Self-Assembled Photonic Crystals Infiltrated with Nanoplatelets and Nanotubes

by

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Abstract

As we move into the next century, photonics will play a significant role in the exploration of the frontiers of science. Photonic materials have the ability to control the flow and generation of photons, and offer greater control over material properties, which can potentially provide solutions to the optoelectronics industry, i.e. improving the current limit in the speed and the capacity of optoelectronics devices.

In 1987, a novel class of artificial structures named as ‘photonic crystal’ (PhC), was invented for the inhibition of spontaneous emission and the localisation of photons, which offers control on absorption, emission and propagation of light. Photonic crystals are long-range periodic materials with a periodicity of the order of the wavelength of light. It is the periodicity in refractive index, which determines the allowed and forbidden bands for the light frequency in the photonic crystals. This periodic structure generate Bragg diffractions which result in forbidden frequency in specific propagation directions, so called photonic stop bands. When light propagation is forbidden in a specific range of frequencies in any direction inside the crystal and polarization a complete photonic bandgap is achieved.

There are three types of photonic crystals: one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) photonic crystals, which depend upon the periodic modulation of the dielectric constant i.e. either created in one, two or three dimensions.

This thesis deals with the fabrication and analysis of 3D photonic crystals which shows strong confinement of light in three dimensions.

In this thesis, we will introduce two different types of 3D photonic crystals i.e. pristine (undoped) and infiltrated (doped) with different nanomaterials fabricated by soft lithographic method i.e. self-assembly.
The fabrication 3D photonic crystal is a very challenging task, one needs to build up high-quality 3D photonic crystals environments. By 1991, Yablonovitch had demonstrated the first three-dimensional photonic band-gap in the microwave regime by drilling an array of holes in a transparent material, where the holes of each layer form an inverse diamond structure – today it is known as Yablono-vite. Over the years state-of-the-art fabrication technologies have been developed to fabricate 3D photonic crystals operating in different range of electromagnetic spectrum ranging from near-infrared to visible wavelength ranges. However, these sophisticated fabrication techniques are expensive and time consuming. Soft lithography is another inexpensive versatile route to fabricate photonic structures.

The research conducted in this thesis targets building up a solid and comprehensive study on the fabrication of 3D photonic crystals in the technically important visible wavelength range.

This project revolves around the fabrication of undoped photonic crystals (pristine) and in-filled photonic crystals with two dimensional layered nanomaterials such as graphene and boron nitride and 1-dimensional materials (single walled carbon nanotubes). Natural gravitational sedimentation method has been used to fabricate photonic crystals using latex polymer as a 3D template.

Despite potential advantages, there are hardly any reports concerning layered nano-filler based photonic crystals (PhCs). In particular, layered two-dimensional based carbon (Graphene), transition metal dichalcogenides (TMDs: Molybdenum disulphide, Tungsten disulphide) and one dimensional materials such as carbon nanotubes are of particular interest due to the high level of optoelectronic functionality they can impart.

One of the biggest issues is to produce large quantity of these nano-fillers and, at the same time maintain the quality as well. Once a stable source of nanoparticles is established achieving a homogenous and controlled distribution of these fillers within a
polymer matrix is still an obstacle commonly encountered in the fabrication of nanostructures.

To overcome this problem self-assembly of latex particles has been used to fabricate two and one dimensional based photonic crystals. During the self-assembly process the individual polymer particles deform into rhombic dodecahedra, due to capillary forces as the polymer dries. Highly ordered polymeric crystals can be produced by this novel technique. This dodecahedra assembly of polymer particles act as a template to assemble nano-fillers, by forcing the nanoparticles to fill the interstitial sites and create three-dimensional, hexagonal patterns. This assembly technique generates a highly uniform distribution of the filler throughout the polymer matrix. One of the key features of our fabricated photonic crystals is the preparation technique i.e. natural, gravitational, sedimentation which makes it very cost effective and efficient.

In this thesis, for the first time, colloidal photonic crystals, embedded with such nano-fillers have been fabricated using a novel and facile latex technology. We also propose that this technique is general and can be applied for a range of other two-dimensional and one-dimensional materials. Critically it is demonstrated that the choice of filler influences the optical and mechanical properties of the resultant crystals.

This thesis also demonstrates that the optical properties can also be manipulated mechanically, post-processing, using stretching, compression and humidity, demonstrating their potential as sensors and visual indicators which will greatly extend their applications in various fields such as optical sensing materials and various optical devices.
Declaration

This thesis and the work to which it refers are the results of my own efforts. Any ideas, data images or text resulting from the work of others (whether published or unpublished) are completely recognized accordingly as such inside the work and ascribed to their originator in the text, bibliography or in footnotes. This thesis has not been submitted in entire or to some degree for whatever other scholastic degree or professional qualification. I agree that the university has the right to submit my work to plagiarism detection service Turnitin UK for originality checks. Whether or not drafts have been so-assessed, the university reserves the right to acquire an electronic version of the final document (as submitted) for evaluation as above.

Self-Assembled Photonic Nanostructures
Infiltrated with Nanosheets and Nanotubes

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Thesis defended by viva voce,
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Chapter 1 Introduction

1.1 Overview

Photonics has presented a large number of significant advances in the last two decades, prompting some new photonic products and technology, with noteworthy financial profits. This technology has provided a whole new range of exciting applications such as low cost photonic circuits, high power lasers, laser defence, optical cavities etc.[1] and could be very useful for sensing with applications in mapping temperature or distance, such as is used in agri photonics for humidity and salinity sensing from the air or IR imaging which can be very useful for security or medical applications.[2-4] Photonics plays a vital role in the modern information industry, in particular in the transmission of high-speed data. Photonic technology has reformed the communication and internet sector, associated with fibre optics.[5] Optical computing is another promising application of photonic technology, which is expected to be much faster and efficient than current computing. Its applications extend from display, lighting, and solar cells to laser systems. This technology is significant, although it is still in its initial industrial stage. In 2008, the photonics products market in the world was worth €277 billion as per data of Optech Consulting in April 2010.[3] This data demonstrates that the development rate of the photonics business is in line with the industry and that the sector is constantly emerging. These statistics represent that even though it is still in its development stage, it has already been proved to be a key enabling technology and requires continuous support from research and development.

In simple terms, photonics manages and manipulates information and energy, in the form of photons or light instead of electricity. It underpins the high traffic internet, and provides the platform for most modern gadgets. Extensive research in the photonics field is due to two significant inventions: Firstly, the laser that was invented 40 years ago and has experienced remarkable development over that time.[6] Lasers are key components in today’s optical communication systems, manufacturing methods, medicine, measurements, entertainment and equipment. Secondly, very-low-loss optical fiber that has also seen tremendous progress over past 3 decades.[7] It is capable of
transmitting information in the form of light up to 100 of miles while still retaining a high optical bandwidth. The laser and these fibres are some of the key elements that are responsible for the revolution in telecommunications, internet communications, optical networking and many other fields. These are remarkable developments and likely to grow further in the future. Despite their superlative transmission properties as data carriers, this technology still depends on other electro-optical components to perform various tasks that lead to limiting of speed and the dissipation of energy or signal. To overcome this, researchers around the globe work on all optical data processing devices, ranging from signal generation to transmission and the single optical chip. Photons can overcome this issue as they can bend, get manipulated and guided, since there is no charge or rest mass property. Yablonovitch (inhibiting spontaneous emission) and Sajeev John (localize and guided photons) independently proposed a new concept of light manipulation by using periodic structures.[8, 9]

Due to the periodic building block arrangement, they called them crystals; and the way they affect the light propagation, they name them photonic. These periodic structures are often called photonic crystals (PhCs). This important invention set the new platform for the current photonics research. Since then, many types of PhCs have been reported both theoretically and experimentally. In these PhCs the refractive index varies periodically over a length scale, comparable to the wavelength of light. These PhCs possess a frequency range, where the propagation of the incident electromagnetic wave or light is forbidden. This gives some promising phenomena; such as light localization and inhibited spontaneous emission, and also it provides an ideal platform to study the light matter interaction in periodic structures.[9] Having control over the propagation of light, PhCs could provide applications in random lasers, waveguide’s, optical sensors, switching, controlled light generation of radiation and filters, etc.[10-12]

Photonic crystals can be divided into three comprehensive category based on their geometry or dimensionality: namely one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) photonic structures.[13, 14] Simplified examples of such PhCs are shown in Figure: 1.1.
Two different experimental methods are widely used to fabricate photonic crystals: nanolithography and self-assembly. Semiconductor industry uses mostly the lithography technique.[15] The biggest drawbacks of this technique is high cost; while self-assembly provide a cost-effective, cheaper, faster, simpler fabrication process.[16, 17] Nevertheless both processes are not free from defects. One example of self-assembled photonic crystals is the colloidal crystal made of silica.[18] A key feature of self-assembly process that it is not limited in their length scale, which means one can tune the operating wavelength of it to its desired applications; on the other hand, it is difficult to control the defects in such photonic crystals.

The process to fabricate photonic crystals has been intensively studied, leading to the development of various methods of making such crystals; like sedimentation, electro-hydrodynamic deposition, colloidal epitaxy, depletion-induced crystallization, convective self-assembly (controlled drying), capillary deposition method and physical confinement.[19] Sedimentation has been proven the most popular method for fabricating these structures.

### 1.2 Primary Objectives and Aims of this Dissertation

The primary objective of this work is to understand the fundamental behaviour of how light couples with the periodic structures. In the first part fabrication of photonic crystals their optical and morphological properties and effect of different parameters such as sphere size; thickness will be studied and presented in details. In the second part, tuning of optical properties will be achieved by infiltrating different 2-D layered materials and 1-D CNTs in these periodic structures. The relationship between
structural and optical will analysed and established. Theoretical bandstucure and simulated optical properties will also be discussed and will be compared with the experimental results. At the end potential application as stress strain sensor of these periodic structures will be presented.

1.2.1 Motive and Goals

Photonic crystals play a key role in the development of planner optical circuits. One of the photonics industry goals is to develop a single device with integrating multiple functions such as generation, guiding and splitting into a single substrate optical computing applications. A vision for all optical chip of the future was presented by Joannopoulos and called as “photonic crystal micropolis”.\[24\] For the researchers in this filed, it has been great goal to strive for. This optical chip can possess significant property to control light in micron-scale optical circuits in very small scale in contrast to those presently utilized in optical networks. The components in micropolis optical chip are imagined to work as low threshold lasers, wavelength division multiplexers (WDM) and switches.\[24\]

Figure: 1.2 Joannopoulos vision of photonic crystal micropolis[24].
1.3 Thesis Structure

Each chapter contains an introductory section, which summarises the relevant literature pertinent to each study.

Chapter 2:

This chapter contains two sections. In the first section, overview on the fundamental concepts that characterize the photonic crystals is presented. Their physical properties will be discussed in terms of their band structure diagrams. Afterwards, the review on the different fabrication procedure to make bare photonic crystals and infiltrated photonic crystals will be presented. In the second section, review on of two dimensional layered materials (Graphene, Boron nitride) and one dimensional nanotubes (Single walled carbon nanotubes) used for infiltration purpose in photonic crystals will be discussed. It will include their fabrication procedure, atomic structure and properties such as electronic, optical, mechanical etc.

Chapter 3:

This chapter reviews the techniques, which has been utilized to characterize the photonic crystals. It will include their operating principle and schematic illustration. Such as Atomic force microscopy, scanning electron microscopy, UV Vis spectroscopy, Mechanical testing, Raman spectroscopy etc.

Chapter 4:

This chapter provides the characterization of different latex polymer, which has been used in this study. It also presents the characterization results for graphene, boron nitride and single wall carbon nanotubes dispersions by using transmission electron microscope, atomic force microscopy, Raman spectroscopy and UV-Vis spectroscopy.

Chapter 5:

In the first section of this chapter self-assembled pristine photonic crystals fabrication procedure will be described. Afterwards their in-depth morphological studies will be presented by using scanning electron microscopy and atomic force microscopy. In the next section, optical spectroscopic results will be presented and will be compared with simulated results. This chapter will describe the effect of particle diameter, incident angle and disorder on the photonic bandgap potions.
Chapter 6:
This chapter discuss the effect of infiltration on photonic crystals properties. Photonic crystals will be infiltrated by using two types of two dimensional nanoplatelets Graphene and Boron nitride. The in-depth behaviour of tuning the optical properties of PhCs by infiltration of these nano materials will be described by using spectroscopy and scattering techniques. This chapter also describes the small angle x-ray scattering measurement to calculate the lattice spacing in the photonic crystal which then will be compared with optical fitting data and microscopic data.

Chapter 7:
This chapter contains two sections. In the first part we will describe the debundling mechanism to achieve isolated single wall carbon nanotubes by dilution process; later a specific concentration where debundling of the single walled carbon nanotubes observed will be chosen to infiltrate the photonic crystals. In the second part fabrication of PhC and their spectroscopic and morphological properties with CNT infiltration will be presented. Application of these photonic materials as stress strain sensor will also be discussed at the end.

