively demonstrate the universality and versatility of the methodology. For each given composition shown and in accordance with the Bragg equation for 1D photonic crystals, the spectral position of the fundamental Bragg peak could be tuned by manipulating the geometric thicknesses or optical thicknesses of the layers constituting the one-dimensional photonic lattice. The thicknesses of the layers could readily be controlled by manipulating either the concentration of colloid in its respective spin-coated dispersion or by the spin-rate of the deposition step or a combination of both. For the work described herein, it was determined that the highest optical quality films could only be obtained if the thicknesses were controlled by both altering the concentrations of the colloids and employing spin-rates in the range of 2000-5000 rpm applied for 20 seconds. The concentrations of each of the colloidal dispersions employed in this study are summarized in Table 3.1.
With regard to spectral features, namely the intensity and bandwidth of the Bragg peaks of the prepared reflectors consisting of the same number of bilayers, as expected they vary from one two-component system to the other. Such phenomena, even though the 1D PCs are non-quarter wave systems, can be understood at least qualitatively by considering eqns. 3.1 and 3.2 which effectively show that the Bragg peak intensity and bandwidth of a given reflector are dependent on the effective refractive index contrast between the two materials making up the 1D PC. In the systems reported here, except in the case of the SiO$_2$/SnO$_2$ 1D PC, it is observed that the higher the refractive index contrast, the greater the intensity, which follow the order: SiO$_2$/ATO ($\Delta n_{\text{eff}} = 0.09$) $<$ SiO$_2$/SnO$_2$ ($\Delta n_{\text{eff}} = 0.12$) $<$ SnO$_2$/TiO$_2$ ($\Delta n_{\text{eff}} = 0.25$) $<$ SiO$_2$/TiO$_2$ ($\Delta n_{\text{eff}} = 0.42$) $<$ ATO/TiO$_2$ ($\Delta n_{\text{eff}} = 0.51$). The lower than expected reflectivity of the ATO dispersions are believed to be due to interlayer interparticle penetration which is evident from the SEMs of Figure 3.3 (see Chapter 5 for further discussion). The bandwidth, owing to the non-quarter wave nature of the fabricated 1D PCs, on the other hand, deviated slightly from this trend but was still observed to change with varying refractive index contrast. The dispersion relations (Figure 3.6), that is how $n_{\text{eff}}$ varies with wavelength (or photon energy), for thin films of SiO$_2$, SnO$_2$, and TiO$_2$ nanoparticles employed in this study were determined by spectroscopic ellipsometry (SE). The method of spectroscopic ellipsometry and how we employed such to determine $n_{\text{eff}}$, film thickness, and extinction coefficient, $\kappa$, and is outlined in Appendix B and briefly discussed here. For each of the samples analyzed, the ellipsometric parameters $\alpha$ and $\beta$, which are intensity independent parameters related to $\tan(\Psi)$ and $\Delta$, respectively (see appendix B and D), through the equations:

$$\alpha = \frac{\tan^2\Psi - \tan^2\Delta}{\tan^2\Psi + \tan^2\Delta}$$
$$\beta = 2 \cos\Delta \tan\Psi \tan\Delta$$

were measured as a function of incident photon energy and a regression analysis was subsequently performed in order to determine the extinction coefficient and index of refraction of the film of interest. $\tan(\Psi)$ and $\Delta$ are determined from the Fresnel coefficients, $r_s$ and $r_p$, of the s and p components of light (see appendix B). Although measuring $\alpha$ and $\beta$ is straightforward, attaining $n_{\text{eff}}$ and $\kappa$ through regression analysis requires detailed knowledge about the film being analysed. For example, a most accurate analysis would account for the porosity of the film, different amorphous and crystalline regions within the film as well as any changes or gradient in the material content across the thickness of the sample. In this initial report, we simplified the SE analysis by assuming that the films are nonabsorbing over the energy range of 1.5-3.0 eV and
acquire the relevant parameters (ie. thickness and $n_{\text{eff}}$) for single layered films (Table 3.1) in two steps. An initial fitting, employed a simple Cauchy Dispersion law to allow the attainment of $n_{\text{eff}}$ and the thickness ($t$). The Cauchy law is the simplest dispersion model for determination of refractive indices, assuming little light absorption over the visible range:

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

**eqn. 3.7**

where A, B and C are the Cauchy parameters, obtained after fitting and $\lambda$ is the wavelength used in the ellipsometric analysis. Materials that show some light absorption in the UV range can be acquired.
modeled by addition of Lorentzian peaks to account for the imaginary part of the complex refractive index.

After obtaining $t$, the material can be remodeled as a mixture of air and a dispersion law for the skeleton material (a known dispersion profile or a Cauchy law can be employed). In this case, the concentration of air in the skeleton material reflects the percentage of porosity.

In this context, spectroscopic ellipsometry (SE) represents an invaluable tool for the characterization of such nanoparticle 1D PCs as the technique allows one to determine the thickness as well as the effective refractive index of every single layer in a given reflector. Such represent the two most important parameters of a 1D PC. As a proof of concept, we attempted to use SE to completely characterize (ie. determine both the thickness and effective refractive index of each layer) a four-bilayer nanoparticle 1D PC of composition $\text{SiO}_2/\text{TiO}_2$ and a three-bilayer nanoparticle $\text{SnO}_2/\text{TiO}_2$ 1D PC. The results of these measurements are provided together in Table 3.2. The data acquired is consistent with structures bearing periodic variation in refractive index along one-dimension. In order to test the validity of the results, using the Scalar-Wave Approximation, we generated a model reflectivity spectrum of 1D PCs based on the parameters extracted from the SE analyses. We subsequently compared the simulated optical spectra to the experimental reflectivity spectra to study the extent to which the two correlate. The agreement was very good for both reflector compositions studied with the best fit being obtained for $\text{SiO}_2/\text{TiO}_2$. In addition, the thicknesses of each of the layers determined by SE agreed very well with values determined by SEM. These results therefore provide credence that SE represents an excellent tool for elucidating the optical constants of nanoparticle 1D PCs, which when combined with appropriate spectral modeling can effectively predict the optical spectra of nanoparticle 1D PCs.

The films prepared, regardless of the composition, demonstrate high optical quality displaying uniform color over a large area with minimal adventitious striations, cracks, and comets, as can be discerned from the photographs shown in Figure 3.5b. Here we observe a series of 1D PCs, each with a different materials composition, effectively demonstrating color reflectivity tuning that spans the entire visible spectral range. It should be noted in the reflectivity spectra of the ATO/TiO$_2$ and $\text{SiO}_2/\text{TiO}_2$ 1D PCs of Figure 3.5a, that the color of each two component composition can be orchestrated to span the entire range of visible spectral wavelengths by simply manipulating the optical thicknesses of the layers comprising the respective 1D PC. This can be achieved by control of dispersion concentration and spin-rate of
the spin-coating deposition step. In our best examples, color uniformity can be achieved over an area of 2 cm x 2 cm with the Bragg peak maximum varying by no more than 5 nm at different spatial locations over the entire area. It is noteworthy that achievement of high optical quality nanoparticle 1D PCs, with a broad composition range of materials, represents a significant step towards the development of any practical device that requires high structural and optical uniformity over large areas.

It should be emphasized that not only do the prepared nanoparticle 1D PCs possess high reflectivity but also significant mesoporosity, which opens up the opportunity, as will be shown in the following section and chapters, for introduction of a variety of materials into the pores (note the analogy again to opals) creating a range of opportunities for the development of new sensing, optical and optoelectronic devices. In addition, the integrated features of high reflectivity and mesoporosity are inherently general to all nanoparticle 1D PCs but what also should be mentioned are the added value properties, characteristic of the individual nanoparticle materials comprising the 1D PC, such as the electrical conductivity and optical transparency of ATO, which should afford new opportunities in a broad range of fields.

Table 3.2. SE characterization of a 4-bilayer SiO$_2$/TiO$_2$ 1D PC and a 3-bilayer SnO$_2$/TiO$_2$ 1D PC.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
<th>$n_{\text{eff}}$</th>
<th>Material</th>
<th>Thickness (nm)</th>
<th>$n_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (1)</td>
<td>148</td>
<td>1.33</td>
<td>SnO$_2$ (1)</td>
<td>149</td>
<td>1.45</td>
</tr>
<tr>
<td>TiO$_2$ (1)</td>
<td>33</td>
<td>1.75</td>
<td>TiO$_2$ (1)</td>
<td>68</td>
<td>1.76</td>
</tr>
<tr>
<td>SiO$_2$ (2)</td>
<td>136</td>
<td>1.34</td>
<td>SnO$_2$ (2)</td>
<td>142</td>
<td>1.47</td>
</tr>
<tr>
<td>TiO$_2$ (2)</td>
<td>31</td>
<td>1.76</td>
<td>TiO$_2$ (2)</td>
<td>78</td>
<td>1.75</td>
</tr>
<tr>
<td>SiO$_2$ (3)</td>
<td>170</td>
<td>1.33</td>
<td>SnO$_2$ (3)</td>
<td>139</td>
<td>1.44</td>
</tr>
<tr>
<td>TiO$_2$ (3)</td>
<td>34</td>
<td>1.75</td>
<td>TiO$_2$ (3)</td>
<td>84</td>
<td>1.75</td>
</tr>
<tr>
<td>SiO$_2$ (4)</td>
<td>167</td>
<td>1.33</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$ (4)</td>
<td>33</td>
<td>1.75</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.7. a) Experimental and simulated reflectance spectra of 4-bilayer SiO₂/TiO₂ nanoparticle 1D PC. b) Experimental and simulated reflectance spectra of 3-bilayer SnO₂/TiO₂ nanoparticle 1D PC. c) Spectroscopic ellipsometry fitting of the SnO₂/TiO₂ nanoparticle 1D PC; α and β are intensity independent parameters related to tan(Ψ) and Δ, respectively.

3.3.1 Planar Defects in Nanoparticle One-Dimensional Photonic Crystals

As discussed briefly in the introduction section, defects can be deliberately introduced into photonic crystals by creating a disruption in dielectric periodicity via the addition or removal of dielectric material in certain regions of the crystal. The effect is a form of optical doping which again is analogous to the electronic doping of semiconductors whereby the deliberate addition of defects creates localized and allowed electronic states within the electronic bandgap. In PCs, a disruption of the dielectric periodicity generates localized photonic states in the photonic...
Figure 3.8. a) SEM images (scale bar = 1 µm) of a SiO$_2$ nanoparticle defect deposited at the center of a TiO$_2$/SnO$_2$ 1D PC. b) and c) include the reflectance spectra of a 5½ bilayer TiO$_2$/SnO$_2$ nanoparticle 1D PC and a 5½ bilayer TiO$_2$/Sb:SnO$_2$ nanoparticle 1D PC bearing 400 nm SiO$_2$ defect layers, respectively. Note the prominent transmission dip present at the center of the Bragg peak of the defect-containing 1D PCs which result from the disruption in dielectric periodicity.

A bandgap which represent narrow ranges of frequencies that are now allowed to propagate through the multilayer structure. In our 1D PCs, a disruption of the dielectric periodicity can be obtained by depositing a layer of different thickness or different refractive index at the center of the multilayer structure. An SEM image of a SiO$_2$ nanoparticle defect deposited at the center of a
TiO$_2$/SnO$_2$ 1D PC is provided in Figure 3.8. This defect containing PC is fabricated by simply spin-coating 2½ bilayers of a TiO$_2$/SnO$_2$ 1D PC (according to the conditions provided in section 3.2 and Table 1) followed by spin-coating of the SiO$_2$ dispersion. Another 2½ bilayers of TiO$_2$/SnO$_2$ nanoparticles are then deposited in an identical manner atop the SiO$_2$ defect layer in order to complete the defect PC. The number and position of allowed photonic states in the photonic stopband can be controlled by modifying the thickness of the defect, which is very easily obtained by a repetition of the deposition process from the same SiO$_2$ nanoparticle dispersion. In Figures 3.8b and 3.8c, we provide the reflectance spectra of a 5½ TiO$_2$/SnO$_2$ bilayer 1D PC and a 5½ TiO$_2$/Sb:SnO$_2$ bilayer 1D PC bearing 400 nm SiO$_2$ defect layers, respectively. Such reflectance spectra contain a narrow region of higher transmittance (i.e., a narrow dip) within the forbidden bandgap frequency range (centered on the photonic stopband). These dips are the fingerprint of the defect states created by intentionally breaking the periodicity. We note however that the periodicity in optical thickness was broken by selecting a material of different composition from the two components of the 1D PC. Thus, both the geometric thickness and effective refractive index of the defect differ from the components of the PC and it is really a combination of each that contributes to the desired effect of the defect. We note that the identical effect could also be achieved in the 5½ TiO$_2$/SnO$_2$ bilayer 1D PC and the 5½ TiO$_2$/Sb:SnO$_2$ bilayer 1D PC by varying the geometric thickness of the central SnO$_2$ or Sb:SnO$_2$ layer, respectively, in such multilayer structures$^{[12]}$. 