Chapter 8:
Chapter 8 provides a conclusion of this dissertation. It will include most important points, which has been achieved and closes with some concluding remarks. Finally highlights the future directions of the research.
Chapter 2 Literature review: Photonic Crystals and Infiltrated Materials

2.1 Photonic Crystals

2.1.1 Background and Concept of Photonic Crystals

How can we achieve control over light or photons? The repeated pattern of atoms in the crystals in electronic materials generates a periodic potential for an electron propagating within the crystal, which represents the conduction properties of the crystals. The wave propagation in periodic structures is similar to the electron’s propagation in periodic potential. In a particular situation, certain waves are prohibited in the crystals lattice, which means there might be some gaps in the band, where waves cannot propagate in particular directions. Extending this situation, if the potential is very strong; this gap inhibits wave propagation in all possible directions, leading to complete bandgap. Photonic crystals are the optical analogue of a semiconductor but work in a macroscopic media (various dielectric constants) instead of at the atomic scale.[9, 20] The periodic dielectric function (periodic index of refraction) is found in the place of a periodic potential.[8, 9, 21] If the index contrast (dielectric constants of the two different materials) is large enough and the materials absorption is very low, then refractions and reflections from interfaces of incident light, are observed similar to the electron in the periodic potentials. This is how light can be controlled. In general, wave or light propagation is forbidden in the photonic crystal for a specific wavelength or certain frequencies, or a spectrum region of energies, for which the crystal forbids the propagation of light at any angle and polarization and is called a complete photonic bandgap (CPBG).[8] One well known example was given by Lord Rayleigh in 1887. He observed that incident light was completely reflected (due to destructive interference of light waves) when it was shown upon a multilayer dielectric mirror.[22] Light propagation in periodic structures/photonic crystals is governed by the four Maxwell’s equations and solution in periodic dielectric medium is required. [23, 24] These equations are:
\[ \nabla \cdot \vec{B} = 0 \]  \hspace{1cm} 2.1

\[ \nabla \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} = 0 \]  \hspace{1cm} 2.2

\[ \nabla \cdot \vec{D} = 4\pi \rho \]  \hspace{1cm} 2.3

\[ \nabla \times \vec{H} - \frac{1}{c} \frac{\partial \vec{D}}{\partial t} = \frac{4\pi}{c} \vec{J} \]  \hspace{1cm} 2.4

where \( \rho \) and \( \vec{J} \) describe and current density, respectively; \( c \) is the velocity of light in vacuum and \( t \) is the time. \( \vec{E} \) and \( \vec{B} \) are the electric field and strength of the magnetic field induction that can be calculated by averaging \( \vec{E} \) and \( \vec{B} \) fields derived from Maxwell equations. The macroscopic values \( \vec{D} \) and \( \vec{H} \), describes dielectric displacement and magnetic field strength, respectively. These equations are not easy to solve in their general form so assuming macroscopic, homogenous, linear and optically isotropic media makes simple the calculations and led to proportional relationship between \( \vec{D} \) and \( \vec{E} \) and \( \vec{B} \) to \( \vec{H} \).

\[ \vec{D} = \varepsilon(\vec{r}, \omega) \cdot \vec{E} \] and \[ \vec{H} = \frac{\vec{B}}{\mu} \]  \hspace{1cm} 2.5

where \( \varepsilon \) and \( \mu \) are the dielectric constant and magnetic permeability. The frequency dependence can be omitted \( \varepsilon(\vec{r}, \omega) \) since dielectric function does not very much and is material dependent in visible frequencies region. The refractive index (RI) is related to \( \varepsilon \) via \( n = \sqrt{\varepsilon} \). The dielectric function is not spatially constant in photonic crystal so this dependence should be taking into account using \( \varepsilon(\vec{r}) \) as general form and \( \mu \) is closed to unity and can be ignored for most dielectric materials. Taking few other assumptions into consideration, such as there are no free charges, no electric current, that is small field strength and a real dielectric constant (no absorption losses) leads to following set of equation by using \( \vec{\rho} = \vec{J} = 0 \).

\[ \nabla \cdot \vec{H} = 0 \] and \[ \nabla \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{H}}{\partial t} \]  \hspace{1cm} 2.6

\[ \nabla \cdot \varepsilon(\vec{r}) \vec{E} = 0 \] and \[ \nabla \times \vec{H} = -\frac{\varepsilon(\vec{r})}{c} \frac{\partial \vec{E}}{\partial t} \]  \hspace{1cm} 2.7

The spatial and temporal behaviour of electric and magnetic fields can be separated using harmonic approach:
Combining with equation (2.6) and (2.7) leads to

$$\nabla \times \vec{E} = -\frac{i\omega}{c} \vec{H}(\vec{r}) \quad \text{and} \quad \nabla \times \vec{H} = \frac{i\omega}{c} \frac{\partial}{\partial t} \varepsilon(\vec{r})\vec{E}(\vec{r})$$

Combining both equations results in a wave equation for magnetic and electric Eigen modes of the system:

$$\nabla \times \left( \frac{1}{\varepsilon(\vec{r})} \nabla \times \vec{H}(\vec{r}) \right) = \left( \frac{\omega}{c} \right)^2 \vec{H}(\vec{r})$$

$$\nabla \times \nabla \times \vec{E}(\vec{r}) = \varepsilon(\vec{r}) \left( \frac{\omega}{c} \right)^2 \vec{E}(\vec{r})$$

These equations represent a linear Eigen value problem on $\vec{H}$ or $\vec{E}$ that can be solved by numerical techniques. The information on photonic crystal can be extracted by periodic dielectric function $\varepsilon(\vec{r})$. Maxwell’s equations provide an exact solution due to its non-interacting nature that leads to an accurate description and prediction of the system. One can apply the same theoretical treatment to different sizes and structures since there are no fundamental length scales. In case of compression or expansion of the lattice constant, mode profile and frequencies can be easily rescaled, due to the inherent Maxwell equation’s scale invariant nature. This nature also assures that various photonic crystals structures with different lattice constants behave similarly.[24]

### 2.1.1.1 Dimensionality Aspect of Photonic crystals

Photonic crystals can be classified into three main categories one-dimensional (1-D), two-dimensional (2-D) and three-dimensional (3-D), which depend upon the arrangement of dielectric medium.[24, 25]

### 2.1.1.2 One dimensional (1-D) Photonic Crystal

One of the simplest examples of a one-dimensional photonic crystal is a dielectric multilayer film called as Bragg reflector.[26-28] Multilayer films (Bragg reflectors) can act as a mirror for light within specific a wavelength range, sum of multiple reflections and refractions that occur at each interface.[26] Figure: 2.1 (a) shows alternating layers of materials (blue and green) with different dielectric constants, with periodicity a (z -
direction), assuming each layer and periodicity extends to infinity. Figure: 2.1 (b) represents the band structure of the multilayer film.[24] The shaded region the Figure: 2.1 (b) indicates the photonic bandgap (PBG); i.e. no electromagnetic modes are allowed in this region. According to the electromagnetic theorem; low frequency modes tend to accumulate in the high dielectric constant layer and vice versa.[24] Terminology of dielectric band and air band comes from the analogy with solid state physics, where the fundamental gap is referred to as the valance band and the empty band above is called the conduction band.

Figure: 2.1 (a) One-dimensional multilayer photonic crystal consisting of alternating layers of materials (blue and green) with different dielectric constants, with a spatial period a. (b) Photonic band structure of a multilayer photonic crystal, reprinted with permission from [24].

### 2.1.1.3 Two dimensional (2-D) Photonic Crystal

A two dimensional photonic crystal is dominated by the fact that the periodicity is in two directions and it is homogenous in the third one.[24, 29-31] This plane is responsible for the PBG and the harmonic modes of the propagating light can be distributed in two different polarizations. Figure: 2.2 represents the typical example where dielectric columns (assumed infinitely tall) are arranged in a square lattice. It forbids a frequency of wave propagation in any direction with in the xy plane, i.e. for specific lattice spacing; there will be a photonic bandgap in this plane.[24] Practically, there are no two dimensional photonic crystal due to the finite size of column in reality. These structures are 3-dimensionsal but traditionally they are called 2-dimensional; since their periodicity is in two dimensions and the wave or light propagates through the same plane as the periodicity. [24]
2.1.1.4 Three dimensional (3-D) Photonic Crystals

Three dimensional photonic crystals are just an optical analogue of the ordinary semiconductor crystal. It has periodicity along all three different axes and therefore localise light in all three dimensions.[24, 32] Since its discovery several examples of possible geometries of such 3-D photonic structures (diamond lattice of air holes, Yablonovite, woodpile stack, inverse opal, alternating two-dimensional crystals of rods and holes) were explained but full bandgaps appears only in some specific ones.[33-43] It took a century to realise the concept of 3- dimensional photonic crystal after Lord Rayleigh (1887) [22] described one-dimensional photonic structures, Yablonovitch shown experimentally 3-D photonic crystals structures in 1987.[9] It was Ho et. Al. in 1990, who reported the structure fabricated on micron scales, where light at infrared wavelengths (woodpile structure) has a complete band gap in three dimensions.[44] It was fabricated by stacking dielectric “logs” (generally rectangular) with alternating orthogonal orientations. Figure: 2.3 (a) shows a four-layer ABCDABCD • • sequence woodpile structure where C and D layers have the same orientation as A and B, but are offset by half of the horizontal spacing and (b) shows the calculated photonic band structure. Lin et al.[45] (1998 b) fabricated a silicon log structure ($\varepsilon \approx 12$) with band gap around 12 $\mu$m, whereas Lin and Fleming (1999) successfully fabricated (3-D) crystal operating at optical wavelength with the minimum feature size of the 3-D structure is 180 nm and has an absolute photonic bandgap at 1.6 $\mu$m.[46]
Figure: 2.3 (a) An electron- micro-graph of a woodpile (silicon) photonic structure. The dielectric “logs” form an FCC (or fct) lattice stacked in the [001] direction (Image courtesy, S.-Y. Lin.). (b) The band structure for the lowest bands of the woodpile reprinted with permission from [24].

2.1.2 Opaline 3-Dimensional (3-D) Structure: Natural, Synthetic and Inverse Opals

Natural opals are a prominent example of photonic crystals composed of silica (SiO₂) spheres, stacked in a close-packed face-centered cubic (FCC) lattice along the <111> direction.[47-51] They possess periodic variations in the dielectric properties at submicrometer length scales.[52] Artificial opals are usually made of silica, polystyrene (PS) or polymethylmethacrylate (PMMA) spheres.[53-60] The voids between the particles are usually filled with water (3~10%), which improves the mechanical stability and improves the dielectric contrast.[61] Many of the bright, iridescent colours found in nature, from butterfly wings, to peacock feathers or certain beetles and jellyfish are due to these periodic structures.[62-65] Figure: 2.4 (a) is the optical image of a natural opal that shows bright iridescent colours; whereas (b) and (c) represent the scanning electron micrographs to show periodicity of the natural opals and artificial opals, respectively.

Figure: 2.4 (a) Natural Opal (b) SEM image of natural opals and (c) SEM micrograph of artificial opal.

Usually, artificial or synthetic photonic crystals do not have a complete band gap but possess incomplete photonic bandgap or pseudogap; however they still possess a brilliant appearance. Sanders (1964) showed that natural opal is formed of close-packed
arrangements of submicron-diameter silica spheres in water as surrounding medium. Figure: 2.5 (a) shows the band structure of an FCC lattice of close-packed dielectric spheres.[18] One can observe small gaps that appear only at specific points in the band diagram. At specific wavelength, \( k \) vectors of these gaps represent a particular direction that is responsible for specific reflected colour. Bright iridescent colours are due to these narrow bands and directionality. Artificial opals tend to be formed when particles self-assemble into an FCC lattice; as one evaporates a solution in which they are suspended (a colloid). Apart from the artificial and natural opals, there is another class of 3-D opals, called Inverse opals which can have complete psuedogap in contrast to natural or synthetic opals as first predicted by Sözüer et al. (1992).[66] The traditional opal structure can be inverted, by infiltrating the void space between the spheres with a high-dielectric material, and then dissolving away the spheres, leaving behind an inverse opal of air holes. Figure: 2.5 (b) represents the band structure of such systems, where air spheres are just touching one another \( (r = a/\sqrt{8}) \), infused in a dielectric \( (\varepsilon = 13) \) medium. The psuedogap is observed between the eighth and ninth bands.

![Figure 2.5](image)

Figure: 2.5 (a) PBG structure of a (fcc) lattice of close-packed dielectric spheres \( (\varepsilon=13) \) in air (inset). Note the absence of a complete photonic band gap. (b) The photonic band structure of an inverse opal structure, reprinted with permission from [24].

2.1.3 Fabrication Methods

The fabrication of PhCs using a top down approach; such as lithography, have been used widely in the microelectronics industry.[40, 67] Lithographic techniques; such as interference, electron beam and holographic, require repetitive patterning of the structure onto the substrate. Nevertheless, these techniques are time consuming, expensive and require sophisticated instruments. Self-assembly provide an alternative solution to lithography.[16, 17] It is a self-organisation/ bottom up technique, which has been proven to be an excellent method to fabricate three dimensional photonic structures. This technique is easy, fast, cost-effective and allows large-area fabrication.[17] This
approach is very similar to the process of natural, self-assembly of silica opals or photonic crystals and has attracted a lot of attention to make periodic or photonic crystals structures over the last two decades.[68] There are various types of self-assembly processes already reported to fabricate colloidal photonic crystals.[19] The self-assembly process is not free form disorders, such as vacancies and dislocations etc., which hampers the optical properties of the fabricated photonic crystals.[69, 70] Therefore improvements and new methods are always needed. There has been a continuous effort to improve the technique. These methods can be mainly categorized as field induced, flow induced and volume induced techniques.[19] In the field induced process it is gravitation or electric field, which is responsible for the self-assembly, restricted flow of continuous flows of particles is in flow induced and solvent evaporation is the driving mechanism in the volume restricted process. Figure: 2.6 represents the classification of the fabrication process of photonic crystals according to their driving force. There are almost 21 methods available to fabricate these photonic structures.[19] It is difficult to discuss all of them in details and also is out of the scope of this thesis. We will describe here the most common used process.

Figure: 2.6 Photonic crystals deposition method classification, presented with respect to their driving force of fabrication. redrawn from [19].
2.1.3.1 Sedimentation Method

Sedimentation method was one of the first techniques to fabricate artificial periodic/photonic structures.[71-74] In sedimentation technique, dispersed colloids are permitted to settle inside the container as illustrated in Figure: 2.7. The higher density of suspended particle is the driving force in contrast to surrounding medium.[75] There are two different competing forces, that are present during sedimentation; thermodynamic (i.e. Brownian motion) and gravitational. For smaller particles (< 500nm), thermodynamics plays an important role, whereas gravity is the dominant force for larger particles.[47, 76] Thickness of the fabricated crystals depends upon initial concentration of solid, which can be tuned.

To achieve better ordering, sedimentation velocity should always be lower than the crystallization rate ($\gamma$) else sediment will end up with amorphous glass state. It is defined as:

$$\gamma \propto \frac{K_B T}{\eta d^2} \quad 2.12$$

![Figure: 2.7 Schematic illustration of a sedimentation cell for colloidal crystallization and inset shows colloids settling under the influence of gravity.](image)

where $\eta$ is viscosity of medium whereas $d$ is the particle diameter. The sedimentation velocity ($U_o$) of an isolated sphere as determined by Stoke’s law is

$$U_o = \frac{d^2 (\rho_p - \rho_{solvnet}) g}{18 \eta} \quad 2.13$$
where \( \rho_p \) and \( \rho_{\text{solvent}} \) are the particle and solvent density respectively, and \( g \) is gravitational acceleration.[77] Equation (2.13) accurately determines the sedimentation velocity for dilute suspensions. Generally, the structures grown by this technique possess FCC structure. The difference in the Gibbs free energy between FCC and hexagonal randomly packed (HCP) is \( \sim 0.005k_B T \), which leads colloids to arrange them in FCC rather than any other arrangement.[78, 79] It can be achieved by slowing down the settling rate of the suspension.[80] Though, there will be the HCP staking in the colloids during sedimentation and cannot be ruled out completely.[81] Literature suggest that in the final product they can take \( \sim 20\% \) volume of the crystals. One of the major drawbacks with it is slow process, which is not suitable for bigger particles. Final product contains \( \sim \) one defect per unit cells and large various sizes of domain’s, which is to simultaneous nucleation at different points. It is found that the settling rate is a linear function of local filling fraction, which is valid for \( \phi_v \leq 5\% \). Figure: 2.8 shows the phase diagram of hard sphere particles. It explains different phases of ordering as function of filling fraction. Liquid to ordered particles starts at \( \phi_v \sim 0.49 \), whereas onwards this till \( \phi_v \leq 0.545 \) mixture of fluid and crystal exists. Beyond this region, \( 0.545 < \text{crystal} < 0.74 \) formation of homogeneous crystal takes place.[82, 83] If the sedimentation rate is too fast, there is a possibility of another state that can exist in between 0.58 and 0.64 volume fractions. It is due to movement hindering by particles.

![Phase Diagram of Hard Sphere particles](image)

Figure: 2.8 Phase Diagram of Hard Sphere particles redrawn from [82].

2.1.3.2 Horizontal Deposition Method (HDM)

Horizontal deposition method (HDM) offers rapid fabrication of structures, which is due to large-area meniscus.[84-88] Meniscus exists along the boundary/periphery,
which increases the area, where crystallization can take place till the centre of the substrate. This technique largely depends upon the suspension concentration and volume. It also saves large volume of suspensions and also rules out the effect of the solvent evaporation. The horizontal deposition method is fast, efficient, and cost-effective to fabricate large-area photonic crystals.[87, 88] Figure: 2.9 shows the schematic of horizontal deposition setup. Meniscus allows to confines the particles thus increases the filling fraction, which led to photonic crystal fabrication. In HDM, thickness of the crystals can be controlled by the concentration and volume respectively. The main drawback of this technique is uncontrollable in thickness. On drying, suspension move towards the meniscus, which led less or almost no suspension in the centre that will cause inhomogeneous thickness. The formation of small domain sizes, coffee ring effect are the other disadvantage of this technique.[87]

Figure: 2.9 Schematic illustration of horizontal deposition set up.

2.1.3.3 Vertical Deposition Method (VDM)

Vertical deposition has been proven to be the most versatile and widely used technique to fabricate 3-D photonic crystals.[89-92] Figure: 2.10 shows the schematic diagram of set up, where glass slide is immersed vertically into the container filled with suspension. It forms a meniscus, where air, liquids and substrate meet. It is based on the convective self-assembly of particles on the substrate. The movement of meniscus helps to form FCC lattice with (111) planes parallel to substrate. Initial ordering of the particles takes place due to attractive force between meniscus and particles and later, evaporation cause meniscus to sweep down and forms well-ordered particles. This technique offers the flexibility to manipulate the thickness of PhCs by tuning the
suspension concentration, particle size, glass slide angle with respect to container walls, which can be reached from 30 to ~ 100. The fast fabrication with low defects makes VDM versatile technique. Photonic crystals obtained by this method, generally contain one point defect per unit cells and ~ 1% stacking faults, which is around 1 magnitude lower than sedimentation process. Nevertheless, there are few major drawbacks associated with this process; such as fast sedimentation of the large particles, which in turn fail to attach to the substrate, steadily increase in the film thickness due to increased particle concentration, formation of different cracking pattern due to uncontrolled evaporation rate or drying. Reproducibility has been one of the major challenges in this process.

![Figure 2.10 Schematic illustration of vertical deposition set up redrawn with the permission from [89].](image)

**2.1.3.4 Physical Confinement Method (PCM)**

Phase behaviour of the materials can be altered by geometrical confinement, which is well known in the crystallization of polymer thin films under confinement. It was Xia et al, who has used the same principle to fabricate colloidal photonic crystals under geometrical constraints. He developed a simple device; and reported colloidal crystal exhibit much better ordering and orientation under physical confinement. Figure: 2.11 show the schematic illustration of the setup. Xia et al. and workers used
polystyrene particles, which were then injected into the confined rectangular glass cell. Authors have shown that it is possible to control the number of layers by tuning the height ratio and particle diameter. This method is able to produce large, defect free and closed packed layers in photonic crystals.

Figure: 2.11. Colloidal crystal growth under physical confinement mechanism redrawn with the permission from [95].

2.1.3.5 Capillary Deposition Method (CDM)

Recently a flow induced method called capillary deposition method (CDM) was developed by Prof Marlow and group.[96, 97] This technique is quite similar to physical confinement technique developed by Xia and workers, where sandwiching the two glass slides made confinement cells and later photoresist was used to separate the glass slides and was fixed by clips.[63] In this method, suspension was injected through a hole drilled on the top of the glass slide. It gives very good reproducible photonic crystals films. On the other side the major disadvantages CDM is use of expensive lithographic facility. In contrast, it offers better quality photonic films in terms of ordering, reproducibility and defects.[98] Figure: 2.12 shows the schematic illustration of the setup. In CDM, deposition occurs due to natural capillary forces, which drag the
suspension from container via glass tubes to sandwich glass substrate. Once the deposition process completed the solvent was then removed through via slow evaporation process. In this method, two sides of the sandwich glass slides are closed and rest two are open for solvent evaporation. This technique also offers predictive thickness and surface flatness of fabricated photonic crystal film.[99]

Figure: 2.12 Schematic illustration of capillary deposition set up Reprinted with permission from [96].

### 2.1.4 Infiltration in Photonic Crystals

To further exploit the photonic crystals properties, they usually infiltrated with various materials to alter the refractive index contrast by introducing luminescent materials mainly emitters. As they tend to modify the spontaneous emission and can be useful for low threshold laser sources applications. This interest has favoured the tremendous improvement observed in last two decade with respect to experimental realizations for a range of infiltrated photonic crystals. The first experimental report was based on cadmium sulphide (CdS) infiltration into 3-D photonic crystals which shows modifying inhibition of spontaneous emission in PhCs.[100] Later researchers moved to titanium oxide (TiO$_2$) infiltration in the photonic crystals as it offers higher index contrast while maintaining the transparency.[101, 102] There are few reports on the photonic crystals research in near infrared region, which has achieved by infiltration with silicon and germanium nanomaterials. [93, 103] Recant growing research was infiltration with
metal nanoparticles such as gold, which has attracted considerable research interest. It allows studying combined effect of photonic bandgap and localized surface plasmon resonance respectively. [104, 105] Few recent studies have been reported enhancement in the optical properties of polymer photonic crystals by infiltration sub nanometer carbon particles. The study suggest ~ 0.1 wt% doping of carbon particles can greatly enhance the optical properties. [106, 107] Infiltration process can be classified in two major categories named chemical and physical infiltration respectively. Chemical infiltration is corresponding to material growth inside the structure, whereas infiltration of materials in already prepared structure is in the category of physical infiltration.

2.2 Literature review: Infiltrated Nanomaterials: (One and Two Dimensional Nanomaterials)

2.2.1 One Dimensional Material: Single Walled Carbon Nanotubes (SWCNTs)

Carbon nanotubes (CNTs) are cylindrically shaped carbon macromolecules made up of rolled two dimensional graphene sheets and considered as quasi one-dimensional systems. Graphene are made of sp² bonded carbon atom arranged in a planer honeycomb structure.[108-110] This unique cylindrical shape of CNTs possess well defined atomic structure, which give rise to its unique properties; such as electronic, electrical, mechanical, optical, thermal, and transport properties etc.[110] In CNTs the in-plane σ covalent bonds are responsible for superior mechanical properties of the CNTs, whereas p orbital, which is perpendicular to the plane of the σ bonds and forms weak delocalized π bonds give rise to electrical properties.[110-112] The dimensions of CNTs are of few nanometres in diameter and several micrometres in length. There are different types of CNTs such as single walled carbon nano tubes (SWCNTs) or multiwalled carbon nanotubes (MWNTs) and can be characterized by their internal structure. It depends upon the number of concentric carbon walls it possesses, shown in the Figure: 2.13. CNTs comprised of single concentric carbon wall referred as SWCNTs, whereas those contains few concentric carbon walls called as multi walled carbon nanotubes.[109] Moreover the physical properties of SWCNTs have turned out to be significantly intriguing. SWNTs offer good uniformity in diameter, which varies between 0.4 and 4 nm. One of the major hurdle of SWNTs for practical uses is the aggregation tendency into bundles due to van der Waals forces.[109]
2.2.1.1 SWCNTs Geometry

A graphene sheet can be arranged in a variety of configurations to form SWCNTs, which gives rise to nanotubes of different types and properties. These different configurations possibility in SWCNTs can be described by the chiral vector. The graphene sheet is rolled in the direction of the chiral vector such that the head and tail of the vector meet at one point. Thus magnitude of the chiral vector gives the nanotube circumference, while the vector’s direction in the graphene plane describes the chirality of the SWCNT, or the direction in which the graphene sheet is rolled with respect to carbon honeycomb structures. [109, 111] This has been represented graphically in Figure: 2.14.

Figure: 2.13 Illustration of (A) SWCNT, (B) (MWNT); different colours represent the different cells or layers reprinted with permission from [109].