The aforementioned defect structures represent dielectric optical microcavities (the optical properties of which were discussed at length in section 1.2) as they essentially consist of two mirrors separated by hundreds of nanometers of an optical medium. Thus, by incorporating an emissive or gain material in the defect region of the PC, these photonic structures become suitable for some of the applications discussed in section 1.2, most notably lasers. In addition, the significant mesoporosity available in such systems coupled with optical amplification paves the way for exciting opportunities for new kinds of sensors whereby vapors and liquids can be gainfully employed as a means to dynamically tune the frequency of the laser emission.
3.4 Results and discussion – One-Dimensional Photonic Ink

Figure 3.9. Schematic of 1D P-Ink. Electrochemically induced swelling of the PFS polymer gel present causes the lattice parameter of the PC to increase which red-shifts the color and Bragg reflectivity of the PC (see spectra on the right).

With the acquisition of porous nanoparticle 1D PCs, made possible as a result of efforts described in the previous section, we investigated the potential of a one-dimensional analogue to the three-dimensional P-Inks described at length in Chapter 2 for applications identical to those intended for the 3D systems. The methodology employed for the preparation of 1D P-ink was analogous to the 3D P-Inks described earlier as it involved; i) preparation of the porous photonic crystal (1D PC) on a conductive and transparent substrate; ii) infiltration of the 1D PC with the PFS based electroactive gel and; iii) electrical actuation of the composite photonic material in a two-electrode electrochemical cell. A schematic of the desired effect is provided in Figure 3.9. Similar to the 3D systems, electrochemical actuation of the polymer causes it to swell or compress, depending on the polarity and magnitude of the applied voltage, and because the polymer lies in good contact with the nanoparticles making up the multilayers in the PC, such behavior is imparted to the PC. The end effect is that electrochemically induced swelling of the polymer gel causes an increase in the lattice parameter of the PC which causes it’s color to red-shift and vice versa.

As mentioned above, the first step in the preparation of 1D P-Ink involves preparation of a porous 1D PC by the spin-coating method described in section 3.2 and 3.3. For this application, we used a 5½ bilayer TiO₂/SiO₂ 1D PC (Figure 3.10a), the reflectance spectrum of which corresponds to the red curve in Figure 3.10c centered at 634 nm. Once the 1D PC was prepared,
Figure 3.10. a) SEM of a 5½ bilayer TiO$_2$/SiO$_2$ 1D PC (scale bar = 1 µm), and b) the same 1D PC following PFS infiltration and SiO$_2$ nanoparticle etching (scale bar = 500 nm). c) Reflectance spectra of the bare 1D PC (red curve), of the PFS infiltrated 1D PC (black curve), and of the SiO$_2$-etched PFS infiltrated 1D PC (green curve).

It was infiltrated with PFS gel components (i.e. PFMVS or PFDVS, a dithiol, and photoinitiator) by drop- and blade-casting and subsequently exposed to UV light for 10 hrs. which again is required in order to effectively crosslink the PFS chains. The reflectance spectrum of the resulting composite (black curve of Figure 3.10c with a stopband maximum at 745 nm) is red-shifted by 111 nm and the stopband intensity decreased by 15% relative to the bare 1D PC. Unlike its 3D opal counterpart, the composite PFS infiltrated NP 1D PC was not electrically tunable in such a state owing primarily to the processing conditions of the 1D PC. Recall that in the preparation of such NP 1D PCs, the multilayered material is thermally treated at 450°C
following the deposition of each nanoparticle bilayer. As a result of such high processing temperatures, it is expected that the particles fuse at their respective contact points rendering the structure compact and unable to dynamically expand and contract following incorporation of the electroactive PFS gel and a suitable oxidizing potential. Therefore, in order to arrive at a structure that is capable of such functional mobility which is superior or at least comparable to the performance of the 3D P-Ink systems, it was necessary to selectively remove one of the nanoparticle layers following PFS infiltration effectively yielding a 1D PC consisting of alternating layers of porous PFS polymer and PFS infiltrated TiO2 nanoparticles. We opted to remove the SiO2 particles since the TiO2 particles possess a significantly larger refractive index and hence afford a final photonic structure with significantly higher reflectivity. Thus, to remove the SiO2 we immersed the PFS infiltrated 1D PC in 1% aqueous HF for 1 min. An SEM of the resulting structure is included in Figure 3.10b confirming the 1D PC structure of the material and it’s corresponding reflectivity spectrum is shown as the green plot in Figure 3.10c. Note that the Bragg peak of the etched 1D PC is blue shifted and the intensity is higher than the bare NP 1D PC. Both such observed phenomena can be attributed to an increase in refractive index contrast (see equations 3.1 and 3.2) between the layers constituting the 1D PC following SiO2 NP removal.

The cyclic voltammogram (Figure 3.11a) of PFS infiltrated NP 1D PC acquired in three-electrode configuration prior to SiO2 etching and as expected, displays two broad redox waves characteristic of polyferrocenylsilanes. Again, the first peak corresponds to oxidation of every other iron atom along the PFS chain, the second to full oxidation of the chain. It was relevant to perform cyclic voltammetry as such measurements confirm that the PFS polymer effectively infiltrates the entire NP PC and makes good electrical contact with the electrode surface, two necessary requirements for P-Ink function and operation.

Electrical actuation of SiO2-etched 1D P-Ink films again was performed by its incorporation into a sealed two-electrode electrochemical cell consisting of the 1D P-Ink composite supported on ITO-glass as the working electrode, a hot-melt ionomer spacer (Dupont), and an ITO-glass counter electrode. As is shown in Figure 3.11b, 1D P-Ink is, similar to it’s 3D analogues, capable of undergoing reversible electrochemically induced swelling and contraction and thus, tuneable color reflectivity. When a positive potential of 2.0 V is applied to the 1D P-Ink for 20s, the reflectance of the material is red-shifted by 200 nm. Again, the process can be reversed simply by applying a reverse bias of -2.0 V. The response time of this device, which
recall is dependent primarily on how rapidly electrolyte can diffuse into the polymer gel, is comparable to that of the original inverse P-Ink. In 1D P-Ink however, not only is the polymer layer porous, as is evident from the SEM of Figure 3.9b, the thickness of the active layer (< 1 µm) is less than an order of magnitude smaller than that in the 3D P-ink systems and thus, electrolyte can penetrate the polymer layer efficiently affording a rapid color change. A tuning range of 200 nm, although representative of a significant portion of the visible spectrum, is in fact inferior to that of 3D inverse P-Ink which recall can be tuned over a range of ~300 nm. Nevertheless, the high reflectivity as well as tolerance of the methodology toward a broad range nanoparticle compositions render this 1D technology as a viable candidate for the desired applications. In particular, we are currently investigating the performance of 1D P-Ink devices bearing each of the materials composition developed as 1D PCs as shown in Figure 3.2, notably with SiO2/SnO2, and SiO2/Sb:SnO2 NP 1D PCs. In such systems, it is expected that the larger electrical conductivity of SnO2 or Sb:SnO2 over that of TiO2 will help facilitate electron transfer to the PFS polymer (particularly on reverse scans owing to the n-type conductivity of such metal oxides) and subsequently lead to enhanced P-Ink device performance.

**Figure 3.11.** a) Cyclic voltammogram of PFS infiltrated SiO2/TiO2 NP 1D PC. b) A demonstration of 1D P-Ink, an example of an electrically tunable 1D PC. The green and red plots correspond to the reflectance spectra of the etched PFS infiltrated 1D PC under no voltage bias and following application of 2.0 V bias for 20 seconds, respectively.
3.5 Summary

Herein, we have established the generality of the spin-coating technique for preparing mesoporous nanoparticle-based 1D PCs from various combinations of a diverse group of metal oxide nanoparticles including SiO$_2$, TiO$_2$, SnO$_2$, and Sb:SnO$_2$. The 1D PC films so prepared, regardless of the composition, demonstrate high structural and optical quality over large areas, which bodes well for their implementation in a range of sensing, optical and optoelectronic devices, especially those whose function and utility would benefit from mesoporosity. We pursued the development of one such optoelectronic device with reduction-to-practice of the first example of an electrically tunable 1D PC which can now potentially serve as a next generation P-Ink device. Electrically tunable 1D PCs could also be integrated very simply into microcavities to afford tuneable LEDs and lasers.

3.6 References

[1] www.kentdisplays.com
Chapter 4
Nanoparticle One-Dimensional Photonic Crystal Distributed Feedback Lasers


4.1 Introduction

As shown in the introductory chapter, the most common resonator structures employed in organic lasing systems are that of a planar microcavity or a 1D PC (commonly referred to as distributed feedback lasers or bandedge lasers).[1] The effect of either resonator structure through phenomena such as reflections, refractions, and interference, is a reorganization of the photon density of states (DOS), \(D(\omega)\) of eqn 1.3, experienced by an optical gain medium embedded within it’s structure. The interaction between the gain medium and resonator structure therefore results in only certain frequencies being favored for lasing. Microcavities support a standing-wave optical field at characteristic cavity mode frequencies and 1D PCs support a standing wave optical field at frequencies overlapping the Bragg stopband edges.

Tessler and co-workers were first to demonstrate an optically pumped organic microcavity laser in 1996.[2] Their laser microcavity, illustrated in Figure 4.1, consisted of a 100 nm thick layer of poly(\textit{para}-phenylene vinylene) (PPV) sandwiched between a pair of mirrors, one a dielectric 1D PC and the other metallic. The laser was fabricated by spin-coating the polymer film onto a broadband, highly reflecting dielectric 1D PC, and then a second partially transmitting silver mirror was deposited on top of the polymer. Following this first study, there have been a number of other studies of organic semiconductor laser microcavities, based on a range of materials.[3-16] It is also important to note that other microcavity configurations have been demonstrated for organic lasers, particularly since the advent of electron beam lithography.
coupled with the solution processability of conjugated polymers. In particular, Fabry-Perot dye laser cavities,\[17\] microring resonators coated around an optical fiber,\[18\] and spherical microcavities\[19\] have been fabricated and exploited for lasing purposes.

With regards to 1D PC resonators, lasers with one-dimensional feedback have been demonstrated using many different organic semiconductors, including derivatives of poly(phenylene vinylene),\[21-27\] polyfluorenes,\[28-34\] and ladder-type poly(paraphenylene).\[35-39\] Such have also been studied in a number of small molecule systems\[40-46\]. In the polymer systems listed above, the 1D PC is most commonly fabricated by interference or electron-beam lithography on Si or quartz. As illustrated in Figure 4.2, the e-beam generated pattern in Si or quartz can then be transferred directly by nanoimprinting into the conjugated polymer or a thermoplastic onto which the conjugated polymer can be subsequently spin-cast. In the case of DFB system using a quartz 1D PC, the conjugated polymer can be directly spin-cast onto the quartz owing to it’s optical transparency. For the small molecule DFB systems, such materials can be simply evaporated onto the 1D PC fabricated by the methods noted above.
Figure 4.2. a) Illustration of the process of nanoimprinting. Here, a Si master is prepared by e-beam lithography. The e-beam generated pattern is then imprinted into a gain material, (SY = Super Yellow, see structure on right) under pressure and heating. The method can be employed to fabricate, b) 1D, and c) 2D, PCs for DFB lasing. The image in a) was taken with permission from reference [20]. Copyright Wiley-VCH. Images b) and c) were taken with permission from reference [1]. Copyright Macmillan Publishers Ltd.

Nanoimprinting can also be used to prepare 2D PC resonators (Figure 4.2) and a number of examples of 2D PC conjugated polymer lasers have been demonstrated thus far.²⁷⁻⁵²
Each of the aforementioned studies made use of resonators fabricated by top-down methodologies. Although numerous bottom-up methods exist for preparing colloidal PCs operating at optical wavelengths (see introduction), little progress has been made toward the fabrication of lasers with bottom-up colloidal PCs serving as the resonator structures. Shkunov et al. produced a bandedge laser system which used a dye solution as the optical gain medium infiltrated into the interstices of a silica opal (resonator). However, because the refractive index contrast between the gain medium and silica spheres was very low, a long attenuation length of Bragg diffraction was present. Thus to achieve the desired resonator effect, the colloidal crystal was required to be relatively thick (i.e., millimeter scale). Recently, a bandedge laser was demonstrated using polymerized crystalline colloidal arrays of mesoporous silica particles. Other types of colloidal PC lasers have also been reported; specifically, lasing in a planar microcavity composed of a partially-reflecting mirror made from a colloidal crystal and the other mirror made from a highly reflecting dielectric 1D PC, and lasing at a planar defect mode of colloidal crystals. In both cases, dye molecules were located between the two mirrors of the colloidal PC microcavities. However, although the aforementioned are indeed relevant and interesting, each of the colloidal PC laser systems reported suffered from a low refractive index contrast between the gain medium and the resonator structure which inevitably lead to high lasing thresholds and a more complicated fabrication process. In addition, other challenges in this field which need to be overcome include the physical durability and the development of a simple and economical fabrication process of the lasing system. We herein report a DFB (or bandedge) lasing system consisting of a gain material infiltrated nanoparticle 1D PC which represents a step toward a solution to each of the aforementioned drawbacks. Most notably, the problems associated with low refractive index contrast are easily overcome by making use of high refractive index nanoparticles as one or both of the layers in the resonator 1D PC.