Figure: 2.14. (a) Illustration of rolled up graphene sheets into SWNT structure (b) Points OO' expresses chiral vector and grey shaded region in the sheet shows unrolled unit cell formed by translational and chiral vector. The angle, \( \theta \), is defined as the chiral angel. The zigzag and armchair SWCNTs are specified in blue and red colours, respectively reprinted with permission from [109].
Roll-up vector $C_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m)$, describes the structure of the SWCNT, where $\mathbf{a}_1$ and $\mathbf{a}_2$ are primitive vectors and $n$, $m$ are integers. The magnitude of translation vector describes the length of the $(n, m)$ SWNT unit cell. The unit cells $(n, m)$ can be used to determine nanotubes diameter ($d_t$) and chiral angle ($\theta$) by following equations;

\[
d_t = \left( \frac{3^{1/2}}{\pi} \right) \left( a_{cc}m^2 + mn + n^2 \right)^{1/2}
\]

\[
\theta = \tan^{-1} \left( \frac{3^{1/2}}{(2n + m)} \right)
\]

where $a_{cc}$ represent the nearest-neighbour carbon to carbon distance, i.e. 0.142 nm. Therefore, different approaches to roll graphene sheet forms three different type of CNTs, known as armchair, zigzag, and chiral, which depend upon the circumferential pattern of the carbon-carbon bonds and angle between them.[109] as shown in the Figure: 2.15.

**Figure: 2.15** Molecular models of SWNT exhibiting different chiralities reprinted with permission from [109].
2.2.1.2 Electronic Properties

There are few certain conditions to form different types of CNTs.[109, 113] Armchair nanotubes are formed, when \( n = m \) and the chiral angle is \( \theta = 30^\circ \). For zigzag, \( n \) or \( m = 0 \) and the chiral angle \( \theta = 0 \). Rest all other CNTs lie between these two conditions, are known as chiral. All three CNTs possess unique electronic properties. The condition for CNTs to be metallic is, \( n - m = 3q \), and to possess semiconducting behavior, \( n - m \neq 3q \). Armchair \( (n, n) \) SWCNTs are always metallic. The zigzag \( (n, 0) \) SWNTs are semi-metallic and two-thirds of the chiral \( (n, m) \) ones are semiconductors. Due to quantum confinement, normal to the axis of CNT, gives rise to interesting properties due to monolayer thickness. Isolated CNT possess unique optical properties (density of states), which generates sharp peaks in electronic absorption spectra or optical transitions.[114] They are called as van Hove singularities; depend on nanotube structure and diameter.[115] It provides valuable information about optical properties of CNTs. Bandgap of semiconducting CNTs is inversely proportional to the nanotube diameter and can be explained by following empirical formula:

\[
E_{\text{gap}} = 2 \frac{E_{\text{c-c}} a_{\text{c-c}}}{d_{\text{cnt}}} \tag{2.16}
\]

where \( E_{\text{c-c}} \) is the carbon-to-carbon tight banding overlap energy, and \( d \) represents the diameter of a nanotube. The bandgap in semiconducting CNT’s is ranges from 0.1 to 2 eV, while metallic tube has no band gap in its unstrained state. An optical spectrum of CNT provides range of useful information such as composition, electronic structures and tube chirality.[115] It has been shown in Figure: 2.16. Figure: 2.16(a) shows a significant difference in SWCNT spectrum at higher energies, which can be noticed up to 2 eV. There are three different peaks that can be distinguished from the background. They are originated from the lowest allowed optical transition in SWCNTs, as shown in Figure: 2.16 (b) and (d). The peaks labelled as \( E_{s}^{11} \) and \( E_{s}^{22} \), correspond to the lowest and second allowed transition respectively in semiconducting SWCNT, whereas the third peak \( E_{M}^{11} \) is associated to the absorption of the first peak in the joined density of states of the metallic nanotubes. Especially, the \( E_{s}^{11} \) transition is a special feature; it reveals the optical band gap of a semiconductor SWNT.[114, 116] Figure: 2.16 (c) has been added for illustrative purposes after background subtraction. Transition energy is related to the nanotube diameter and chirality and shows \( 1/d \) dependence, which is based on the Van Hove singularities.
Figure: 2.16: (a) & (b) Absorption Spectrum of SWCNT and colloidal graphite, where points A, B and C referring to electronic transitions between bands in semiconducting to metallic tubes in (b). (c) Shows absorption spectrum of SWCNTs after background subtraction. Reprinted with the permission from [116] (d) Schematic illustration of electronic transition in band structure.

2.2.1.3 Other Properties

In addition to its excellent electronic properties, CNT also possess wide range of other exciting properties. The thermal conductivity at room temperature for a multi-walled carbon nanotube was reported by Kim et al in 2001 to be ~ 1,000 W/m.K, i.e. higher than natural diamond and basal plane of graphite.[117] Another important property is hydrophobic nature of CNT, which prevent wetting for most aqueous solvents and have been used for molecular adsorption.[118] CNTs also demonstrated exceptional mechanical properties. CNTs possess almost five times higher Young’s Modulus compare to steel in a range of 1,500 – 5,000 GPa and tensile strength ~ 50 GPa, which is fifty times higher than high-carbon steel.[119-121]

2.2.2 Synthesis methods

Extensive research efforts have been carried out to synthesize CNTs. There are three main approaches to produce CNTs;

1. Arc discharge
2. Laser ablation
3. Chemical Vapour Deposition

2.2.2.1 Arc Discharge

Arc discharge is a versatile technique to produce high quality both SWCNTs and MWCNTs, which has been used earlier to produce fullerene.[122, 123] The quality of CNTs can be tuned by controlling the parameters such arching current and inert gas
pressure. Metal catalyst is an integral part to produce SWCNTs in the arc discharge process. In a chamber, arc discharge creates vapours of inert gases at pressure ~ (50 and 700 mbar) between two graphite electrodes. A direct current (50 to 1,000 Amps) is then passed ~ 20 Volts, which creates a high temperature discharge between the electrodes, results in carbon atoms vaporization, which forms carbon products, by depositing on the carbon cathode. One of the major drawbacks of this approach is resultant products are mixture of components, which then need purification of CNTs from soot and other impurities.[124]

2.2.2.2 Laser Ablation
Guo et al. and workers were the first group demonstrated laser ablation technique to produce CNTs and in particular, SWCNTs.[125] In a typical experiment, a graphite target doped with Fe, Ni or Co was kept in windowed quartz tube and then placed in a chamber filled with inert gas (helium/argon gas). The chamber is maintained at high temperature ~1,200°C and pressure ~500 Torr. A laser, YAG or CO₂ laser is used (pulsed or continuous - main difference is that the pulsed laser requires much higher light intensity ~ 100 kW/cm² in contrast to 12 kW/cm² with continuous laser) to vaporize graphite target. It vaporizes the carbon atoms onto the collector, which create hot plume of carbon forms, i.e. expands and hence cools rapidly. On cooling down, carbon atoms condense to form clusters, which used to grow CNTs.[126] Tuning the composition of the target can produce both SWCNTs and MWCNTs. MWCNTs has been produced using pure graphite electrodes, whereas addition of small amount of Co, Ni, Fe etc. to the graphite electrodes allows to grow SWCNTs. This approach produces high-quality of SWCNTs with controlled nanotube diameter distribution. On the other hand it is limited for mass production and requires expensive lasers.

2.2.2.3 Chemical Vapour Deposition (CVD)
Though arc discharge and the laser ablation process are the conventional approach to produce carbon nanotubes but scaling up issue makes them unsuitable. Chemical vapour deposition is potentially better technique over both of them.[108, 127] It uses catalyst metal nanoparticles and carbonaceous vapours/gases. The growth principle of CNTs in CVD is based on the decomposition of volatile or specifically hydrocarbon (or alcohol) precursors, in the presence of a metal catalyst. In a typical process, plasma or resistive heating coil is used to decompose the precursors (methane, carbon monoxide and acetylene) into its reactive carbon atoms at ~ 650-900°C. Afterwards carbon atoms
directed and passed through the heated substrate in presence of catalyst for a period of time. At optimize condition, carbon nanotubes were formed on the substrate surfaces. By tuning the parameters such as metal catalyst and reaction conditions, SWCNTs or MWCNTs can be produced in large scale by using this approach. Over the time, there has been continuous efforts to improve the CVD process such and plasma-enhanced chemical vapour deposition (PECVD) and thermal CVD has been developed.[128]

2.2.2.4 High-Pressure Carbon Monoxide (HiPCO)

High Pressure Carbon Monoxide method was discovered by Dr. Smalley's and his team in 1999 and still is one of the most popular methods to produce SWCNT.[129] In this method, carbon mono oxide gas, source of carbon material is injected at high pressure (up to 10 atm) into a furnace at temperature around ~ 800-1200°C. Iron particles as catalysis are also created in the furnace by thermal decomposition of gaseous iron pentacarbonyl. On the surface of catalyst, carbon monoxide reacts to form carbon dioxide and carbon atoms, which bond together to form carbon nanotubes. Resultant nanotubes have the average diameter of approx. 1.1 nm. Over other methods HiPCO method has been proven to be best method to produce high quality CNTs and also offers easy purification and large scale manufacturing.

2.3 Graphene

In 2004 Andre Geim and Kostya Novoselov at The University of Manchester extracted single-atom-thick crystallites from bulk graphite. They pulled graphene layers from graphite and transferred them onto thin SiO$_2$ on a silicon wafer in a process called either micromechanical cleavage or the Scotch tape technique.[130, 131] This discovery led them to win the Physics Nobel Prize in 2010. Statistics reveals that there are more than ~ 24000 papers has been published since years 2000 and makes graphene most discussed topics in physics and material science.[132] Figure: 2.17 shows optical picture of graphene flakes. It can readily seen from the figure observed from the image that there is a homogeneous variation in the optical contrast for different layers. The trace in image (b) shows steplike changes in the contrast for 1, 2, and 3 layers trace, which has been averaged over 10 pixel lines.
Figure: 2.17 Optical picture of a graphene flakes on 300 nm SiO$_2$ imaged with white light a, green light. Mono-layer graphene is clearly visible in image (a), image (c) shows indiscernible three layers Image sizes are 25x25μm$^2$. Reprinted with the permission from [133].

2.3.1 Graphene Structure & Properties

Graphite comprises layers of atomically thin graphene, which is coupled together due to van der wall forces.[134] The distance between two successive graphene layers is 0.34 nm. This is much larger than the distance between two carbon atoms 0.142 nm. Due to weak van der wall forces, it is easy to isolate graphene layers from graphite.[131] Graphene layers are the basic building block of other forms of carbon allotropes.[135] If rotated along one axis, graphene layer end up with carbon nanotube and can also be wrapped to create fullerene like structure. Due to sp$^2$ hybridization, graphene forms $\sigma$ bonds in plane with nearest neighbouring atoms, which are responsible for mechanical robustness of graphene (Young’s modulus, Y~1 TPa), whereas valance electron in $p_z$ orbital forms the delocalized $\pi$ bonds, responsible for electronic, and chemical properties of graphene.[134, 136]

Graphene possess unusual energy dispersion relation. There are two carbon atoms per unit cells in the graphene. They can be understood as two different conical points in the Brillouin zone (BZ) and called such as K and K'. In monolayer graphene the band crossing took place between these two points. A close look to the band structure reveals that there is linear behaviour between electron energy and wave vector close to crossing points which resembles to Dirac behaviour of massless fermions.[135, 137, 138] Figure: 2.18 shows the schematic illustration of the structure, where it possesses two carbon sublattices A and B [fig (a), blue and orange colour]. Due to quantum-mechanical hopping between sublattices A and B, graphene forms two energy bands.[139]
Electronic density of Graphene vanishes linearly with energy close to Dirac point. It makes graphene to behave neither as a metal nor a semiconductor (or insulator) because of absence of gap in the spectrum.[140]

In graphene, valance and conduction bands touch each other at the Fermi level rather than overlapping as observed by band structure. Close to the crossing points, effective mass of electrons in this region is zero, due to linear dispersion relation; it holds a new transport mechanism in graphene where charge carriers can travel ballistically.[137] It allows graphene to conduct electricity better than metals, whilst having resistivity on the order of $10^{-6}\,\Omega\cdot\text{cm}$ at room temperature. The velocity of electrons in graphene is $\sim10^6\,\text{m/s}$, about 1/300 of the velocity of light.

Optical transparency of the graphene is another key property. Monolayer graphene shows surprisingly high absorption rate $\sim2.3\%$ of incident white light. Interestingly, it is exactly equal to $\pi\alpha$, where $\alpha$ is the fine structure constant ($e^2/\hbar c$).[133, 141]

Monolayer graphene is also one of the strongest known materials. Young’s modulus of graphene is remarkably high $\sim1\,\text{TPa}$ with an ultimate tensile strength of 130 GPa, which makes it harder than diamond and almost $\sim300$ times stronger than steel. Although graphene is mechanically robust, it is still possible to stretch it. Literature suggested that graphene can be stretched up to 20% of its initial length.[136, 142]

Graphene also demonstrates markedly high thermal conductivity $\sim5000\,\text{W} \,\text{m}^{-1} \,\text{K}^{-1}$ in contrast to SWCNTs, which demonstrate $3500\,\text{W} \,\text{m}^{-1} \,\text{K}^{-1}$.[143, 144] Ho et al. reported the experimental thermal conductivity of bulk graphite as $\sim2000\,\text{W} \,\text{m}^{-1} \,\text{K}^{-1}$. In another study, Nika et al. compared and demonstrated the thermal conductivity between bulk
graphite and graphene and proposes thermal conductivity for mono layer graphene depends largely on the flake size and ranges from 3000-5000 W m\(^{-1}\) K\(^{-1}\).[145]

2.3.2 Graphene: Fabrication Methods

To produce better quality and large area graphene is still a challenge. Advancement in the production of graphene with properties suitable for the particular application is necessary to exploit graphene potential. There are many different techniques are available these days to produce graphene of different, shapes and quality. Some of them are described below in the Figure: 2.19:

Figure: 2.19 Several methods of mass-production of graphene[146].

2.3.2.1 Mechanical Exfoliation

Mechanical exfoliation method to produce graphene was developed by Geim and Novoselov using highly oriented pyrolytic graphite as a precursor.[130, 135] In a typical process, graphite flakes was kept on adhesive tape, and then the tape was repeatedly closed and peeled off. Later, adhesive side of the tape was placed on a substrate. Once the tape was removed, the substrate contains several graphite flakes and residue in the tape. There were few major drawbacks with this method such as large amount of residue on the substrate, and small graphene flakes which makes them unsuitable for industrial applications.[147] Figure: 2.19 illustrate the various fabrication methods according to size, & quality for any particular application.
2.3.2.2 Chemical Vapour Deposition (CVD)

Chemical vapour deposition of graphene is more recent method to grow large area uniform polycrystalline graphene films.[148] In a typical process, a metal substrate kept into a furnace and heated ~ 1000°C and at the same time methane and hydrogen gases were flowed under specific vacuum conditions. It produces carbon atoms from the methane to be deposited onto the surface of the metal. A square metre of graphene film has already been achieved using this method.[149] There are few drawbacks associated to this process such as; it requires transfer of graphene film from the copper support to other substrate, also carry impurities and wrinkle formations.

2.3.2.3 Liquid Phase Exfoliation (LPE)

Liquid-phase exfoliation considered as one of the most feasible approach to exfoliate layered materials such as graphene because of its versatility and minimal efforts.[150-152] This approach utilizes different solvents that exfoliate few-layer nanoflakes. Nonetheless, concentration used to vary for different solvents. A relationship between the nanoflakes, structure and its dispersability in solvents has been established due to inconsistency dispersion. There are two empirical parameters called surface energy and Hansen solubility on which this theory is based on and will be explained below. [153] These parameters play an important role to decide or select solvents.

Surface energy/Surface tension[154]

The surface energy (SE) can be described as imbalanced forces arise due to unbalanced bonding at the surface of molecules or atoms. It is excess energy per unit area, which is corresponds to unsatisfied bonds on the surface and its unit is J/m². To reduce the surface energy by reducing surface area is called as surface tension (ST) and given in units of N/m. The relation between these two is given below. The work done per unit increase of area is

\[
\frac{dA\gamma}{dA} = \gamma + \frac{\partial\gamma}{\partial A}
\]

where A is the surface area and \(\gamma\) is SE. ST and SE are equal for isotropic materials such as liquids but different for anisotropic solids. As per thermodynamic principle, the most stable state possesses least free energy. Due to molecular mobility the structure of isotropic liquid stay with minimum area/unit volume i.e. sphere. It means \((\partial\gamma/\partial A)\) will be zero for liquids; hence ST and SE will numerically remain same even though area is changed. In the case of anisotropic solids, SE depends on crystallographic orientation.
of crystal. Furthermore, SE changes with change in surface atoms either by stretching or compression, leading to $\partial\gamma/\partial A$ value. Hence, ST does not equal to surface energy for solids.

Surface energy role in solvent selection

Various studies have proposed that the SE has been used one of the key parameter in selecting solvents for nanotubes, graphene and other layered materials.[150, 151, 153] It has been suggested that best solvents are those who have SE close to that of the dispersing solids. It can be described by using Gibbs free energy equation:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

$\Delta G_{\text{mix}}$ and $\Delta H_{\text{mix}}$ are the Gibbs free energy and enthalpy of mixing respectively. $T$ is the temperature, and $\Delta S_{\text{mix}}$ is the entropy of mixing. Enthalpy of mixes approaches to zero for an ideal mixture and gives negative free energy value. Bergin et al. describes exfoliation of the carbon nanotubes in solvents by applying thermodynamic simulations.[155]

Later Cunningham et al. developed a model of studying the balance of Van der Waals interaction under solvent nanosheet conditions.[153]

Based on their assumptions, the enthalpy of mixing can be estimated by the following equation:

$$\frac{\Delta H_{\text{mix}}}{V} \approx \frac{2}{T_{\text{NF}}} \left(\sqrt{\gamma_{\text{NF}}} - \sqrt{\gamma_{\text{sol}}}\right)^2 \phi$$

$V$ is the mixture volume, $T_{\text{NS}}$ is the thickness of nanoflakes, $\gamma_{\text{NF}}$ and $\gamma_{\text{sol}}$ are the nanoflakes and solvent surface energy, respectively, $\phi$ is the dispersed nanoflakes volume fraction. This equation foresees that the optimal condition for the dispersion, when solvent surface energy is very close to the nanosheet.

Hansen Solubility Parameters (HSP)

HSP is based on the principle “like dissolve like” and predicts molecular affinities, solubility-related phenomena.[156] In this concept each molecule is assigned with three different parameters based on interaction forces: dispersion forces ($\delta_D$), permanent dipole-permanent dipole forces ($\delta_P$), and hydrogen bonding ($\delta_H$).
HSP have existed since 1967 and provides a useful meaning to predict molecular affinities, solubility and solubility-related phenomena [29]. HSP concludes that if there is not a significant difference between a solute’s solubility parameters from the one of the selected solvent; then, they will possess high affinity and will dissolve and can be explained by following equation:

\[ R_a = \sqrt{4(\delta_{D,\text{Sol}} - \delta_{D,\text{NF}})^2 + (\delta_{P,\text{Sol}} - \delta_{P,\text{NF}})^2 + (\delta_{H,\text{Sol}} - \delta_{H,\text{NF}})^2} \]  \hspace{1cm} 2.20

Where \( R_a \) is the interaction radius. \( \delta_{D,\text{Sol}}, \delta_{P,\text{Sol}}, \) and \( \delta_{H,\text{Sol}} \) are dispersion, polar, and H-bonding for solvents. \( \delta_{D,\text{NF}}, \delta_{P,\text{NF}}, \) and \( \delta_{H,\text{NF}} \) are the dispersion, polar, and H-bonding for nanoflakes. Thus, the smaller the interaction radius value will leads to higher solubility. For the case of multicomponent it can be calculated from the following equation:

\[ \delta_{blend} = \sum \phi_{\text{comp,n}} \delta_{\text{comp,n}} \]  \hspace{1cm} 2.21

Where \( \phi_{\text{comp,n}} \) and \( \delta_{\text{comp,n}} \) are the volume fraction and the HSP value of the specific component in the solvent mixture, respectively.

To exfoliate graphene, process involves sonication of graphite in solvents such as N-methyl-2-pyrrolidone (NMP), N’N-dimethylformamide (DMF), and \( \gamma \)-butyrolactone (GBL).[150] Liquid-phase exfoliation of graphite oxide is also being used to exfoliate of graphene. [157]

### 2.4 Boron Nitride Nano sheets (BNNs)

Boron nitride is an inorganic material and can be synthesize in low dimensions or as nanoflakes similar to graphene flakes or sheets. BNNs structure is similar to graphene and possesses equal numbers of nitrogen and boron atoms. BNNs structure closely resembles to carbon as sharing the same total number of electrons between the neighbouring atoms and exists in various crystalline forms.[158, 159] Two dimensional BN flakes were produced from a BN crystal in 2005.[131] In contrast to carbon based flakes materials, BN have remained much less explored.
2.4.1 Structure and Properties

Figure: 2.20 illustrate the structure of boron nanosheets with alternating boron and nitrogen atoms. BNNs are transparent and insulating in behaviour. BN can be classified into four forms:[160, 161]

1. Hexagonal BN (h-BN)
2. Rhombohedral BN (r-BN)
3. Cubic BN (c-BN)
4. Wurtzite BN (w-BN)

Boron layers are held together due with Van der Walls forces in stacks form. Being insulators, BNNs present wide bandgaps ~ 5.0–6.0 eV.[158] Pakdel et al suggested that boron nanosheets (BNNs) have optical bandgap ~5.7 eV, which suggest it is a promising protective shield encapsulating nanomaterial.[159] These nanosheets can also find applications as catalysts or field-emitters suggested by Terrones et al.[162]

Due to the ionic bonding between B and N, BNNs are electrically insulating, with a large electronic band gap (~ 4 - 6 eV).[158] The electrical resistivity of BNNs are in the order of $10^{17}$ and $10^{14}$ Ω cm at room temperature and at 200°C respectively. BNNs composites can serves as electrical insulator in electronics.

Hexagonal boron nanostructures possesses notably high specific heat and thermal conducting properties.[163] Literature suggested that thermal conductivity in BNNT is much higher than CNT. In particular, for single walled boron tube, measured value was ~350 W/m/K at room temperature, which makes them suitable for applications in macroscopic refrigerators and energy-saving buildings.[163] These nanosheets also possess excellent thermally stable properties. Experiments suggested that multi-walled BNNTs are oxidation resistance up to 840°C in air and for lower diameters tubes, it show oxidation resistant up to 900°C.[164, 165] BN nanostructures also possess superior mechanical properties, which makes them very useful nanofillers. Hernandez et al. reported elastic modulus of BNNTs is ~ 0.84~ 0.91 TPa with diameters ranging from 0.81 to 2.08 nm.[166]
Figure: 2.20 (a) Structure of h-BN layers. (b) Atomic structure of monolayer h-BN on Ni(111) substrate. Crystal structures of hexagonal boron nitride reprinted with the permission from[161].

2.4.2 Fabrication Methods

There are numerous approaches to synthesise boron nanotubes and nanosheets by using various methods such as CVD, sputtering technique, pulsed laser deposition, laser ablation, liquid phase exfoliation and mechanical exfoliation.

CVD, generally used to prepare high performance materials and widely used technique in semiconductor research to fabricate thin films. The process comprises adsorption and reaction of precursor materials. Decomposition of precursor molecules release the gas phase products, which later decomposes onto the substrate surface.[167-171] The first successful attempt to grow single- or few-layer h-BN was using ultrahigh vacuum systems using borazine as the precursor materials and single-crystal transition metals as the substrates.[172] Zettl’s group reported mechanical exfoliation method to produce well-ordered BNNs, with the thicknesses range between 3.5 and 80 nm and prepared by peeling off BN layers from h-BN powder with adhesive tape, attached to a 300 nm thick SiO$_2$ substrate.[173] Solution exfoliated of BN layers from h-BN flakes using sonication using presence of polar solvents and/or reagents.[174, 175] Han et al. (2008) produced mono-and few-layered nanosheets by chemical exfoliation.[176] Li et al used ball milling process to obtain BN nanosheets under N$_2$ atmosphere.[177] Gao et al demonstrate that CVD offers controlled fabrication of thin BNNSs of large lateral sizes and it was synthesized without using catalysis process around ~ 1100 – 1300°C range.[178]
Chapter 3 Investigation Methods

This chapter basically describes the characterization techniques that are utilized in carrying out the experiments described in the following chapters (4, 5, 6, 7). The methods include atomic force microscopy, scanning electron microscopy and transmission electron microscopy to probe the surface of used 2 dimensional nanomaterials such as graphene, boron nitride and one dimensional single walled carbon nanotubes. These techniques were also used to determine the particle size of used polymer latex and also to measure interparticle distance between polymer spheres after fabricating photonic crystals; DSC to measure glass transition temperature, optical spectroscopy to measure photonic bandgap of photonic crystals; small angle x-ray scattering measurements to probe interparticle spacing in pristine and infiltrated photonic crystals; Raman spectroscopy to determine the number of graphene layers; and the tensile testing to analyse mechanical properties such as hardness and young modulus of the infiltrated photonic crystals.