A close consideration of conventionally employed DFB lasing structures described earlier and shown in the literature immediately reveals the viability of using our NP 1D PCs as resonators in DFB lasers. The nanoparticle 1D PCs can be prepared with excellent optical quality over large areas and most significantly, such PCs are porous which allows for infiltration with functional materials, such as conjugated polymers or laser dyes, which in turn can lead to the fabrication of composites whereby the emitter’s emission can be modulated by the photon density of states of the 1D photonic crystal. We exploit this interaction in order to produce efficient distributed feedback lasing from a composite Rhodamine 6G infiltrated (Section 4.3)
and a poly(phenylene vinylene) (PPV) infiltrated nanoparticle one-dimensional photonic crystal (4.4).

4.2 Experimental Section

*Materials and Instrumentation:* SiO$_2$ nanoparticles were purchased from Aldrich (Ludox SM-30). TiO$_2$ nanoparticles used in this work were prepared according to literature protocol$^{[57]}$ and their synthesis is described in section 3.2 of chapter 3. Rhodamine 6G was purchased from Exciton and was used as received. PPV was prepared by the precursor route reported originally by Wessling$^{[58]}$. Gel Permeation Chromatography (GPC) data was acquired relative to polystyrene standards in THF on a Viscotek GPCmax The spin-coater was a Laurell WS-400A-6NPP/LITE. Reflectance spectra in the range 350 to 850 nm were collected using an Ocean Optics SD2000 fiber–optic diode–array dual–channel spectrometer interfaced with an ocular tube of an Olympus BX41 binocular microscope by fibre optics, using the microscope’s light source (Olympus TH4–100) and a 20x working distance objective (Olympus 20X/0.40 BD LMPlan FI). SEM was performed using a Hitachi S–5200 (10 – 15 kV, 15 mA). Laser Confocal Microscopy was performed on a Leica TCS SP2 model with a HeNe laser operating at 1.2 mW under 50x magnification. Ellipsometry was performed with a Sopra GES5E spectroscopic ellipsometer. For the R6G lasing measurements, the light source we used the second harmonic of 1064 nm Nd:YAG TEM00 pulsed laser (Quanta System, repetition rate 1 Hz, pulse duration 5 ns). Spectra have been recorded with a nitrogen cooled CCD (Spex 2000) coupled to a polychromator (Triax 190 from J-Horiba), with a bandpass of 0.2 nm for signal detection. Excitation laser light has been removed by using a proper notch filter (Edmund Optics). To measure the laser emission of the PPV infiltrated NP 1D PC sample we used the second harmonic of an amplified Ti:Sapphire tunable laser (Coherent Mira). The selected wavelength was 800 nm, in order to have the second harmonic at 400 nm. The laser emission was collected normal to the substrate, by an optical multichannel analyzer (OMA) (1.2 nm resolution). X-ray data were collected on a Bruker-Nonius Kappa-CCD diffractometer using monochromated Mo-K$_\alpha$ radiation and were measured using a combination of $\phi$ scans and $\omega$ scans with $\kappa$ offsets, to fill the Ewald sphere. The data were processed using the Denzo-SMN package.$^{[59]}$ Absorption corrections were carried out using SORTAV$^{[60]}$. The structure was solved and refined using SHELXTL V6.1$^{[61]}$ for full-matrix least-squares refinement that was based on $F^2$. All H atoms bonded to C atoms were included in
calculated positions and allowed to refine in riding-motion approximation with U~iso~tied to the
carrier atom. H atoms bonded to the O atoms were refined independently with isotropic
displacement parameters.

**Preparation of PPV Precursor:** The monomer p-xylene-bis(tetrahydrothiophenium chloride) was
obtained via the reaction of dichloro-p-xylene (0.75 M) with tetrahydrothiophene (2.25 M) at
50°C in a 80:20% by volume methanol:water solution under N₂ overnight. The product was
subsequently obtained by evaporation of the methanol followed by precipitation from cold
acetone. Precipitation was not immediate and so the solution was stored for three days at 4°C
after which needle like crystals of the desired monomer were obtained. The solid was collected
by filtration and dried under vacuum on a Schlenk line. The PPV polyelectrolyte precursor was
then subsequently prepared by reacting 2.145 g of monomer with an equimolar quantity of
sodium hydroxide (0.4 M) at 0°C for 1 hr. under N₂. The total volume of NaOH solution was
added dropwise over 20mins. The reaction was stopped by simply neutralizing with 0.4 M HCl
to a pH of 6.8. At this point the solution became relatively viscous. The polyelectrolyte was
separated from residual monomer and NaOH by dialysis against deionized water for 3 days. The
dialysis tubing used had a molecular weight cut-off of 3500 Da.

**Preparation of oxide nanoparticle based one dimensional photonic crystals:** see section 3.2

**Preparation of composite emitter/NP 1D PCs:** Composite R6G/NP 1D PC was prepared by
immersing an 11 bilayer SiO₂ and TiO₂ NP PC into a 10⁻³ M R6G in water solution for 24 hrs.
Composite PPV/NP 1D PC was prepared by spin-coating or drop-casting 1 wt.% aqueous
precursor PPV solution into an 11 bilayer SiO₂ and TiO₂ NP PC. The infiltrated PC was then
heated at 225°C for 3 hrs. under an N₂ atmosphere in order to convert the PPV precursor to the
fully conjugated PPV polymer.
4.3. Results and Discussion – Composite Rhodamine 6G / Nanoparticle One-Dimensional Photonic Crystal Distributed Feedback Laser

To maximize the necessary photonic crystal effect as a resonator in DFB lasers, SiO$_2$/TiO$_2$ NP 1D PCs consisting of eleven bilayers, compared to the previously reported four bilayer NP 1D PCs (chapter 3), were fabricated entirely by spin-coating with good structural and optical quality over 2 cm x 2 cm areas. The effective refractive index of the SiO$_2$ layers and the TiO$_2$ layers were again determined by spectroscopic ellipsometry to be 1.33 and 1.75 at 633 nm respectively. From the effective refractive indices as well as layer thicknesses, the porosities of the SiO$_2$ and TiO$_2$ layers were determined to be 38% and 34% respectively.

In section 1.3 of the introductory chapter, we qualitatively established the theoretical basis for DFB and microcavity lasers. Prior to considering the actual measurements made on our novel DFB systems, we apply the same formalism by solving the transfer matrix of a 1D PC bearing the aforementioned parameters (ie. refractive indices and thicknesses).[62] Figure 4.3a shows the calculated transmission spectrum of a 1D PC consisting of 11 layers of SiO$_2$ alternating with 11 layers of TiO$_2$, with thicknesses of 145 and 65 nm, respectively (such values are approximations to the actual thicknesses employed). The most notable feature of the transmission spectrum is the presence of a broad photonic stopband which of course represents the range of photon frequencies that cannot propagate along the direction of refractive index periodicity in the 1D PC. From the transmission spectrum it is also possible to derive the distribution of photonic density of states (Figure 4.3b) within such a 1D photonic structure, which most importantly for the work described herein, is high at both the red and blue edges of the photonic stopband.

From Figure 4.3b, it is evident that the presence of the photonic crystal causes a reorganization of the photon density of states available to an emitting species embedded within it’s structure. Therefore, for an emitting species confined within the NP PC, it is expected that emission wavelengths overlapping the PC bandedges will be enhanced and those overlapping the stopgap will be suppressed. Recall Fermi’s golden rule (eqn 1.3) which again was considered in detail in section 1.3. Fermi’s golden rule states that the transition rate $W_{ij}$ of a transition (from wavefunction $j$ to wavefunction $i$) occurring at frequency $\omega$ is proportional to the photon density
Figure 4.3. a) Transfer-matrix calculated transmission spectrum of an 11 bilayer SiO₂/TiO₂ nanoparticle 1D PC. b) The calculated photonic DOS of the same structure.

states at $\omega$. In the 1D PC, the DOS at the bandedge, $g(\omega_{be})$, is elevated and consequently, the rate of spontaneous emission at emission wavelengths lying at band-edge wavelengths is increased. If the rate of spontaneous emission is increased, so too is the rate of stimulated emission and herein lies the origin for the possibility of laser gain in such photonic materials.

For proof-of-concept that our NP 1D PCs could function as band-edge (DFB) lasers we selected Rhodamine 6G (R6G) as the emitter; its molecular structure is shown in the inset of Figure 4.4a. This organic dye possesses a high molar absorption coefficient (about $1.2 \times 10^5$ L mol⁻¹ cm⁻¹ at 532 nm), a photoluminescence quantum yield of 0.86 at room temperature. R6G is an active material with a remarkably high photostability, low cost, and an optical gain range extending from 550 to 600 nm with a maximum in optical gain at 570 nm.⁶³,⁶⁴ In addition to R6G’s optical properties, this particular dye was specifically chosen because of its cationic character which makes it ideally suited for ion exchange with nanoparticle surface hydroxyl protons, thereby providing a high dye loading of the porous photonic structure.

Having prepared the nanoparticle based PCs by the spin-coating method followed by a mild sintering post-treatment, the R6G dye was absorbed into the photonic structure by immersing the PC in a $10^{-3}$ M R6G in water solution for 24 hrs. A cross-sectional confocal optical microscopy image is provided in Figure 4.4b effectively demonstrating that the dye
Figure 4.4. a) SEM cross-section image of a SiO$_2$/TiO$_2$ nanoparticle 1D PC (scale bar = 1 μm). b) Confocal microscopy image of the dye-loaded nanoparticle 1D PC (scale bar = 1.5 μm). Note that the thicknesses of the images correlate well. c) Photographs of two R6G infiltrated NP 1D PCs under UV excitation below lasing threshold.

uniformly permeates the entire photonic structure. Note that the thickness of the confocal image correlates well with the thickness of the NP PC depicted in the SEM of Figure 4.4a. The limited spatial resolution of confocal optical microscopy does not allow the distribution of dye within the SiO$_2$ and TiO$_2$ layers to be elucidated. Nevertheless, it should be emphasized that the porosity of the nanoparticle 1D PC along with the coulombic interaction between the nanoparticles of the PC and the dye are key features of this system as such enables uptake of a large quantity of dye which in turn provides the opportunity of creating a lasing architecture from a nanoparticle-based
1D PC. Figure 4.4c includes a photograph of two R6G infiltrated NP 1D PCs under UV excitation below threshold. It is evident from the photographs provided in Figure 4.4c that the R6G, eventhough it is present in the solid state, is still strongly emissive under UV excitation within the 1D PC. Such behavior can be attributed to the spatially segregated mesopores within the PC which is believed to effectively separate the dye emitting centers which in turn inhibits fluorescence self-quenching.

The experimental reflectance spectrum of the SiO$_2$/TiO$_2$ 1D PC infiltrated with R6G is provided in Figure 4.5b, (blue line). It displays an intense broad band reflectivity from 550 to 650 nm, with a maximum at about 600 nm which correlates well with the predicted minimum of transmittance (Figure 4.3a). This effect is of course a direct manifestation of the photonic stopband of the 1D PC which again is created by the periodicity of the dielectric lattice.

The optical setup (a schematic of which is provided in Appendix D) used to acquire photoluminescence measurements is described in detail in the experimental section. For such measurements, the pulsed second harmonic of a neodymium doped yttrium aluminum garnet laser was employed as the pump with a repetition rate of 1 Hz and a pulse width of 5 ns. As showed in Figure 4.5a, the pump laser light impinges on the sample obliquely with respect to normal incidence. The resulting emission is vertical with respect to the sample surface, most notably in the direction parallel to the dielectric periodicity. The pulse energy density used in our experiments was always maintained at a value an order of magnitude below the bleaching of the sample (0.6 J/cm$^2$). The pump beam was focused onto a spot with an area of about 1 mm$^2$ and all luminescence measurements were carried out under ambient conditions. Laser light has been carefully removed by using a proper notch filter.

By exciting the sample with a pump energy density of 40 μJ/cm$^2$, a narrow emission peak (Figure 4.5b, orange line) is clearly detectable at about 548 nm (∼18 250 cm$^{-1}$) corresponding to the energy where the blue edge of the photonic stopband overlaps the R6G spontaneous emission. This result is in good agreement with the theoretical predictions of high photonic DOS shown in Figure 4.3b, around 544 nm (18400 cm$^{-1}$). In addition and again as predicted by each of the calculations of Figure 4.3, it is important to note that almost all dye emission beyond 548 nm is suppressed owing to the presence of the photonic stopband. The observation of such phenomena effectively establishes that the stimulated emission at 548 nm is associated with the DFB structure, a result of the coupling of the emission of R6G with the blue bandedge of the nanoparticle 1D PC.
Figure 4.5. a) Schematic representation of the sample and lasing measurement. b) The experimental reflectance spectrum (blue line) and photoluminescence (orange line) of the dye-loaded nanoparticle 1D PC excited by pulsed laser light at 532 nm with an energy density of 40 mJ/cm². The inset shows the molecular structure of the R6G dye. c) Photoluminescence spectra of the sample below (blue line) and above (purple line) the lasing threshold. Inset: overall PL intensity as a function of the excitation energy density at 532 nm. The threshold energy density is approximately 12 mJ/cm². d) A photograph of the emission from the sample excited by pulsed laser light at 532 nm with an energy density of 40 mJ/cm².

The inset of Figure 4.5c includes the intensity of the 548 nm emission of the sample as a function of the incident laser excitation energy density over a range of 6 to 40 μJ/cm². With increasing excitation energy density, we observed an abrupt change in the photoluminescence
intensity at 548 nm. The corresponding onset energy density upon which the aforementioned phenomena of amplified emission appears can be considered as the lasing threshold of the system; it was determined to be approximately 12 μJ/cm². It is worth mentioning here that such a threshold is one of the lowest reported for a bottom-up nanofabricated laser device. Figure 4.5c shows representative luminescence spectra of the sample below (blue line) and above (purple line) the threshold power. The emission above the threshold has been collected by using neutral optical filters on the signal detection in order to reduce the intensity. The photoluminescence spectrum below threshold shows the broadband emission of the organic dye, which is slightly modified by the photonic stopgap profile. However, once the sample is excited above the threshold excitation power we obtain a narrow emission of about 8 nm FWHM, corresponding to a cavity quality factor Q ~ 70. The observation of this phenomenon establishes that the stimulated emission at 548 nm can be associated with the DFB structure created by the 1D PC. As expected, the amplified emission takes places strictly at energies corresponding to the spectral regions with high density of allowed photonic states, which are only determined from the intrinsic properties of the periodic dielectric structure.

4.4 Results and Discussion - Composite pol(phenylene vinylene) / Nanoparticle One-Dimensional Photonic Crystal Distributed Feedback Laser

The methodology employed for the preparation a composite PPV/NP 1D PC DFB laser was analogous to that already described for the R6G/NP 1D PC lasing system. Again as the resonator, an 11 bilayer SiO₂/TiO₂ NP 1D PC, bearing the same optical properties as described in section 4.3.1, was employed. The emitter PPV was then subsequently introduced into the photonic structure according to methods described in section 4.2. The traditional “precursor route” was selected as the synthetic method of choice for the emissive polymer, the scheme of which is shown in Figure 4.6. The monomer p-xylene-bis(tetrahydrothiophenium chloride) was obtained via reaction of dichloro-p-xylene with excess tetrahydrothiophene. The monomer was then precipitated from acetone and allowed to stand for three days at 4°C yielding large needle-like crystals. To the authors knowledge, the crystal structure of p-xylene-bis (tetrahydrothiophenium chloride) has yet to be reported and thus it is also included in Figure
4.6b. The PPV polyelectrolyte precursor was then subsequently obtained upon treatment of p-xylene-bis(tetrahydrothiophenium chloride) with NaOH solution. Following neutralization, the precursor polyelectrolyte was purified by dialysis and subsequently used as acquired from the dialysis tube for infiltrating the 1D PC. The polydispersity of the polymer was determined by GPC (see Appendix C) to be 3.7 which is similar to values reported in literature.

Having prepared the nanoparticle based 1D PCs by the spin-coating method followed by a mild sintering post-treatment, precursor PPV was drop-cast or spin-cast onto the NP PC in order to infiltrate the pores of the PC. Regardless of the method of PPV infiltration though, an undesired polymer overlayer (which is strongly attenuating) was always present. Such however was easily removed by gently scraping the overlayer with a glass slide. Here the polymer is easily removed as it is significantly softer than the polymer/NP composite and thus the latter
Figure 4.7. a) SEM image of an 11-bilayer SiO$_2$/TiO$_2$ NP 1D PC (scale bar = 1 μm). b) Cross-sectional confocal microscopy image of the PPV-infiltrated NP 1D PC (scale bar = 1 μm); note that the thickness correlates well with the thickness of the SEM in a). c) Photograph of the PPV/NP 1D PC composite under UV excitation.

remains intact suffering minimal structural or optical degradation. Once the PC is infiltrated and the overlayer removed, the precursor was thermally converted to the desired conjugated structure by heating at 225°C for 3 hrs. under N$_2$. A cross-sectional confocal optical microscopy image is again provided in Figure 4.7b effectively demonstrating that the polymer uniformly permeates the entire photonic structure which is of course again made possible by the mesoporosity of the
nanoparticle 1D PC. The photograph of Figure 4.7c, which is of the PPV/NP 1D PC composite under UV excitation is a true testament to the emissive nature of the PPV infiltrated 1D PC.

PPV is a versatile emissive and semiconducting polymer as it has found widespread use in organic light-emitting diodes\cite{65} and transistors.\cite{66} However, the fully conjugated and unsubstituted structure lacks solubility in commonly used solvents and so to ensure solution processability of PPV, one of two approaches are usually adopted. The first simply involves employing an alkoxy-substituted derivative of PPV, such as poly(2-methoxy-5-[2'-ethylhexyloxy]-p-phenylenevinylene), MEH-PPV, which of course allows for processing from organic solvents. The second involves the preparation of a polyelectrolyte precursor which can be processed from aqueous solution and subsequently thermally converted to the desired conjugated polymer. For the lasing application described herein, either route is suitable however we opted for the polyelectrolyte precursor method for reasons highlighted below. For example, an attractive feature associated with generating a composite PPV/NP 1D PC whereby the PPV is obtained via the precursor route stems from the PPV’s subsequent insolubility following thermal conversion. Once infiltrated and thermally converted, the resulting composite (ie. PPV/NP 1D PC) is quite robust and highly resistant to common solvents. In addition, this particular polymer was specifically chosen because it’s respective precursor is cationic thereby rendering it ideally suited to interact favorably with the negatively charged surface of the nanoparticles. This interaction in turn ensures a high polymer loading of the porous photonic structure.

The properties of PPV generated from the precursor route are governed primarily by the conjugation length of the polymer, which in turn are highly dependent on the purity of sample and the conditions used for the thermal conversion (i.e. temperature and atmosphere).\cite{67} A decreased conjugation length is common with PPV obtained \textit{via} the precursor route which is certainly undesired for electronic applications where high carrier mobility is often sought but can actually be beneficial for optical applications such as lasing. A decreased conjugation length decreases the interaction between emitting centers and so minimizes deleterious mechanisms of fluorescence self-quenching. Typically, PPV obtained from the precursor route is emitting of green-yellow light, has good photostability and exhibits approximate photoluminescence efficiencies of \(~22\%\).\cite{68} To the authors knowledge, DFB lasing from PPV obtained from the precursor route has not been demonstrated but lasing from such a polymer embedded in a microcavity architecture was shown in 1996.\cite{1}
Figure 4.8. a) Absorption and spontaneous emission spectrum of a pure 300 nm thick PPV film. b) Emission spectra of a 1 µm thick PPV film with increasing excitation energy. Inset: Input-Output (i.e. excitation energy – output intensity) characteristics of the emission at 520 nm (i.e. the lasing wavelength). For high excitation the sub-linear increase is ascribed to degradation of the sample. c) Reflectance spectrum of a PPV infiltrated NP 1D PC (blue plot) along with the emission spectrum of the composite above threshold. d) Input-output (i.e. excitation energy – output intensity) characteristics of the emission of the composite. Inset: transmission spectrum of the NP 1D PC (black plot) and laser peak of the PPV infiltrated NP 1D PC.

The absorption and spontaneous emission spectrum of a pure 300 nm thick PPV film is shown in Figure 4.8a. The absorption has a maximum ~400 nm and thus it was this wavelength that was selected as the excitation pump wavelength. The spontaneous emission of the thermally converted polymer is broad extending over a range of 500-690 nm which is indeed advantageous for this application as it does not imposes significant restrictions on the position of the 1D PC.
Bragg reflectance. The reflectance spectrum of a PPV infiltrated NP 1D PC is shown in Figure 4.8c (black line). The broad band between 530 and 630 nm, with a peak reflectance at 570 nm corresponds to the photonic stopgap of the NP 1D PC. A comparison of NP PC reflectance and the PPV spontaneous emission reveal a significant overlap, which is of course a pre-requisite for the development of the desired band-edge PPV/NP 1D PC laser.

The optical setup used to acquire photoluminescence measurements is described in detail in the experimental section. For such measurements, the DFB was pumped by 100 fs pulses at 400 nm at a repetition rate of 1 kHz, obtained from the second harmonic of a Ti:Sapphire amplified laser. The beam, incident at an angle of ~20 degrees to the surface normal, was focused on a circular excitation area (1.1 × 10^{-4} cm^2) and the emission was measured with an optical multichannel analyzer (OMA, 1.2 nm resolution).

As mentioned previously, the spontaneous emission of PPV exhibited good overlap with the Bragg peak of the constructed 1D PC. It is worth noting that the ideal system would be one whereby the blue edge of the stopgap of the NP 1D PC exactly overlaps the gain maximum of the emitting polymer. Such a system is very challenging to construct however owing to the difficulty in precision controlling of the stopband position as well as the sensitivity of the polymer conjugation length (and thus the gain spectrum) on the fabrication conditions. Nevertheless, although the aforementioned condition certainly represents the ideal, it’s realization is not absolutely necessary to obtain stimulated emission as we achieved this situation by simply ensuring sufficient overlap of polymer emission with the blue edge of the PC. As shown in Figure 4.8c, above an excitation energy density of 550 μJ/cm^2, a narrow peak (FWHM~3 nm) centered at 520 nm can be observed. The observed lasing wavelength correlates well with the blue edge of the PC stopgap and thus the vertical DFB photonic structure provides an efficient feedback to light inside the cavity.

In Figure 4.8d we plot the input-output (i.e. excitation energy – output intensity) characteristics of the emission of the composite material. It shows the typical signatures of laser action: a clear threshold at approximately 100 nJ, with concomitant line narrowing (from ~40 to ~3 nm) and a linear increase for higher excitation energies. Note that the linear increase is obtained over a very large range of input energies (from 100 to 1400 nJ) which is worth emphasizing as this effect is seldom achieved with organic lasers as usually saturation and degradation play a major role at higher excitation conditions. The threshold corresponds to an energy density of 550 μJ/cm^2, of absorbed light, as the exciting laser beam is focused on an area
of $1.1 \times 10^{-4}$ cm$^2$. This value is in good agreement with thresholds for other organic DFB lasers reported in literature.$^{[21-39]}$ It is expected that the threshold can be lowered by increasing the number of layers of the DFB structure as this would augment the feedback mechanism. The desired effect achieved by employing the porous photonic matrix as the laser resonator can also be deduced by analyzing the emission of a pure PPV film (i.e. no 1D PC present) as a function of laser excitation energy (Figure 4.8b), the same excitation energy range employed for excitation of the lasing composite. The emission of the pure PPV film as a function of the excitation energy is very broad with no apparent linewidth narrowing upon increasing excitation energy, lending further credence to band-edge lasing in the composite PPV infiltrated 1D PC.

In accordance with eqn. 3.4, the stopband as well as the blue edge of the stopband of an NP 1D PC can be manipulated to span the entire range of visible spectral wavelengths by varying the optical thicknesses of the layers comprising the structure (easily achieved with our methodology by controlling the nanoparticle concentration of the dispersion and the spin-rate of the spin-coating deposition step). Therefore, by incorporating a suitable dye into a porous NP 1D PC, solid state dye lasers can now be fabricated for operation at optical and IR frequencies.