3.1 Morphological Characterization

3.1.1 Atomic Force Microscopy

Atomic force microscopy (AFM) was invented by Binning at al in 1986. Since then it has proven to be a versatile technique and played a crucial role in Nano sciences.[179, 180] AFM has been used widely to study topographical, mechanical, viscoelastic properties of materials.[181] AFM utilizes a cantilever, which measures the force between the tip and the sample surface. When the cantilever approaches the sample, the changes in the frequency of vibration of the cantilever can be used to directly measure the topography, and at the same time the shift in phase. The cantilever behaves like a spring and the tip-surface interactions can be explained by Hooke’s law of force:

\[ F = -kZ \]  \hspace{1cm} 3.1

A general block diagram is shown in Figure: 3.1
There are three different modes in which AFM operates (1) Contact (2) Semi-contact or intermittent (3) Non-contact.

**Contact Mode:** This mode operates on the principle of constant force (constant average distance) by which atomic resolution can be achieved. In this mode, scanning at constant distance (maintaining fixed sample height relative to the tip), while the cantilever deflection is being recorded. To scan hard surfaces this mode is been typically used where tip directly approaches the specimen. This mode is not useful for soft materials like polymers or biological samples. Contact mode is relevant when one deals with the repulsive region of the inter-molecular force curve given in Figure: 3.2

*Intermittent– contact Mode (Semi Contact Mode)*
Although contact mode is popular to achieve greater resolution, it’s not useful for soft specimen. For such specimens semi-contact mode is being used. In this mode the cantilever oscillates at a frequency close to its free resonant frequency ($v$) given by:

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$  \hspace{1cm} (3.2)

Where $k$ is the spring constant, and $m$ is the mass of the cantilever, therefore lateral forces are significantly reduced. Forces interactions in this mode correspond to the repulsive region in the force-distance diagram shown in figure (3.1). While scanning in the height mode, the surface topography is recorded as a height image and in phase mode imaging; the phase shift of the oscillating cantilever relative to the driver electronics is also recorded. Phase shift of the cantilever oscillation provides qualitative characterisation of material properties, for example adhesion or elasticity, chemical composition and friction.

![Interatomic forces vs. distance curve](image)

Figure: 3.2 Interatomic forces vs. distance curve redrawn from [182].

*Non-contact AFM mode:*

In this mode, scanning perform ~ 50–150 Å above the sample surface. Scanned images are constructed by scanning the tip above the specimen surface. Attractive forces are
much weaker compared to contact mode, so small oscillation is used to detect small forces by measuring the change cantilever’s amplitude, phase and frequency. Non-contact mode operates in the attractive regime of the inter-molecular force curve. Non-contact mode is suitable to image soft surfaces. On the other hand, it is extremely sensitive to external vibrations and condensed water lying on the specimen’s surface. This mode is very useful to scan biological samples.

3.1.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was invented due to the lack of resolution and magnification of conventional microscope. SEM provides bunch of information ranging from surface topography, crystalline structure, and chemical composition etc.[183, 184]

It also offers the flexibility to use different mechanical stages, to measure specimen under different conditions and positions. In order to produce images, SEM uses a focused primary-electron beam, which scans the sample surface in a raster fashion. The resolution limit of SEM is 5 nm, which is also the spot size of the beam. The focused electron beam in SEM penetrates the specimen and interacts with atoms, which is shown in Figure: 3.3 (a). After the interaction, electron scatters in two ways; inelastic scattering and elastic scattering. Inelastic scattering is responsible to produce secondary electrons, backscattered electrons, x-rays, thermal energy and light as shown in Figure: 3.3 (b). In inelastic scattering, secondary and backscattered electrons are used to extract analytical information from the specimen. Secondary electrons produce the surface images of the specimen. It can also be produce by backscattered electrons (<50eV) which originate from within a few nanometres of the surface.[183, 184] Elastically backscattered electrons provide information about elemental composition with surface morphology. This type of scattering depends upon the atomic number of specimen and characterized by high energy. The Accelerating voltage defines the amount of energy carried by the primary electrons. Electrons with higher energy produce a larger interaction volume and generate higher energy signals, while low accelerating voltage provides information from the surface of the sample. Sample composition strongly affects the depth and shape of the interaction volume. For example, the beam penetration for carbon is about 1 µm at 10 kV, and decreases with increasing atomic number.[184]
3.1.3 Transmission Electron Microscopy (TEM)

Ruska and Knoll constructed the first TEM in 1930s, an achievement for which Ruska was awarded the Nobel Prize in physical science in the year of 1986.[185] Today, TEM can accomplish a resolution in the scope of 50 picometer (0.05 nm) and a magnification up to 10 million times. The wavelength of electron is $10^5$ times smaller than visible light and it is related to energy by Broglie’s equation. [185] For example, wavelength of 100 keV electrons is 0.00370 nm i.e. smaller than the size of an atom (0.1 nm). Since the 1970s, various types of TEMs have been developed, which are fit to purpose to resolve atoms in crystals by high resolution transmission electron microscopy. Over the time TEM has turned into an exceptionally valuable instrument to characterize extensive range of materials including life sciences samples. In TEM, light (scatter fewer electrons) and heavy atoms show weak and strong contrast respectively, depend upon electron scattering. There are two type of scattering, i.e. elastic and inelastic. For material analysis both are useful. In inelastic scattering, there is inelastic collision, which displaces atoms within the material, and thus can cause specimen damage. Specifically in the case of light elements and biological samples, this limits the applicability of the TEM. Figure: 3.4 shows the typical working principle of TEM. A gun is used to emit the electrons, which is made of LaB$_6$ for thermal emission or field emission gun (FEG) respectively. [186] Emitted electron is then accelerated by an electric field, normally to energies of 60–300 keV. Field emission gun ensures coherency of electron beam. Accelerated electrons then travel through vacuum chamber and focused by adjustable electromagnetic fields makes they go in spiral paths. Later,
condenser aperture allows passing coherent beam and almost parallel beam hits the specimen. Image formation is achieved by collecting diffraction pattern on fluorescent screens through charge-coupled device. To overcome, the aberration issue aberration correctors have been developed for TEM image correction and it has improved TEM resolution under the atomic diameters for most chemical elements.[186]

Figure: 3.4 Schematic of transmission electron microscopy column. Diffracted electron beams exhibited by dashed lines redrawn from [185].

Figure: 3.5 shows various types of electron interaction with samples. In conventional TEM elastically scattered electrons offers basis for diffraction contrast, high resolution and phase contrast imaging, whereas inelastic scattered electron are useful for Electron Energy Loss Spectroscopy (EELS) measurement, which provide information on energy loss while passing through the specimen and transfer the energy to phonons or plasmons etc.[186] Dimension of the TEM specimens are circular (3.05 mm in diameter) discs. TEM works with various types of samples and sizes ranging from sample dispersed on a grid, fastened to a metal ring etc.
Figure: 3.5 Possible ways an electron can interact with a sample. Scattered electron beams are travelling in straight direction while photon beams are curved redrawn from [185].

3.2 Optical Characterization

3.2.1 Ultraviolet-Visible (UV-Vis) Spectroscopy

UV-Vis Spectroscopy is a tool to measure the absorption, or transmission spectra of compounds, which is measured after passing through sample.[187, 188] This absorption/transmission in the sample takes place due to various electronic transitions. UV-Vis spectroscopy works on the basis of Beer’s Lambert Law, which is stated below:

\[ A = \log \frac{I_0}{I} = \varepsilon l c = \alpha c \]  

Where A = absorbance, \( I_0 \) = incident intensity, I= transmitted light Intensity, C = concentration of light, \( l \) = sample path length, \( \alpha \) = absorption coefficient, \( \varepsilon \) = molar absorvity. From the above equation absorption A can be calculated if \( l \) and \( c \) are known.

In the case of solid samples sample thickness will be accounted instead of concentration.[187, 188] Usually the working spectrum range for UV-Vis spectrometers is from 190nm to 900nm. The building block of a UV-Vis Spectrometers is shown in the Figure: 3.6. The main components in UV-Vis spectrometers consists a lamp, which is usually deuterium for range in ultraviolet region, tungsten and halogen lamp for visible and near infra-red region, Photodiodes, and a photomultiplier tubes for detection. When the light from a source incident on the sample, it absorbs certain light resulted in reduction in transmitted light. Transmitted light then can be plotted as a
function of wavelength i.e. also represents sample’s absorption spectra. UV-vis spectroscopic data offers qualitative and quantitative information of a given compound or molecule.

Figure: 3.6 Basic layout of double beam UV-Vis spectrometer.

3.2.2 Specular & Diffuse Reflectance Spectroscopy

Reflection consists of two components: specular and diffuse. The amount of light reflected by an object or surface, and how it is reflected, is highly dependent upon the smoothness or texture of the surface. The smoother surface gives mirror-like reflection, whereas rough or textured surface gives diffuse reflection as shown in the Figure: 3.7. At a point when surface imperfections are more diminutive than the wavelength of the incident light (as on account of a mirror), essentially the majority of the light is reflected. Nonetheless, generally all surfaces have convoluted surfaces that show a diffuse reflection, in all directions. Diffuse reflectance is measured by using the integrating sphere. Integrating spheres [schematic illustration in the Figure: 3.7 (c)] is an ideal tool to measure transmission of turbid, translucent or opaque materials, where conventional techniques failed due to light scattering of the sample. An integrating sphere is a hollow optical device, either constructed from or coated internally with a white diffusing material. It has the ability to collect most reflected or transmitted radiation, because of the its geometry. [189] In our study we used Diffuse Reflectance accessory come with Cary 5000 UV-Vis spectrometer to analyse total reflectance from of photonic crystal surface.
Figure: 3.7 Schematic Illustration of (a) Specular and (b) Diffuse reflection and Integrating sphere to measure diffuse reflection.

3.2.3 Raman Spectroscopy

Raman spectroscopy is employed normally to study the vibrational and rotational modes of molecules and was discovered by an Indian physicist named Sir C.V. Raman, however, Raman scattering was pioneered and developed a few years later by George Placzek.[190, 191] When incident light interacts with matter, photons will undergo transmission, absorption, reflection or scattering. At the molecular level, photons usually interact with matter through two major processes, namely absorption and scattering. Scattering process can be either elastic where both the incident photons and scattered one have the same energy, or inelastic scattering where photons can lose or gain energy due to changes in the vibrational, rotational and electronic energy in a molecule during the scattering. Among those energy changes in inelastic scattering the most prominent are transitions between vibrational energy levels. [190] Elastic scattering is also known as Rayleigh scattering (without change of the frequency on incident monochromatic radiation $\omega_0$) and inelastic scattering usually called Raman scattering. The Raman shifts refer to the frequency shift due to the energy difference between the incident and scattered photon. Raman scattering can be classified into two
types: Stokes and antistokes. In quantum terms, the scattering is explained as an
extinction of molecule into a virtual state, having a higher energy, after the excitation,
the excited molecules return to the original ground electronic state, emitted photon will
have equals the energy of the previously absorbed photon.[190] Inelastic scattering
arises when the final state is changes in contrast to initial one. In Stokes Raman
scattering the band of frequencies will be less than the incident one ($\omega_0 - \omega_M$). In
contrast to that, in anti-Stokes Raman scattering band of frequencies will be greater
($\omega_0 + \omega_M$), where $\omega_M$ is a vibrational frequency of a molecule. Figure: 3.8 is a schematic
diagram of these bands. This nomenclature is in analogy to Stokes’ law for fluorescent
light.

Raman spectroscopy measures both the intensity and wavelength of the inelastic
scattered light. A Raman spectrum is a plot of the intensity of scattered photons versus
the Raman shifts, for a specific incident wavelength of light. In fact, due to different
material having different vibrational modes, the Raman spectrum will vary from one
material to another material. This makes Raman spectroscopy a very practical
 technique for molecular recognition and hence analysis of Raman spectra potentially
allows for identification of the material as well as studying the structure of the material
of interest. Raman spectroscopy is a powerful tool to study range of different kind of
sample s ranging from solid to liquid samples. A Raman spectrometer consists of a
laser as a photon source, which is transferred through a number of mirrors, a filter and
polariser to the beam expander that adjusts the diameter and collimates the laser beam.
The laser beam is directed onto a high-performance rejection band filter (notch filter).
After that it passes through a microscope lens to be focused on the sample mounted to
the sample stage. The beam reflected from the sample passes back through the
microscope optics and through a monochromator. Raman shift is detected and analysed
using charge-coupled device (CCD camera), optical illumination and detection system
(APD) for performing standard SNOM imaging or photomultiplier module (PMT),
followed by data acquisition and curve fitting using computer software.[191] Raman
spectroscopy is a very attractive and non-destructive technique for studying the phonon
and electronic structure of carbon based materials such as nanotubes and 2-D layered
materials, in particular graphene. It provides bunch of information such as CNTs,
diameter, diameter distribution, nanotube (n, m), no of layers in 2-D materials, nature
of defects etc. [192]
3.3 Light Scattering Characterization

3.3.1 Dynamic Light Scattering (DLS)/ Photon Correlation Spectroscopy (PCS)

Light scattering characterization remains a non-invasive way to determine macromolecular shape, size, diffusivity, and molar mass. In static light scattering technique, size, and shape is analysed via measurements of detection of scattered light at various angles around a sample solution, whereas in dynamic light scattering technique (DLS), size and shape of the particles is assessed by comparing light intensity measurement between short time intervals to calculate how quickly particles diffuse through solutions at a fixed angle.[193, 194]

DLS/PCS method allows the measurements down to nanometer scale, which makes this technique so popular. DLS works well with different range of samples; such as polymers, nanoparticles, emulsions, and various colloids etc. A schematic is shown in the Figure: 3.9 demonstrate the basic working principle of the technique. In a typical method, a laser light beam incident on the specimen and the scattered light was collected by photon detectors.
In a solution, particles are always moving constantly in random fashion and their motion uncorrelated with rest of all the other particles. An incident laser light on the suspension or moving particles tends to scatter. The sum of the scattered light from two different particles and the resultant phase of scattered light will keep on changing either in destructive or constructive way due to randomness in the motion of particles in the solution. It creates the constant fluctuations in the scattered light intensity over the time and measured by DLS.