### 4.5 Summary

In conclusion, we demonstrated lasing from composite materials consisting of either R6G or PPV infiltrated NP 1D PCs. As emphasized earlier, it is the porosity of the NP 1D PC which is key to the preparation as it allows for the emitting species to be introduced into the photonic structure after it has been fabricated and thermally stabilized. The obtained thresholds and FWHMs of the lasers are good although improvements can be made if: i) a larger number of bilayers are introduced into the 1D PC; ii) if the R6G is dispersed in a polymer solvent; iii) if a better matching between photonic band-edge and gain maximum of PPV are established, or if the active polymer were to be incorporated into a microcavity architecture (see section 1.3)$^{[69]}$. Note that the porosity of the medium, which is essential for construction of the laser device, also offers other interesting opportunities. The use of “functional” one-dimensional nanoparticle photonic crystals that show a shift in stopband wavelengths by selective absorption of analytes, paves the way to a possible realization of laser based switches and sensors.
4.6 References


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5.1 Introduction

As shown in the previous chapters, more recent advances in the field of 1D PCs have involved fabricating such photonic structures from novel nanomaterials primarily to impart added functionality to the photonic material.[1,2] In section 5.3 of this chapter, we present a novel selectively-transparent and conducting photonic crystal (STCPC) fabricated entirely from transparent conducting oxides (TCOs). These STCPCs, fabricated in the form of a nonquarter-wave 1D PC, are made of alternating layers of sputtered indium-tin oxide (ITO) and spin-coated antimony-doped tin oxide (ATO) nanoparticles and represent a significant advance over existing 1D PCs because they combine intense broadband reflectance with the transmissive and conductive properties of the metal oxide building blocks. Moreover, due to this unique combination of properties, such materials can expectedly be integrated into any number of opto-electronic devices where control of light propagation can be exploited to enhance efficiency. For example, the benefits of using PCs as a back-reflector for thin film photovoltaic devices have been both theoretically,[3,4] and experimentally,[5] demonstrated, and as an extension of this idea it has been suggested that PCs fabricated from materials that are both conductive and transparent can be used as intermediate reflectors in micromorph solar cells.[6] In addition, such 1D STCPCs, because they are simultaneously reflective and conductive, can be employed as a mirror and anode in an Organic Light Emitting Diode microcavity. In section 5.4, we describe the performance of OLED microcavities bearing our newly developed STCPCs as the partially reflective anode.
5.2 Experimental Details

Materials Aqueous dispersions of Sb:SnO₂ nanoparticles were purchased from Alfa-Aesar (Nanotek). For OLED Fabrication, Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) used as hole injection layer was provided by H. C. Starck. N,N’-diphenyl-N,N’-bis-(1-naphthyl)-1-1′-biphenyl-4,4’-diamine (α-NPD) used as hole transport layer, and tris-(8-hydroxy-quinolinato)aluminum (Alq₃) used as emissive layer were provided by Norel Optronics Inc. and used as received. 2,3,6,7-tetrahydro-1,1,7,7,-tetramethyl-1H,5H,11H-10-(2-benzothiazolyl) quinolizino-[9,9a,1gh] coumarin (C545T) used as fluorescent dopant emitter was purchased from Luminescence Technology Corp. and used as received. High purity (99.99% trace metals basis) LiF was purchased from Sigma-Aldrich and thoroughly degassed in high vacuum prior to use.

Optical Characterization: The transmission spectra of normally incident light over a circular area of 7.1mm² were measured with a UV/Vis spectrometer (Perkin Elmer, Lambda 18). Spectroscopic ellipsometry analyses were performed on a Sopra GES-5E ellipsometric porosimeter at a fixed incidence angle of 70.15° in the range 1.5–3.0 eV. A regression analysis was performed on the data attained from these ellipsometry measurements in order to fit the dispersion relations of these 1D STCPCs and reference films to a Cauchy model. The statistical measure of the quality of fit attained for the ellipsometric measurements performed on our ATO and ITO reference films was fairly high (R² > 0.99). However, as a result of the roughness of the interfaces, the statistical measure of the quality of the fit attained for our 1D STCPCs was not as good. The statistical measure of quality of fit for the green 1D STCPC was 4.2 x 10⁻³ (R² = 0.96). A comparable measure of quality of fit for the red 1D STCPC was also attained (R² = 0.94). In order to directly determine the porosity of the ATO nanoparticle films, ellipsometric porosimetry of an ATO nanoparticle film on a polished silicon wafer was performed (Appendix D). The porosity was determined to be 41% which is consistent with the porosity of other films prepared from nanoparticles of similar size.⁷

STCPC Fabrication: 0.7 mm thick Corning glass substrates were cut into ~2.5 cm x 2.5 cm squares and subsequently cleaned in a 3:1 (v/v) solution of sulphuric-acid/hydrogen-peroxide and then rinsed with distilled water. 1D STCPCs were deposited onto these glass substrates by
alternately spin-coating ATO nanoparticle films and sputtering ITO films as described below. Additional samples were similarly prepared on polished silicon wafers for SEM imaging.

**Preparation of Sputtered ITO films:** ITO films were deposited in a custom built sputtering system (Kurt J. Lesker Co.) by RF magnetron sputtering from a ceramic In$_2$O$_3$:SnO$_2$ target (90:10 wt %). The base pressure of the sputtering chamber was 1x10$^{-7}$ Torr before argon was introduced into the chamber at a flow rate of 20 sccm. The chamber pressure was set to 3 mTorr during the deposition, which was carried out at room temperature. The forward and reflected power was 97 W and 0 W, respectively, and the DC biased voltage was 75 V. The substrate-to-target distance was ~14 cm and the film growth rate was 4x10$^{-2}$ nm/s. The sputtering process was terminated when the desired thickness, as measured from an *in situ* quartz crystal thickness monitor (SQM-242 from Sigma), had been deposited.

**Preparation of ATO nanoparticle films:** A 50 wt% (solid content) solution of ATO nanoparticles in water were purchased from Alfa-Aesar (Nanotek). The dispersion was diluted under vigorous stirring with water causing some aggregation and subsequent flocculation. The aggregates were removed by centrifugation at 6000 rpm for 12 min. The resulting supernatant which contained well dispersed ATO nanoparticles at a concentration of 10.1 wt.% was then collected and to such was added poly(ethylene glycol) at a concentration of 1.25 wt.% At the dispensing stage in the spin-coating process, the dispersion was filtered through a 0.45 µm pore Nylon syringe filter. Dispersions were spin-coated at speed of 2000 rpm for 20 seconds.

**OLED Fabrication:** OLEDs were fabricated in a Kurt J. Lesker LUMINOS® cluster tool at a base pressure of ~ 10$^{-8}$ Torr using stainless steel shadow masks to define the device structure. Freshly deposited substrates (ITO final layer) were ultrasonically cleaned with a standard regiment of acetone and methanol followed by UV ozone treatment for 15 minutes. PEDOT:PSS (CLEVIOS™ P) was deposited on cleaned substrates by spin-coating in ambient air at 2000 rpm, followed by curing under vacuum at 150°C. The various organic molecules were deposited from alumina crucibles (Knudsen cells) in a dedicated organic chamber. LiF was also deposited in the same chamber from an alumina crucible. The Al cathode contacts (3 mm diameter circles) were deposited from a pyrolytic boron nitride crucible, in a separate metallization chamber without breaking vacuum. Film thicknesses were monitored using a calibrated quartz crystal microbalance. Each cathode circle defined one OLED device, with 9 devices per 2.5 cm × 2.5 cm
substrate. A total of up to four different device structures were fabricated on a single substrate to eliminate possible run-to-run variability caused by subtle variations in process conditions.

**OLED Characterization:** Current-voltage (IV) characteristics of the OLEDs were measured using an HP4140B pA meter in ambient air. Contact to the top Al cathode was made using a Ag wire loop to avoid piercing the organic layers underneath. Luminance measurements were taken using a Minolta LS-110 Luminance from the substrate side of the devices. Electroluminescence (EL) spectra were measured using an Ocean Optics USB2000 fiber spectrometer at 10 V applied bias.

5.3 – Results and Discussion: Selectively-Transparent and Conducting Photonic Crystals

Our 1D STCPCs are fabricated by alternately sputtering and spin-coating ITO and ATO nanoparticle films, respectively, in order to build up the desired multilayer structure. For example, in order to construct a single bilayer within the 1D STCPC an ITO film is sputtered onto a ~2.5 cm x 2.5 cm Corning 1737 glass substrate and an ATO nanoparticle film is subsequently spin-coated on top of this ITO film. Following each ATO deposition in the fabrication process, the structure is annealed at 450°C for 15 minutes to effectively remove organics added to the nanoparticle dispersion to improve film quality. Using this procedure, any number of bilayers can be successively deposited in order to build up the 1D STCPC to a desired thickness. Moreover, the thicknesses of the sputtered ITO and ATO nanoparticle films can be easily manipulated in order to set the spectral position of the Bragg-diffraction peak in accordance again with eqn. 3.4. This methodology is well suited for incorporating defects, as shown in section 3.3.1, into the multilayer 1D STCPCs structure as such can be achieved by appropriately tuning the thicknesses of selected layers during the fabrication process. The stopbands (ie. Bragg peaks) exhibited by the 1D STCPCs reported herein are again a consequence of the 1D periodic variation in refractive index. However, it must be emphasized that the appreciable refractive index contrast is attributed to the porosity of ATO layer which note is the result of the ATO nanoparticle packing. The effect of the porosity is a decrease in the refractive index of the ATO layer and thus, the creation of the desired index contrast. Such a contrast is not possible with bulk ITO and bulk ATO as both materials possess similar refractive indices and are thus poor candidates for 1D PC fabrication.
Figure 5.1. a) Cross-sectional SEM image of a 1D STCPC comprised of 5.5 bilayers of sputtered ITO and spin-coated ATO nanoparticle films. The inset shows a highly magnified image of a layer of smaller ATO nanoparticles sandwiched between two sputtered ITO films. b) and c) demonstrate how the reflectance and transmittance of the STCPC varies with an increasing number of layers (indicated by the legend) in the STCPC.

A cross-sectional SEM image of a 1D STCPC comprised of 5.5 bilayers of sputtered ITO and ATO nanoparticle films is shown in Figure 5.1a. The ITO and ATO nanoparticle films are most easily distinguished by the inset where the ATO nanoparticles are easily visible. Owing to
the moderate surface roughness of the ATO nanoparticle film, the sputtered ITO films grow in a
columnar fashion atop the ATO nanoparticles. Such roughness also seemed to create undesired
thickness variations throughout the ITO layer as the targeted thickness of the ITO layer in Figure
5.1 was 80 nm and such was achieved under identical conditions on flat Si. However, the SEM
image of Figure 5.1 reveals columns within the ITO film having a height in excess of 90nm. It
can also be noted that owing again to the porosity of the ATO layer, a degree of infiltration of
ITO into the ATO layer is expected during the sputtering process. As will be discussed further
below, such infiltration can significantly affect both the optical and electronic properties of the
multilayer structure. This particular point will be discussed further below with reference to
Figures 5.4 and 5.5 which compare the modeled and measured reflectance of our 1D STCPCs.

The evolution of the reflectance and transmission spectra of a set of 1D STCPCs with
increasing numbers of bilayers, is shown in Figures 5.1b and 5.1c, respectively. These spectra
display intense photonic stopbands (Bragg-peaks) from 500 nm to 700 nm as a 1D STCPC
comprising just 3.5 bilayers exhibits a Bragg peak greater than 60% while that of a 1D STCPC
comprising 7.5 bilayers exceeds 90%. Most interestingly, Figure 5.1c reveals the large
transmittance of the 1D STCPCs over the near-infrared spectral region despite their high
reflectance in the vicinity of ~600 nm. For instance, the average transmittance of the
aforementioned 3.5- and 7.5- layered STCPCs from 700 nm to 900 nm is 80 % and 74 %,
respectively. In addition and again of particular interest, the average transmission of these 3.5-
and 7.5- layered 1D STCPCs is 60% and 44% from 400 nm to 500 nm, respectively, but quickly
decreases as the wavelength decreases to lower values due to absorption within both the
sputtered ITO and spin-coated ATO nanoparticle films. The aforementioned is a testament to the
true selectivity of the reflectance of such materials, which as we show below is desired for
certain applications.

In accordance with eqn. 3.4, the reflectance peak of our 1D STCPCs can be tuned by
appropriately tuning the thickness of their respective individual layers. This is demonstrated in
Figure 5.2, which shows the reflectance spectra of four 1D STCPCs of ~80 nm thick ATO
nanoparticle films and ITO layers that have equivalent thicknesses of, ~80 nm, 90 nm, 95 nm,
and ~110 nm when deposited onto a flat substrate. The reflectance spectra of these 1D STCPCs
comprising equal thickness ATO layers and the aforementioned ITO layer thicknesses peak at
~475 nm, ~520 nm, ~565 nm and ~625 nm and thus appear blue, green, yellow and red in color,
Figure 5.2. Reflectance spectra of a blue, green, yellow and red 1D STCPCs which peak at ~475nm, ~520 nm, ~565 nm and ~625 nm. A photograph of each 1D STCPC is shown as an inset above its reflectance peak.

respectively. A photograph of each of the blue, green, yellow and red 1D STCPCs are included in Figure 5.2 above their corresponding reflectance spectra. These 1D STCPCs are of excellent optical quality (see Appendix D which includes optical micrographs of the surface of such STCPCs), possessing virtually no striations and only a small concentration of “comets”. Again, as mentioned in Chapter 3, in our experiences, comet formation can be almost entirely prevented by working in meticulously clean environments (ie. a clean room) as well as by filtering dispersions at the dispensing stage of the spin-coating process through 0.20 µm pore Nylon syringe filters.[2,7]

As previously mentioned, the optical and physical properties of the ATO and ITO films within our STCPCs differ from that of corresponding ATO and ITO reference films that were
deposited onto polished silicon surfaces. To gain some insight into these differences, similar to the analyses of Chapter 3, we performed spectroscopic ellipsometry measurements on individual ATO and ITO reference films and also on green and red 1D STCPCs. For each of these samples, the ellipsometric parameters \( \alpha \) and \( \beta \) were again measured and a regression analysis was subsequently performed in order to determine their extinction coefficient (\( \kappa \)) and index of refraction (\( n_{\text{eff}} \)). To simplify the analysis, we assume that these layers are homogeneous media separated by smooth interfaces. The measured effective extinction coefficients of both the ATO nanoparticle and ITO reference films and the ATO and ITO layers within the 1D STCPCs were small, on the order of \( 10^{-2} \) or lower for \( \lambda > 400 \) nm. Furthermore, the effective index of refraction of the reference films and of the ATO and ITO layers within the red and green 1D STCPCs are plotted in Figure 5.3a.

The effective index of refraction of the sputtered ITO reference film is plotted as the topmost solid line in Figure 5.3a, where it can be seen to decrease monotonically from a value of 2.19 at a wavelength of 400 nm to 1.81 at a wavelength of 900 nm. It can be noted that these values are comparable to those reported in the literature.\(^8\) The ellipsometry measurements performed on the red and green 1D STCPCs reveal that the effective index of refraction of the ITO layers within the red 1D STCPC is lower than that of the ITO reference film, and that the effective index of refraction of the ITO layers in the green 1D STCPC are even lower than those in the red 1D STCPC (see Fig. 5.3a). As previously mentioned with reference to Figure 5.1, the sputtered ITO layers grow on top of the ATO nanoparticle film in a columnar fashion and, as can be seen in the SEM images shown in Figures 5.4b and 5.4c, comprise some degree of porosity as a consequence of spaces existing between adjacent ITO columns. Moreover, these SEM images suggest that the porosity in the ITO layers is greater in the green 1D STCPC as compared to the red 1D STCPC, which is consistent with the fact that the effective index of refraction of the ITO layers in the green 1D STCPC are lower than those in the red 1D STCPC. The thicknesses of the ITO layers in the 1D STCPCs also differ from those of the reference samples. Specifically, the thicknesses of the ITO layers in the green and red STCPC, as determined from the ellipsometric measurements, are 89 nm and 108 nm, respectively. Here we mention once again that the equivalent thickness of the ITO layers in the green and red 1D STCPCs are just \(~60\) nm and \(~100\)nm when deposited onto glass substrates. Furthermore, these thickness values are in agreement with the SEM images shown in Figure 5.4. For example, the scaled height of the up-
Figure 5.3. a) Effective index of refraction of the ATO and ITO reference films as well as the effective index of refraction of the ATO and ITO layers within the green and red 1D STCPCs shown in Figure 5.2. The index of refraction of the reference films are represented by solid lines, while the effective index of refraction of the layers within the green and red 1D STCPCs are represented by dotted and dashed lines, respectively. The lines appearing in the top half of the plot represent ITO layers and those appearing in the bottom half represent ATO layers. b) Measured (solid line) and modeled (dashed line) reflectance from the green 1D STCPC. The dotted reflectance spectra is calculated assuming that the thicknesses and indices of refraction of the ATO and ITO layers within the 1D STCPC are identical to those of the ATO and ITO reference films (ie. the thickness of the ITO and ATO films are assumed to be 60 nm and 73 nm, respectively, while the indices of refraction are plotted as the solid lines in Figure 5.3a). c) Measured (solid line) and modeled (dashed line) reflectance from the red 1D STCPC. The dashed line represents the reflection spectra similar to that shown in Figure 5.3b but for the red, rather than the green, 1D STCPC (ie. the thickness of the ITO film is assumed to be 100 nm rather than 60 nm).
down arrows overlaying Figures 5.4f and 5.4g are 89 nm and 108 nm; the heights of these up-
down arrows match those of the ITO columns in their respective 1D STCPCs reasonably well.

The effective index of refraction of the ATO nanoparticle reference film, plotted as the bottommost solid line appearing in Figure 5.3a, is observed to decrease monotonically from a value of 1.39 at a wavelength of 400 nm to 1.33 at a wavelength of 900 nm. The smaller value of the effective index of refraction of the ATO nanoparticle films, as compared to solid ATO, is a result of their high degree of porosity which was estimated to be 41% from ellipsometric porosimetry measurements (see Figure 3 in Appendix D). An SEM image revealing the porous nature of the ATO nanoparticle reference film is shown as Figure 5.4a. Also, the thickness of the ATO reference film was determined to be 73 nm. The thickness of the ATO nanoparticle film in the green 1D STCPC was determined to be the same as that of the reference film; however, as shown in Figure 5.3a, the effective index of refraction of the ATO layers within the stack is larger than that of the reference film. This increase in the effective index of refraction is attributed to some degree of infiltration of ITO into the spaces between the nanoparticles in the ATO film during the ITO sputtering process. The height of the ATO nanoparticle film in the red 1D STCPC was determined to be 88 nm and, similarly to the ATO layers within the green 1D STCPC, their effective index of refraction is larger than that of the reference film. In agreement with the SEM images, the fact that the thickness of the ATO nanoparticle layers within the red 1D STCPC is determined to be larger than in the reference film or in the green 1D STCPC suggests that the interface between the ATO and ITO layers is not as sharp as desired (a degree of interpenetration is present) and that the effective index of refraction at the boundary between these layers takes on some intermediate value between that of the ATO nanoparticle and sputtered ITO films. Nevertheless, it can be noted that the thicknesses of the layers within the 1D STCPCs determined from our ellipsometry measurements are in agreement with the SEM images shown in Figure 5.4. For example, a cross-sectional SEM image of the green 1D STCPC is shown in Figure 5.4d and the scaled height of the stacked black and white squares overlaying this image are 73 nm and 89 nm, respectively. Although it is difficult to distinguish a definite boundary between the ATO and ITO layers it can be seen that the column of stacked black and white squares have the same periodicity of the green 1D STCPC. A similar analysis, but for the red rather than the green 1D STCPC, is shown in Figure 5.4e wherein the scaled height of the black and white squares overlaying the SEM image are 108 nm and 88 nm, respectively.
Figure 5.4. a) Top-view SEM image of an ATO nanoparticle reference film. b) Top-view SEM image of ITO sputtered onto an ATO nanoparticle film – the sputtered ITO would form a 60 nm thick film if deposited onto a flat substrate. c) Top-view SEM image of ITO sputtered onto an ATO nanoparticle film – the sputtered ITO would form an ~ 100 nm thick film if deposited onto a flat substrate. d) Cross-sectional SEM image of bilayers within the green 1D STCPC shown in Figure 2. e) Cross-sectional SEM image of bilayers within the red 1D STCPC shown in Figure 2. f) Higher magnified image of that shown in Figure 3e. g) Higher magnified image of that shown in Figure 3f.

We have also used the indices of refraction and thicknesses determined from the ellipsometry measurements to model the reflectance spectra from the green and red 1D STCPCs. Transfer-Matrix calculations were performed using scalar-wave approximation and the results, plotted in Figures 5.3b and 5.3c, reproduce the measured reflectance spectra reasonably well. For comparison, the Bragg-reflectance peaks calculated assuming that the thicknesses and dispersion relations of the ATO and ITO layers within the 1D STCPCs are the same as those determined
from the ATO and ITO reference films are also plotted in Figures 5.3b and 5.3c and it can be seen that the reflectance peaks calculated assuming these properties are larger, wider and blue shifted with respect to the actual reflectance peaks.

We have also investigated the conductivity dependence of our 1D STCPCs on both their number of bilayers and the thickness of their sputtered ITO layers. Specifically, the sheet resistances of the 1D STCPCs were measured using a four point probe (Four Dimensions, Inc. Model 101C) and the results from the 1D STCPCs containing 3.5, 5.5 or 7.5 bilayers are plotted in Figure 5.5. The sheet resistances of the green, yellow and red 1D STCPCs shown in Figure 5.2 are also plotted in Figure 5.5. The sheet resistance of these two sets of 1D STCPCs, measured before and after undergoing a 16 hr. bathing in air at 500ºC, are plotted alongside the sheet resistance measured from a set of four reference films that include individual ~80 nm thick ATO nanoparticle and sputtered ITO films and two different bilayers comprising ITO films of differing thicknesses sputtered onto ATO nanoparticle films.

From Figure 5.5, the annealing treatment decreases the sheet resistance of the ATO nanoparticle reference film from $8.5 \times 10^6$ to $6.8 \times 10^5 \, \Omega/\square$, but increases that of the ITO reference film from 70 to 210 $\Omega/\square$. Sintering nanoparticle films is known to increase their conductivity, and ATO nanoparticle films of comparable thickness to those in our stacks exhibiting sheet resistances on the order of $10^4 \, \Omega/\square$ have been fabricated.$^{[9,10]}$ In fact, ITO films are typically subjected to post-deposition annealing treatments in order to reduce their resistance, however, the resistance of ITO films have been shown to increase upon annealing in air at temperatures above 300ºC owing to crystallization effects.$^{[11]}$

As shown in the SEM images of Figures 5.4b and 5.4c ITO films sputtered onto nanoparticle films possess a small degree of porosity and in order to verify their conductivity we have prepared and measured the sheet resistance of single bilayers. To prepare these bilayers a ~73nm thick ATO nanoparticle film was first deposited onto a Corning 1737 glass substrate and ITO films were subsequently sputtered onto this film. The sheet resistances of these bilayers, wherein the thicknesses of the ITO layers would be ~60 nm and ~80 nm if deposited onto a flat substrate, are plotted in columns 3 and 4 of Figure 5.5, respectively. When these bilayers were subjected to the annealing treatment, their sheet resistance was reduced to within an order of magnitude of the ~80 nm thick ITO reference sample.
The sheet resistance of the first set of 1D STCPCs comprising 3.5, 5.5 and 7.5 bilayers, are plotted in columns 5 through 8 of Figure 5.5, and are 78.6, 56.5 and 54.7 $\Omega/\square$, respectively. These values are comparable to the 70 $\Omega/\square$ measured for the single ~80 nm thick sputtered ITO reference film. Furthermore, the annealing process did not significantly change the sheet resistance of these 1D STCPCs as all values measured after the annealing process are within 20% of those measured before annealing. The sheet resistance of the green, yellow and red 1D STCPCs are plotted in columns 8 through 10 of Figure 5.5, and are 74.4, 56.5 and 35.9 $\Omega/\square$, respectively. Once again, the sheet resistance of the 1D STCPCs measured before and after the annealing treatment are within 20% of each other with the exception of the 1D STCPC containing the 100nm thick ITO layers, which increased from 35.9 to 49.7 $\Omega/\square$. 

Figure 5.5. Sheet resistance of various 1D STCPCs plotted along with certain reference films.
5.4 Results and Discussion – OLED Microcavities Containing Selectively-Transparent and Conducting Photonic Crystals

In section 1.3.1 of this thesis, an introductory discussion pertaining to OLED microcavities was provided. It was highlighted that a microcavity architecture (owing to its unique properties discussed at length in section 1.2) represents one route to overcome the problem of the poor color purity associated with the characteristically broad emission of organic emitters in OLEDs. In particular, by incorporating an OLED inside a microcavity (Figure 5.6a), and coupling the device emission to a cavity mode, the spectral linewidth of the device emission can be significantly narrowed, and the directionality of the emission as well as the emission light intensity are improved. Each of the aforementioned cavity effects lead to purer color generation. Recall that a planar microcavity consists of solely two mirrors (either metallic or dielectric (as in the case of a 1D PC, see section 1.1.1.2) or both) sandwiching a medium with a thickness comparable to optical wavelengths. In an OLED microcavity, this medium between the two mirrors constitutes the active layers of the OLED (i.e. emitter, ETL, HTL, electrodes). The most commonly employed OLED microcavity architectures employ: i) two metal mirrors\textsuperscript{[12-15]} (typically silver) made of the same metal but deposited with different thicknesses to afford one mirror that is only partially reflective and the other almost completely reflective (to reflect the Fabry-Perot nature of optical cavity); and ii) one mirror being a dense dielectric 1D PC, typically SiO\textsubscript{2}/TiO\textsubscript{2} or SiO\textsubscript{2}/Si\textsubscript{x}N\textsubscript{y} and the other mirror (which also serves as the cathode of the LED) being a metal\textsuperscript{[15-22]}, typically made of aluminum. With regards to the former, excessive use of metals are unfavored in such excitonic applications as they easily engage in energy transfer with excitons of the organic emitter which in turn decreases the external quantum efficiency of the LED. With regards to the latter, that is microcavities made with dielectric 1D PCs, because neither SiO\textsubscript{2} nor TiO\textsubscript{2} nor Si\textsubscript{x}N\textsubscript{y} are conductive, a layer of ITO (or another suitably conductive and transparent oxide or metal) must be deposited atop the 1D PC to serve as the anode (hole injector) of the OLED (following ITO deposition, the remainder of the OLED structure is fabricated of course). Although necessary, the deposition of such an additional layer is not favorable as it; i) adds an additional step to the fabrication process and complicates the modeling of the structure; ii) it modifies the Bragg reflectivity of the 1D PC (as it disrupts the periodicity
Figure 5.6. a) Device structure of OLED microcavity containing an STCPC as both the anode as well as partially reflecting mirror. b) Measurement setup employed for the analysis of the EL properties of STCPC containing OLED microcavity. c) Molecular structures of the emitting species, Alq₃, the hole transporting species, NPB, and the hole injecting species, PEDOT:PSS, of the OLED microcavity.