The diffusion rate of particles in the solution and fluctuations in the scattered light intensity are related to each other and they both are related to hydrodynamic radii of the particles. These fluctuations in the scattered light are measured via a second order correlation function, which then leads to measure decay rate at which then can be converted to diffusion constant $D$ via the equation:

$$D = \frac{\Gamma}{q^2} \tag{3.4}$$

where, $q$ represent scattering vector magnitude, and can be calculate by following equation:

$$q = \frac{4\pi n_0}{\lambda_0} \sin(\theta/2) \tag{3.5}$$

where $n_0$ is the solvent index of refraction, $\lambda_0$ represent incident light wavelength in vacuum, and $\theta$ is represent scattering angle. At last, using Stokes-Einstein equation the diffusion constant can be understood as the hydrodynamic radius $r_h$ for a diffusing sphere

$$r_h = \frac{kT}{6\pi \eta D} \tag{3.6}$$

where $k$ represent Boltzmann’s constant, $T$ is the temperature in kelvin, and $\eta$ is viscosity of the solvent. In our study we used Malvern Zetasizer instrument to measure critical micelle concentration of surfactant in water.
3.4 Coherent Small Angle X-Ray Scattering (c-SAXS)

Small-angle X-ray scattering (SAXS) is an important non-invasive nano-scale structural characterization tool in the research fields of soft matter physics. It measures the scattering of x-rays, originated from electron density fluctuations in materials. It is a unique scattering characterization tool in terms of resolution, which is provided by new generation synchrotron sources.[195, 196] The synchrotron source provides large photon flux and high collimation. Guinier & Fournet, Brumberger wrote an excellent book, which provides a up-to-date description of this technique.[197]

![Schematic representation of dynamic light scattering setup adopted from LS instruments.](image)

![Schematic layout of a SAXS setup depicting the incident, scattered and transmitted X-ray beams, the 2D detector, and the definition of the scattering vector (q).](image)

A schematic illustration of SAXS technique is shown in the Figure: 3.10. In a typical experiment a highly collimated X-ray beam of specific wavelength incident on a specimen leads to scattered the light. In next step scattered light intensity in forward direction is collected via detector. To overcome any absorption or scattering by air, initially transmitted beam is fully absorbed by using beam stop placing in front of the detector and flight path before and after the sample is in vacuum. Later, scattered photons measured at scattering angle. For the specimens scattered or collected photons
varies with the incident number of photons per second per unit area and also with distance between specimen and detector. The scattered photons into unit solid angle (normalized to the incident photon flux) are the ones, which is measured in various experiments.

Since energy of incident radiation is very high the scattering at small angles is fully elastic in contrast to excitation of sample, which then led to the incident and scattered wave vectors magnitudes equal, $|k_i| - |k_s| = 2\pi/\lambda$ and the refractive index is close to unity. The momentum transfer or scattering vector, $q = k_s - k_i$ and its magnitude can be explained such as:

$$q = |q| = \frac{4\pi}{\lambda} \sin \left( \frac{\theta}{2} \right)$$

3.7

The electrons are the sources of X rays scattering in the specimen, so electron density difference, $\Delta \rho$, is the dispersion in the irradiated volume is probed. The scattering power of atoms is proportional to their atomic number, and samples with high electron density, such as silica, will display a high contrast for X-rays. For a dispersion of monodisperse, homogeneous and spherically symmetric particles, $I(q)$ can be written as:

$$I(q) = \Delta \rho^2 n V^2 P(q) S(q)$$

3.8

where $n$ represent the particle number density and the volume of the particles represented by $V$. $P(q)$ represent particle form factor and $S(q)$ is the structure factor. Hence, it contains information related to the interactions among the particles; in the dilute case $S(q) \sim 1$.

### 3.5 Thermo Analytical Characterization

Thermo analytical techniques encompass a group of techniques, in which properties of specimen are monitored against time and temperature. Basically methods of thermal analysis allow the study of all chemical processes associated with heating/cooling such as decomposition, pyrolysis, ignition, phase changes, calorimeter etc. All this can be studied on a small amount of the sample in a highly automated way. There are couple
of techniques but here we will discuss two of them which have been used under the scope of this thesis.

3.5.1 **Thermal Gravimetric Analysis (TGA)**

TGA is the oldest and simplest technique for thermal characterization. In TGA, the mass change of sample is measured as a function of temperature under a controlled atmosphere. Consequently, the thermal stability can also be investigated by TGA. [198]

A schematic of TGA apparatus is shown below in Figure: 3.11. The apparatus consists of a temperature-controlled furnace and dual balance beams with sample pens and attached thermocouples. The furnace is usually continuously purged with a gas, such as air, oxygen, nitrogen or argon. In a typical experiment, a small amount (3~5 mg) of powdered sample is placed in one of the sample pans, while the temperature of each pan and the instantaneous sample mass are recorded. Both loss and gain of mass can be observed with increasing temperature. Loss of mass is attributed to vaporization of the material, whereas a mass gain most likely indicates a reaction with a gas, such as oxidation.[198]

![Schematic illustration of TGA.](image)

Several factors can influence the accuracy of the measurement. The heating rate must be slow enough for temperature gradients within the sample and the furnace to be minimized. Increasingly rapid heating rates will appear to shift the features to higher temperatures and broaden to them. This effect will be more pronounced in larger or denser samples. It is therefore desirable to use powdered samples in very small quantities and to heat them slowly. To facilitate this, balances used in TGA system are highly sensitive, with resolutions as fine as 0.1µg.
A second consideration, partly compensated for by the system design, involves the change in the density of the gas with temperature and the resultant change in buoyancy of the sample pan and convective currents. For example, the apparent change in mass for a sample and a pan with volume 1 cm\(^3\) due solely to buoyancy effects in air between 20°C and 1000°C is 0.5mg. Since the typical sample mass is the same order, those buoyancy effects must be considered. In addition temperature gradients result in convection currents of gas within the sample chamber that can affect accurate measurements. While different TGA systems use different methods to compensate for these effects, the system used for our experiments used as identical reference pan, which is assumed to stay at constant mass, and fluctuations of the reference pan are subtracted off. Gas is flowed through the narrow furnace horizontally to reduce convention. Finally all TGA systems are calibrated with known standards to give more accurate readings.\[182\]

3.6.2.1 Theory

The mass change of a sample is measured during a heating programme. If degradation occurs and releases a volatile component, mass loss is detected. The resolution in change of sample mass is better than 1µg. TGA is typically presented as a plot of measured mass loss (Y-axis) against temperature (X-axis) Figure: 3.12 (a). The natural shape of mass loss is sigmoidal, with most mass loss occurring at the main reaction temperature, but, nevertheless, some residual mass loss occurs afterwards.

![TGA and DTG Diagram](3.12(a) Curve of TGA and (b) DTG.)

An alternative data presentation is a derivative plot Figure: 3.12 (b), often called derivative thermogravimetry (DTG), where the Y-axis is the rate of mass loss against temperature (dm/dT) and X-axis is the experimental temperature. The derivative plot
appears as a board peak over a range of temperature. This curve is useful for overlapping reactions, giving double peaks and/or shoulders.

3.5.2 Differential Scanning Calorimetry

DSC is a versatile tool to study polymer transitions, glass transition temperature ($T_g$), melting and boiling points, crystallization, oxidative stability, rate and degree of cure, and liquid crystalline transitions, etc. It measures the energy (heat flow) required to maintain zero temperature difference between the sample and the reference ($\Delta T = T_s - T_r \approx 0$), as both are placed in identical environments and subjected to the same temperature conditions at a controlled rate.[182] A schematic diagram of the instrument is given in Figure: 3.13.

![DSC Apparatus Schematic]

Figure: 3.13 Schematic representation of a DSC apparatus redrawn from [182].

DSC is particularly useful technique to characterise thermophysical properties of polymers including melting temperature ($T_m$), percent crystallinity, crystallisation when cooling from the melt and the glass transition temperature ($T_g$). Figure: 3.14 show the ideal curve obtained for a polymer sample.
Glass transition is a second order transition (no enthalpy is associated with such transitions) and plays a crucial role in defining the physical properties of polymers. Below the glass transition temperature ($T_g$) noncrystalline polymers are in a glassy state, where polymer chain movement is dramatically reduced. Above the $T_g$ the polymer behaves as if it is a liquid or in a rubbery state. Polymers possess higher heat capacity above $T_g$, they can absorb more heat and therefore the glass transition is an endothermic process. At a certain temperature above $T_g$, known as the crystallization temperature ($T_c$) molecules may gain enough mobility to arrange themselves into a crystalline form. It is an exothermic process because they release heat during this transition. The highest temperature peak in Figure: 3.14 corresponds to the melting transition ($T_m$) at which ordered polymer regions break up and become disordered. When the polymer crystals melt they absorb heat therefore it is an endothermic transition.

### 3.6 Mechanical Analysis

Mechanical properties of the materials can be studied using various characterisation strategies. These tests can be performed under controlled and different environment and over wide temperature ranges as numerous mechanical properties can be influenced by temperature and environment changes. Mechanical analysis measures and offers insight...
about specific properties of the materials such as tensile, creep, viscoelastic and strength etc. [199]

### 3.6.1 Tensile Testing

The mechanical response of a material to an external force includes elastic, plastic and viscoelastic deformations. [199] In elastic deformation, the force is proportional to the displacement. The materials will return to its original dimensions on removing the stress as illustrated in Figure: 3.15 (a). This ability is referred as elasticity and energy is conserve in this situation. The force distance relation of the elastic deformation obeys Hooke’s law of $\sigma = E \varepsilon$. The force per unit area, $\sigma$, is called the stress:

$$\sigma = \frac{F}{A_0} \quad 3.9$$

And the stretch $\lambda$ is the ratio of deformed to initial length and defined as

$$\lambda = \frac{L}{L_0} = \lambda - 1 \quad 3.10$$

Young’s modulus, a measure of the intrinsic resistance of a solid to a stress, can be obtained from their linear regime as:

$$Y = \frac{\Delta \sigma}{\Delta \varepsilon} \quad 3.11$$

The elasticity is independent upon the loading rate. For most materials, elastic deformation restricted to a small deformation region and strains instantaneously. When the deformation continues to increase, plastic deformation may occur. Plasticity describes a material undergoing non-reversible deformations in response to applied forces. Plastic deformations dissipate energy, which is proportional to the shaded area in the figure.

The mechanical response of viscous materials is time dependent. Polymer exhibits viscoelastic behaviour, i.e. both viscous and elastic characteristics, upon application of external force. Hysteresis is observed in the force displacement curve of viscoelastic materials, with the area of the loop being equal to the energy dissipation after a loading – unloading cycle as illustrated in Figure: 3.15.
The viscous component can be discovered by Newton’s law with a low strain rate,

\[ \sigma_s = \eta \frac{d\varepsilon}{dt} \]  

with \( \eta \) being the viscosity and \( d\varepsilon/dt \) the strain rate.

Polymers are frequently utilized within applications that oblige great mechanical implementation. The characterization of stress-strain curves of solid polymers is very important. Solid polymers can be categorized into three different classes of behaviours: brittle, ductile and rubber like. Figure: 3.16 shown below represent the typical stress-strain profile for a typical polymeric material subjected to tensile testing. At low stress and strain, it behaves as linear elastic solid material and point the where its start behaving as non-linear is known as proportional limit, presented in the figure by point A. The point B represents the yield point at maximum load in stress and strain. This point also indicates the plastic/permanent deformation and its corresponding stress and elongation are called yield strength and elongation at yield. Moving on beyond this region neck forms due to considerable amount of stretch in the material which also known as plastic region.
After this point any further elongation causes stress increase or strain hardening in the material and led to rupture of the polymeric material, which is shown by point C in the figure. At this point stress and strain referred as an ultimate strength and elongation at a break respectively. The stress strain behaviour is influenced by many parameters such as rate of strain, temperature, structure of the materials, molecular characteristic of the materials etc.