Because our STCPCs are simultaneously selectively reflective as well as electronically conductive, such 1D photonic materials are ideally suited for integration into OLED
microcavities. In such a device, for the first time, the 1D PC is capable of serving two necessary functions: i) as one partially reflecting mirror of the optical microcavity; and ii) as the anode of the diode. The devices were fabricated directly onto the STCPC with an overall structure of (STCPC) / poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) / \( N,N\)-di(naphthalene-1-yl)-\( N,N\)-diphenyl-benzidine (NPB) / tris(8-hydroxyquinoline) aluminum (Alq\(_3\)) / LiF / Al as illustrated in Figure 5.6a. The molecular structures of the hole-injecting layer, PEDOT:PSS, the hole transport layer, NPB, and the emitter/electron transport layer, Alq\(_3\), are also included in Figure 5.6c. We highlight here that such work represents the first example of the incorporation of a transparent and conducting oxide photonic crystal into an OLED architecture. The use of such a PC creates now a cavity region that consists purely of organic materials (optically homogenous) which in turn significantly simplifies the microcavity fabrication and simulation process. Let us now consider the performance of an OLED microcavity bearing STCPCs.

The green and black plots of Figure 5.7a correspond to the reflectance spectra of a green-reflecting STCPC and a microcavity of composition (green STCPC) / PEDOT:PSS (60 nm) / NPB (70 nm) / Alq\(_3\) (45 nm) / LiF / Al, respectively. The most notable feature of the reflectance spectrum of the STCPC is again the observance of a photonic stopband in the visible spectrum centered at 541 nm. With regards to the reflectance of the OLED microcavity containing the green reflecting STCPC, what is observed as expected is intense broadband reflectivity over a range of 450 – 700 nm with a narrow transmission dip with a peak transmissivity of 60% centered at 540 nm. Thus, the narrow transmission dip is a direct manifestation of the resonant cavity mode which arises as a result of the spacing between the two mirrors of the microcavity. The high transmissivity (~60%) and small FWHM (~21 nm) of the cavity mode are a testament to the quality of the optical microcavity constructed.

In addition, as discussed in section 1.4 and again expressed mathematically in eqn.1.10 and 1.11, the peak wavelength of a resonant cavity mode is dependent on the optical thickness of the cavity region and the Bragg peak wavelength of the 1D PC. For our studies, to vary the position of the cavity mode, we altered only the Bragg peak wavelength, thus modulating the magnitude of the first term in eqns. 1.11 and 1.12, and held the optical thickness of the cavity region constant. Figure 5.7b includes the reflectance spectra of cavities bearing equal cavity thicknesses but fabricated from three different STCPCs, one exhibiting blue reflectance (Bragg peak at ~ 475 nm), green reflectance (~ 548 nm), and red reflectance (~ 614 nm). The cavity
modes lie at 498 nm, 536 nm, and 570 nm for the cavities bearing blue, green, and red reflecting STCPCs, respectively. Thus, by employing STCPCs with peak reflectivities that span the range of 494-614 nm, it is possible to achieve cavity reflectances which span a range of 498-570 nm. This range is particularly well suited for the commonly employed green emitter Alq3 as such exhibits an electroluminescence FWHM over a range of 488-571 nm. Thus, because of the good overlap of the Alq3 emission with the cavity modes of the STCPC containing microcavities, the emission of Alq3 can be simultaneously narrowed and amplified over it’s entire EL range using STCPC-based microcavities.

Since Alq3 exhibits a peak electroluminescence at 524 nm, we employed the green reflecting STCPC in an OLED microcavity in order to effectively gauge the optical effect of the STCPC-based microcavities on the EL properties of Alq3. Again, as mentioned in section 1.3 of Chapter 1, it is expected that i) the peak Alq3 electroluminescence overlap the peak transmissivity (ie. the cavity mode) of the microcavity, ii) that the spectral linewidth of the emission of the Alq3 embedded within the microcavity be significantly narrowed compared to the Alq3 EL from a noncavity-based OLED, and iii) that the peak intensity of the EL emission
Figure 5.8. a) Normalized EL spectra from a noncavity OLED (dotted black) and a microcavity OLED (green) under 10 V bias. The OLED structure was of that depicted in Figure 5.6a. b) Normalized EL spectrum and cavity reflectance overlayed. Note the good overlap of the cavity mode and the cavity emission which is indicative of a resonant cavity effect. c) Photograph of microcavity OLED of a) under a 10 V bias. d) Chromaticity diagram highlighting the CIE coordinates of the cavity EL(•) and noncavity EL(+) coordinates. Pure colors lie at the edges of the diagram.

from the cavity be greater than the peak intensity of the EL emission from a noncavity OLED. The observation of such phenomena is indeed indicative of a resonance effect between the cavity mode of the microcavity and the emission of the Alq₃ emitter. Figure 5.8 includes the EL spectra from a green-STCPC containing OLED microcavity (green curve) and non-cavity OLED. It is evident that ii) listed above is satisfied as the FWHM of the Alq₃ emission is reduced from 100 nm in the non-cavity OLED to 24 nm in the STCPC-based OLED microcavity. This value is
Figure 5.9. \( IV \) curve of green STCPC containing OLED microcavity with device structure shown in Figure 5.6. The turn-on voltage of our OLED microcavity is 3.3 V. The inset includes a measurement of brightness vs. current density. A maximum luminance of 12,030 cd/m\(^2\) is achieved at a current density of 450 mA/cm\(^2\).

comparable to previous literature reports of OLED microcavities\(^{[12-24]}\) however, it is expected that this value can be even further reduced by increasing the reflectivity of the STCPC (which can be simply achieved by increasing the number of bilayers in the STCPC structure). In addition, although the EL data of Figure 5.8a is normalized, the non-normalized data shows that the EL emission of the microcavity is more intense than the non-cavity OLED at an applied voltage bias of 10 V. Figure 5.8b displays both the reflectance and the EL spectrum of the STCPC based cavity. As expected, the EL spectrum of the OLED microcavity overlaps the cavity mode very well as the EL peak maximum lies within 4 nm of the cavity peak transmittance. Also, the FWHM of the cavity mode is nearly identical to the Alq\(_3\) cavity based emission. The observance of such a phenomenon satisfying requirements (i-iii) listed above effectively confirm that a microcavity effect is indeed operative in our fabricated system.

Additional device characteristics of our STCPC containing OLED microcavities are provided in Figure 5.9. The \( IV \) curve of the OLED microcavity with the device structure shown in Figure 5.6 displays obvious diode behavior. The turn-on voltage of our device was determined
to be 3.3 V. The inset of Figure 5.9 displays how the luminance varies with current density of the OLED microcavity. The maximum luminance of the device is 12,030 cd/m² at a current density of 450 mA/cm² which is comparable to reported OLED microcavities but less than the best microcavities reported to date. We are currently performing additional measurements on our microcavity OLED to determine the current efficiency and power efficiency of the device. We are also performing each of the above measurements on noncavity OLEDs bearing the same organic structure and prepared with the same ITO as used in the STCPC in order to determine the enhancement factor of our OLED microcavity over that of the noncavity OLED.

For such STCPCs to be integrated into commercial OLED displays, it must be possible that the entire photonic crystal be patternable via photolithography. As a proof-of-concept, although the demonstrations of Figure 5.10a)-c) are rather crude and only performed on the macroscale, we patterned a transistor pattern, lines, and the letters “UT” into a blue-reflecting STCPC. The patterning proceeded first by spin-coating a commercial photoresist onto the
surface of the STCPC. It is relevant to note here that the uppermost layer of the STCPC is a dense layer of ITO and thus, the resist does not penetrate the material. Following spin-coating, a suitable mask was placed over the photoresist and exposed to UV light. The resist was then developed in toluene and the exposed regions subsequently etched with Zn powder and concentrated HCl. Much to our surprise, considering the significant porosity of the NP layers in the multilayer structure, the etch, at least on the macroscale, was observed to proceed anisotropically (ie. from top - down) by simply patterning the surface. We are currently investigating what is the lower limit of this patterning process.

5.5 Summary

In conclusion we have fabricated the first examples of conductive 1D PCs for optical wavelengths. It is worth mentioning here that 1D STCPCs represent the first example of photonic crystals based on the highly technologically relevant material of ITO as the 1D photonic materials are comprised of alternating layers of spin-coated ATO and sputtered ITO films. These novel 1D STCPCs exhibit intense Bragg reflectivity but are simultaneously highly transmissive over spectral regions outside of their respective stopband. For example, 1D STCPCs comprised of 5.5 bilayers of ~80 nm thick ITO and ATO layers deposited on 0.7 mm thick glass substrates exhibit a peak reflectance greater than 80% at a wavelength of ~580 nm and have an average transmission of 78% over the spectral region ranging from 700 nm to 900 nm. Also, we have shown that the spectral position of their Bragg-peaks can be tuned by the thicknesses of either their ITO or ATO nanoparticle layers. Furthermore, the sheet resistance of these 1D STCPCs is comparable to that of sputtered ITO. Given their high conductivity as well as tunable optical properties, we demonstrated the integration of such 1D STCPCs into OLED microcavities to simultaneously serve as the anode of the diode and as a one of the two mirrors of the optical cavity. The aforementioned represents the first example of such a capability as well as the first example of ITO-based PC integration in OLEDs. We observed an impressive cavity effect as the FWHM of the OLED emitting species, Alq₃, was reduced to 24 nm. We are currently pursuing the incorporation of our STCPCs into other relevant devices in the areas of lasing (potentially a good anode for an organic injection laser), electrochemistry (an electrode material), optical telecommunication, and multi-junction photovoltaics (as a back reflector in an a-Si or organic solar cell) for the end-purpose of efficiency enhancement.
5.6 References


Chapter 6
What is Next?

6.1 Photonic Crystals

Although it has been twenty years since the concept of a photonic bandgap was proposed\cite{1,2}, the original goal of the realization of a three-dimensional material with a complete photonic bandgap for visible light, has eluded researchers. Nevertheless, this idea inspired the now incredibly active area of photonic crystal research, which has resulted in the fabrication of specialized materials capable of controlling light in fascinating ways. As highlighted in the introductory section of this thesis, numerous PC constructs fabricated from a broad range of materials as well as synthetic methodologies involving top-down and bottom-up nano- and microfabrication have emerged. Most notably, PC materials with complete photonic bandgaps lying in the infrared and microwave regions of the EM spectrum have been fabricated\cite{3,4}. Therefore, owing to such a vast pool of resources now available, the foundations are established for commercialization of specific photonic crystal based technologies. In fact, photonic crystals with bandgaps in the microwave and radio frequencies are currently used in antennae that direct radiation away from the heads of cellular telephone users. Moreover, numerous start-up companies have emerged attempting to bring PC materials and devices to market.

Omniguide Communications (Cambridge, MA), based on the research of Yoel Fink and J. D. Joannopoulos at MIT and Mesophotonics (Southampton, England) led by G. Parker are start-up ventures pursuing the development of photonic crystal waveguide technology\cite{5}. Such technology would essentially allow for low-loss transmission of light around tight corners (which is not possible with conventional fiber optic waveguides) and over appreciable distances. The realization of miniature waveguides is pivotal for the development of an all-optical computer\cite{6,7}, a proposed device capable of logic function driven purely by photons rather than electrons. In such a device, miniature waveguides would serve as the interconnects (ie. wires for photons) between various components of an all optical integrated circuit. In addition to waveguides, researchers hope to also build diodes and transistors from PCs which will further enable the development of an all-optical computer. Although Omniguide and others have demonstrated PC waveguiding, Parker believes that a prototype optical computer is still 25 years away. Other notable PC-based ventures include Blaze Photonics (Bath, England)\cite{8} and Redfern Polymer Optics (Sydney Australia)\cite{9} which are start-ups pursuing the development of photonic crystal
glass fibers (similar to the work described in section 1.1, Figure 1.3) and photonic-crystal polymer fibers, respectively, again for the purposes of waveguiding with little dispersion.

To continue the development of the research described in Chapter 2 and Chapter 3 of this thesis, a University of Toronto start-up company, Opalux Inc., was created in 2007. Within a relatively short time frame, Opalux has now emerged as a global leader in the development of technologies based on colloidal photonic crystals. The company is attempting to commercialize technologies dubbed Photonic Ink and Elast-Ink, which are broad wavelength tuneable opaline systems designed for display applications (see Chapter 2 and 3) and anticounterfeiting protection, respectively. With regards to Photonic Ink, it is the inverse PFS 3D opal which at present demonstrates the best device performance. However, Opalux is now actively pursuing the development of Photonic Ink based on one-dimensional photonic crystals (ie. 1D P-Ink) owing to the higher reflectivities, lower device thickness, and tolerance toward a broad range of materials compositions that such a device offers. In time, provided that effort is still directed toward the development of 1D P-Ink, it is expected that the performance of 1D P-Ink will surpass that of its 3D counterpart.

Indeed, as the aforementioned certainly attests, the field has been advancing at high speed since its inception. To maintain the same rate of progress, it will be necessary for researchers to overcome the difficulties associated with the fabrication of small 3-D periodic structures with feature sizes of less than 1 μm. Only then will complete PBGs be attained in the visible spectrum and in turn photonic crystals will be able to realize their full potential. Nevertheless, it is certainly expected in the next decade or two that research currently being conducted will give birth to commercial photonic crystal based lasers and light-emitting diodes (LEDs).

### 6.2 Lasers

Although the field of organic semiconductor lasers is young at little more than a decade old, it too is progressing at a rapid pace primarily because organic lasers offer new challenges and opportunities for organic light-emitting materials beyond organic light-emitting diodes. Organic semiconductors are very appealing for lasing applications since they are easily processable from solution and offer the prospect of emission tuneability via simple structure manipulation. Certainly the greatest effort in the field is currently being directed toward the first demonstration of electrically pumped organic lasers. It is expected that the realization of
such a device will impact technology development in the same way that electrically pumped inorganic lasers have. However, such function has yet to be achieved as organic lasers cannot support high enough current densities to achieve a necessary population inversion for lasing. Recent reports\textsuperscript{[17]} claiming to have achieved electrically pumped organic lasers have yet to gain widespread acceptance owing to both insufficient data provided to make such a claim as well as a poor correlation between theoretical predictions and the data provided. Therefore, intense research continues toward this end particularly on systems bearing a microcavity structure (ie. analogous to an OLED microcavity) as this is regarded as the simplest and most promising architecture for the desired application. We therefore hope that one of our systems, particularly the OLEDs microcavities bearing conductive STCPCs described in Chapter 5, could potentially contribute to such a realization. Nevertheless, it is relevant to note that a key recent breakthrough, made possible by the reduction of polymer lasing thresholds, is the demonstration of direct optical pumping of polymer lasers by gallium nitride diode lasers.\textsuperscript{[18]} Such indirect electrical pumping gives many of the advantages of electrical pumping and paves the way for organic semiconductor lasers to become practical sources, initially for use in a range of spectroscopic applications.

In Chapter 4, lasing was demonstrated in a laser dye infiltrated- and organic semiconductor infiltrated-nanoparticle 1D PC. Note that a central feature of the 1D PC employed in these proof-of-concept studies is the nanoparticle generated porosity, which enables the uptake of a high loading of R6G dye or PPV polymer, an attribute not possible with conventional 1D PCs consisting of dense constituent layers. Following intrapore emitter adsorption considerable porosity can be arranged to remain in the composite 1D PCs, which bodes well for future work whereby adsorption-desorption of vapors and liquids can be gainfully employed as a means to dynamically tune the wavelength of the laser emission, suggesting exciting opportunities for new kinds of sensors. In addition, a logical extension of the work described herein would involve the development of a microcavity where one or both of the mirrors are made of NP 1D PCs. It is expected that the lasing performance of the analogous microcavity will be superior to the NP DFBs described in Chapter 4 as the DOS of the cavity mode greatly exceeds the photonic DOS at the band edges. In Figure 6.1, we demonstrate our first efforts toward the development of microcavity laser systems bearing NP 1D PCs capable of vapor detection. Here, a microcavity, which consists of two SiO$_2$/TiO$_2$ NP 1D PCs as the mirrors sandwiching a blend of polystyrene and MEH-ppv (which note serves as the gain medium, see Figure 6.1a), is shown in Figure 6.1b
Figure 6.1. Fabrication and sensing capability of NP 1D PC microcavities. a) Photographs of an NP 1D PC (left) and an NP 1D PC (right) onto which a MEH-ppv/polystyrene blend (i.e., the gain medium) has been transfer printed. The emission of the gain medium is evident as the photograph on the right is taken under UV excitation. To complete the optical microcavity, either a metal is evaporated or another NP 1D PC is laminated atop the gain medium as is shown in b). When exposed to toluene vapor, the Bragg reflectivity of the 1D PC is red-shifted which causes a red-shifting of the cavity mode and expectedly in turn, a change in the lasing wavelength.

prior to and after exposure to toluene vapor. To prevent infiltration of the polymer gain medium into the 1D PCs it is transfer printed as solid film on PDMS. Subsequently, the capillary condensation of toluene vapor into the pores causes a red-shift of the Bragg diffraction of the porous 1D PCs which in turn shifts the cavity mode. The shift of the cavity mode will thus cause a shift in the lasing wavelength. This system should offer good sensitivity owing to the narrow laser emission and because the Bragg peak and cavity mode shifts are dependent on the refractive indices of the vapors to be sensed, the system should also be relatively selective.

The demonstration of lasing in our NP 1D PCs has also inspired us to further our involvement in such a highly intriguing field. Thus, owing to the availability of high quality Si
quantum dots in our laboratory, we recently directed our attention to the fabrication of laser systems containing quantum dots as the gain medium. Klimov et al.[18] have recently demonstrated gain narrowing from the archetypal quantum dot system, core-shell nanoparticles of CdSe/ZnS. Also, a single report[19] of lasing in top-down fabricated Si quantum dots has been provided, however it has yet to gain widespread acceptance as a legitimate demonstration of Si quantum dot lasing. We therefore attempted to make use of our bottom-up synthetic Si quantum dots in a polystyrene (PS) matrix as the gain medium of a planar microcavity laser. Figures 6.2a
and 6.2b show the red-orange emission of the Si quantum dots under UV excitation in solution and as a thin film, respectively. The microcavity consisted of a tailor made 1D PC (a SiO$_2$ NP/ITO 1D PC similar to the type highlighted in Chapter 5) and an Ag film as the two mirrors separated by the Si quantum dots (0.15 wt.%) in PS with an optical thickness of $\lambda/2$, where $\lambda$ corresponds to the Bragg peak maximum of the 1D PC. In Figures 6.2c and 6.2d, we provide direct evidence for lasing from our Si quantum dot microcavity. The black curve of Figure 6.2c corresponds to the reflectance of the microcavity, the most notable feature here again being the sharp transmission dip (i.e., the cavity mode) centered at 680 nm. Because the photon density of states is high at the cavity mode, we expect, provided that the Si quantum dot active layer experiences sufficient gain, at a certain pump energy density, lasing should ensue solely at cavity mode frequencies. In fact, this is precisely what is observed as the red curve of Figure 6.2c corresponds to the emission spectrum of the microcavity above the lasing threshold. We see that the peak is very narrow (~3 nm) and almost perfectly overlaps, as expected, the optical cavity mode. Consistent with the aforementioned are the power characteristics displayed in Figure 6.2d. The output power of the microcavity has a nonlinear dependence on the input power, with a kink at the lasing threshold which occurs at an energy density of 1 mJ/cm$^2$.

The above results are indeed significant as one of the great challenges to date in photonics has been to modify silicon for the purposes of enhancing its light emission properties.\textsuperscript{[20]} The effort is primarily driven by the desire to integrate novel optical circuitry into well-established electronic designs to make possible new information processing and storage architectures. Since the overwhelming majority of existing electronics is manifest in Si, it seems intuitive that one elegant approach would be to integrate Si-based photonic devices into Si-based electronic devices. With the efforts described herein, we have taken one step closer to the realization of this goal.

### 6.3 OLEDs

With regards to OLEDs, the future is bright indeed as commercialization is already a reality and steady expansion is evident. Two companies, Sony and Samsung, certainly lie at the forefront of the field. Sony currently sells Walkmans, MP3 players, and 15 inch TVs employing OLED monitors.\textsuperscript{[21]} Samsung Electronics and LG Electronics have released mobile phones,
digital cameras, and TVs making use of OLED displays. In addition, Samsung projects that by 2011, they will have large (40+ inch) HD OLED TVs available for sale.\textsuperscript{[22]}

Indeed OLEDs represent a technology that is here to stay. If one compares OLEDs to liquid crystal displays (LCDs), OLEDs are brighter, offer better contrast, wider viewing angles, use less power, and provide faster response times.\textsuperscript{[21]} OLED screens can also be one-third thinner than LCDs, since they do not need a backlight, and that makes them particularly suitable for portable electronics devices. One major drawback though is cost as OLEDs are currently more expensive to manufacture than LCDs. Nevertheless, it is expected, with continued research and development that the cost of OLED fabrication will be reduced to below that of LCDs rendering OLEDs the more viable display technology.

With regards to OLED microcavities, it is certainly accepted that such an architecture represents the best way to achieve color saturation and enhanced luminance from OLED devices. However, challenges such as integration of various microcavity design concepts with current OLED fabrication methods as well as the inherently poor viewing angles\textsuperscript{[23]} of such devices, hinder greater development and widespread usage. To date, microcavity designs typically require specialized device architectures that are not compatible with existing device structures. The ideal solution is to have direct drop-in replacements for various layers of the OLED to change its performance characteristics. The selectively transparent and conductive Bragg stacks described in Chapter 5 being based on ITO are therefore particularly interesting since they can be used as a direct drop-in replacement for regular ITO. Poor viewing angles in OLED microcavities stem primarily from the 1D nature of the 1D PCs employed as well as the microcavity itself as such only support highly directional output from the OLED device. For some applications, directional output is sufficient however most display applications prefer as wide a viewing angle as possible. Perhaps the use of omnidirectional reflectors, developed by Joannopoulos \textit{et al.}\textsuperscript{[24]} as the mirrors of the optical cavity represent one way of circumventing the significant angle dependence of OLED microcavities.

### 6.4 References


[8] www.blazephotonics.com
Figure 1. $^1$H-NMR of methylvinylsilaferrrocenophane ($C_6D_6$, 400MHz). The structure of methylvinylsilaferrrocenophane is shown as an inset.
Supporting information for Chapter 3
Figure 1. Spectroscopic Ellipsometry method demonstrating how $\alpha$ and $\beta$ are related to $\tan \psi$ and $\Delta$, which in turn allow for the determination of thickness, $t$, and effective refractive index, $n_{eff}$.
Appendix C

Supporting information for Chapter 4

Crystal data and structure refinement for p-xylene-bis(tetrahydrothiophenium chloride).

Empirical formula C16 H32 Cl2 O4 S2
Formula weight 423.44
Temperature 150(1) K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P 21/n

Unit cell dimensions
\[ a = 7.0933(2) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 10.1351(5) \text{ Å} \quad \beta = 101.544(3)^\circ. \]
\[ c = 14.8789(6) \text{ Å} \quad \gamma = 90^\circ. \]

Volume \[ 1048.03(7) \text{ Å}^3 \]

Z 2
Density (calculated) \( 1.342 \text{ Mg/m}^3 \)
Absorption coefficient 0.526 mm\(^{-1}\)

F(000) 452
Crystal size \( 0.18 \times 0.18 \times 0.14 \text{ mm}^3 \)

Theta range for data collection 2.79 to 27.46°.
Index ranges \(-9 \leq h \leq 9, -13 \leq k \leq 13, -19 \leq l \leq 19\)

Reflections collected 6538
Independent reflections 2376 \[ \text{[R(int) = 0.0389]} \]
Completeness to theta = 27.46° 99.2 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.933 and 0.845

Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 2376 / 0 / 125

Goodness-of-fit on \( F^2 \) 1.088

Final R indices \([I>2\sigma(I)]\) \[ R1 = 0.0381, wR2 = 0.0856 \]
R indices (all data) \hspace{1cm} R1 = 0.0549, wR2 = 0.0958

Largest diff. peak and hole \hspace{1cm} 0.362 and -0.336 e.Å\(^{-3}\)

**Figure 1.** GPC of poly(phenylene vinylene), PPV, PDI = 3.7.
**Figure 2.** A typical setup for making the lasing measurements presented in Chapter 4.
Appendix D

Supporting information for Chapter 5

Definition of Sheet Resistance:

Figure 1. An optical micrograph taken over an area of ~1mm$^2$ area of the yellow 1D TCPC portrayed in Figure 2 is shown here to exemplify the high quality of our 1D TCPCs. This 1D TCPC is comprised of 5.5 bilayers of ~80nm thick ATO nanoparticle films and ITO layers that have an equivalent thickness of ~80nm when deposited onto a flat substrate. The reflectance spectrum of this 1D TCPC peaks at ~580nm.
Figure 2. The ellipsometric parameters a) $\alpha = \frac{\tan^2\psi - \tan^2 A}{\tan^2\psi + \tan^2 A}$ and b) $\beta = 2 \cos \Delta \frac{\tan \psi \tan A}{\tan^2 \psi + \tan^2 A}$ as measured and fit for the green 1D STCPC shown in Figure 2. The position of the analyzer, $A$, was set to 45° and the statistical measure of goodness of fit was $4.2 \times 10^{-3}$ ($R^2 = 0.96$). A comparable measure of goodness of fit for the red 1D STCPC (not shown) was also attained ($R^2 = 0.94$). The dispersion law assumed the Cauchy model with little light absorption in the visible range.

Figure 3 ellipsometric porosimetry of 80 nm ATO nanoparticle film.
**Figure 4.** An example of a 1D PC consisting of alternating layers of SnO$_2$ nanoparticles and sputtered ITO.