3.6.2 Indentation Testing

In late 19th century Hertz research work on contact mechanics laid the foundation of indentation testing. He developed the elastic theory for contact between two elastic solids considering some constraints: strains are small and are within elastic limit, considered solid as elastic half-space, surfaces is continuous, non-conforming and frictionless.[201] Later, Johan August Brinell developed a procedure by using carbide ball indenting into metal called as Brinell test to calculate the hardness of materials.[202] After Brinell Meyer (1908) proposed an empirical formula to overcome the shortcomings of Brinell test and suggested hardness is material property and should be defined as:[203]

$$H = \frac{4P}{\pi d^2} \quad 3.13$$

To overcome, optical post-measurements of the indentation diameter in Mayer test, Tabor further developed the effective strain of the indentation $\varepsilon_i$ by a spherical indenter and approximated by:[204]
\[ \varepsilon_i = 0.02 \frac{d}{D} \] 3.14

It helps to develop the stress strain curves. Geometry of the indenter from ball to diamond shape was developed by Robert L. Smith and George E. Sandland defines as Vickers test, where diamond indenter that had four faces with angle 136°. [205] They then defined hardness as:

\[ DPH = \frac{2Psin\left(\frac{136}{2}\right)}{d^2} \] 3.15

Later, Stanley P. Rockwell invented the Rockwell hardness test to overcome the problem of measuring the imprinted diameter through a microscope and was no more required.[206] It laid the foundation to develop instrumented indentation. To analyse the indentation data, there are couple of methods has been proposed over the time. A method proposed by Oliver and Pharr is now the most commonly used to calculate the hardness and elastic modulus from the load -unloading curve.[207-212]

3.6.2.1 Oliver and Pharr Analysis

Oliver and Pharr introduced one of the most accurate and widely accepted method to analyse mechanical properties of the system such as hardness and elastic modulus. The basic principle of the method is shown in Figure: 3.17. In this method, an indenter with known elastic modulus and Poisson ratio is brought into contact with specimen. Indenter applied force which begins to indent the specimen and the displacement is measured as a function of applied force.[208]

![Figure: 3.17 (a) schematic of specimen under load (b) schematic of loading geometry and (c) load vs displacement curve redrawn from [208].](image)
The sample’s reduced modulus, $E_r$, is measured by fitting the data along the unloading portion of the applied load ($P$) shown in figure (c). During unloading, the measured displacement ($h$) as a function of applied force can be converted into a stiffness value i.e. $S = \frac{dP}{dh}$. Contact depth ($h_c$) between the indenter and sample surface can be calculated by using following equation

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{\frac{dP}{dh}}$$  \hspace{1cm} 3.16

Where $\varepsilon$ is constant and depend upon the indenter geometry. In our case is $\approx 0.75$.

Projected contact area of conical indenter is given by:

$$A = 24.5h_c^2$$  \hspace{1cm} 3.17

And Indentation hardness of the sample is thus calculated from:

$$H = \frac{P_{max}}{A_c}$$  \hspace{1cm} 3.18

Finally elastic modulus is estimated from the equation:

$$E = \frac{dP}{dh} \frac{1}{2} \sqrt{\frac{\pi}{A_c}}$$  \hspace{1cm} 3.19
Chapter 4 Materials: Fabrication, Characterization and Results

This chapter is divided into two sections. In the first section, we will discuss the physical properties of the polymer latex and surfactant used in this thesis. In the second section the experimental procedures to obtain dispersions of 2-D, layered materials such graphene and boron nitride and one dimensional materials, such as single walled carbon nanotubes will be presented. Later, optical, morphological and statistical analysis will be carried out to determine their state of exfoliation and their size in the dispersion.

4.1 Materials

4.1.1 Latex Polymer

Latex is class of colloidal dispersion, which contains polymer particles, water and surfactant. Polymer particles are usually dispersed in water and prepared by emulsion polymerization. The latex polymer particle’s diameters are usually around a few hundred nanometres in size.[213-216] Latex has a wide range of applications, ranging from paints, coatings, pressure sensitive adhesives, - to thin films. Capillary forces and convective particle flux, caused by water evaporation, is responsible for the formation of latex particle films. Later stages involve particle deformation and inter-diffusion, leading to highly transparent thin polymer films.

The film formation process is commonly divided into 3 stages and these are summarised diagrammatically in Figure: 4.1.[213] During the first stage water evaporates from the dispersion at a constant rate whilst the polymer particles, moving under the effect of Brownian motion, become increasingly concentrated. The rate of water evaporation from colloidal suspension is the same as water alone, as further water evaporation, leads to increased concentration, the particles come into closer proximity. At this stage volume fraction of the polymer reaches 60-70%. In the second stage, particles comes close and are in irreversible contact and appear at the surface of the latex. At this stage the evaporation rate of water progressively decreases. Forces accompanying drying exceeds the mechanical (both elastic and viscous) resistance of the particles, resulting in particle deformation. This deformation takes places in such a
manner that polymeric material fills the void spaces and FCC packed spheres transform into rhombic dodecahedra, producing a void free, but still mechanically weak film. At this stage the film interface still exists between polymer particles. The compaction and deformation step is considered to be favourable due to the influence of capillary pressure between the particles and the significant reduction in the total area of the particle - water or particle – air interfaces. Remaining traces of water in the film will evaporate through inter – particle channels and then by diffusing through the coalesced layer, there may be a polymer “skin” over a wet layer. In the next stage healing of the polymer particles will occur at the particle – particle interface, rate of water evaporation slows down further in this stage. Inter particle membranes, due to the presence of absorbed surfactant breaks up and this material is expelled into film interfaces. Dissolution of this membrane brings polymer particles into intimate contact and permits inter-diffusion between the neighbouring particles. Later polymer boundaries gradually disappear due to polymer mixing which is often called “auto–hesion”, “maturation” or “gradual coalescence”. During this stage the films properties changes significantly, as polymer diffusion generates entanglements, substantially improving the mechanical strength and resistance character of the film.

This third stage generally leads to optical clarity of the film. However latex can appear optically, without particle deformation. To achieve a cohesive film it is necessary to dry the latex above the “minimum film formation temperature” or MFFT. It can be defined as: the minimum temperature at which a cast latex film becomes continuous and clear. Latex remains opaque and powdery below this MFFT. It is generally accepted that film formation described in stage two cannot take place below the MFFT. And stage three cannot occur below the glass transition of the polymer latex.

![Illustration of three different stages Latex formation stages](image)

Figure: 4.1 Illustration of three different stages Latex formation stages redrawn from [182].
4.1.2 Surfactants

Surfactants are used extensively for nanomaterials dispersions such as carbon nanotubes and graphene, via non-covalent functionalization in aqueous solution. Surfactants (SURFace ACTive AgeNTS), are small mobile molecules that, at relatively low concentrations, can absorb onto a surface or an interface and change the surface or interfacial free energy. [217, 218] A surfactant molecule contains polar (hydrophilic) and nonpolar (hydrophobic or lipophilic) groups as shown in Figure: 4.2, and can be classified according to their physical properties or functionalities. There are usually four types of surfactant called anionic, cationic, non-ionic and zwitteronic. [219] In our case non-ionic surfactant has been used. As surfactant molecules are added to aqueous solutions they tend to accumulate at fluid-fluid and fluid-solid interfaces. After a certain concentration of molecules the surfactant forms micelles due to aggregation. This particular concentration, the critical micelle concentration, (CMC) is different for every surfactant.[220] Below the CMC, but very close to it, premicellar surfactant aggregation occurs, which means that surfactant molecules aggregate into oligomers having an aggregation number lower than that of micelles. Beyond the CMC, any surfactant added to the aqueous solution will not increase the number of unimers, but rather will contribute to the formation of additional micelles. The premicellar and micelle formation mechanism is shown in Figure: 4.2. In this study non-ionic surfactant Triton–X100 was used to stabilize and to overcome the reaggregation issue of the nanomaterials such graphene, boron nitride and carbon nanotubes. According to Scolari et al,[221] to be able to obtain good dispersion, optimum surfactant concentration should be used which they found to be slightly higher than the CMC. In this study, the surfactant concentration was chosen to be well above the CMC and is described in further section.

Figure: 4.2 Mechanism of surfactant micelle formation in aqueous solution redrawn from [182].
The physical properties and structural formula are shown in Table 4.1.

Table 4.1 Literature values of physical properties of Triton –X 100 surfactants used and its chemical structure

<table>
<thead>
<tr>
<th></th>
<th>Molecular weight (g/mol)</th>
<th>Density (g/cm$^3$)</th>
<th>CMC (mM)</th>
<th>Structural formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton X - 100</td>
<td>625</td>
<td>1.07</td>
<td>0.22-0.25</td>
<td><img src="image" alt="Structural formula" /></td>
</tr>
</tbody>
</table>

4.1.3 **Materials: Latex Polymer type 1 (255 nm): Details and Characterization**

The type of latex used in this work and its morphological parameters are provided in the Table 4.2 below:

Table 4.2 physical properties of latex (255 nm) provided by manufacturer

<table>
<thead>
<tr>
<th>Monomer Composition</th>
<th>Units</th>
<th>PW-1203B MAA/MMA/BA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (glass Transition Temperature)</td>
<td>°C</td>
<td>34</td>
</tr>
<tr>
<td>Solid Content</td>
<td>%</td>
<td>54.9</td>
</tr>
<tr>
<td>PS(pd)</td>
<td>nm</td>
<td>255(0.025)</td>
</tr>
</tbody>
</table>

Latex polymer was provided by company named NeoResins, Netherlands. The components used to form this latex include: random copolymer of butyl acrylate (BA), methyl methacrylate (MMA) and methacrylic acid (MAA): in a molar ratio of BA: MMA: MAA of 41:56:3. Figure: 4.3 below show the optical image of latex polymer in the glass vial and drop casted film on the glass cover slip at the room temperature.
Figure: 4.3 Optical image of latex polymer in the glass vial and drop cast film on a glass substrate.

To characterize the latex polymer, atomic force microscopy was used. A glass cover slip cleaned with acetone, methanol and deionized water and blown with nitrogen gas to achieve good adhesion was used for this study. Later, the latex polymer was drop cast onto this substrate to achieve a thin film of polymer latex, the film was dried at the room temperature. The thickness of cast film was about ~ 100 μm. The measurements were performed in the ambient air and to avoid thermal drift all the scanning was performed in less than a minute.

An NTMDT NOVA AFM was used to characterize drop casted latex film. It is capable of scanning a region up to 150 μm x 150 μm. Figure: 4.4 shows representative latex particle morphology in height mode on a latex film, dried at room temperature.

Figure: 4.4 (a) shows a surface scan of a latex polymer film in height mode. A perfect hexagonal dense packing of polymer latex with some minor defects, in the form of misalignment in the colloidal structure and empty lattice sites were observed. AFM imaging reveals that latex particles are monodisperse and display well-ordered long-range packing, which is consistent with a face centered cubic structure. Figure: 4.4 (b) shows a line scan profile, used to calculate the particle size. Interparticle distance was measured between two adjacent polymer particles to calculate the diameter, which was found to be ~ 250±5nm. Figure: 4.4 (c) show 3-D image, particles are stacked uniformly in a lattice and the boundaries between the individual particles are clearly visible. This is as expected, since the film was dried at room temperature, and below the $T_g$ of latex polymer. Ordering of the particles has been shown in Fig. 3.16c, was analysed by two-dimensional Fast Fourier transform (FFT). The FFT shown in the
Figure: 4.4 (d) display the hexagonal symmetry. The two-dimensional power spectrum, which consists of six high intensity spectral spots in a hexagonal arrangement, is indicative of the extended ordering.

Figure: 4.4 AFM topography image of multilayers latex polymer (diameter- 255nm) deposited on the mica surface, taken in intermittent-contact mode (a) height image (scan size 5x5 um) (b) topographical cross-sectional line scan profile of height image (c) 3-D height image and the corresponding (d) 2D-FFT diagram showing the same particle size and almost perfect hexagonal, dense packing with only some minor defects visible, in the form of misalignment in the colloidal structure and empty lattice sites.

4.1.4 Latex Polymer Type -2 (290 nm) Details and Characterization

This latex polymer is different in the sphere diameter size. This latex polymer is also used as the template for CNT assembly (chapter 7), provided by DSM NeoResins (Waalwijk, The Netherlands) is based on a random copolymer of methacrylic acid (MAA), acid: acetoacetoxyethyl methacrylate (AAEM), methyl methacrylate (MMA), and butyl acrylate (BA) in a molar ratio of MAA/AAME/MMA/BA of 3/10/50.3/36.7%. The polymer particle size is 290 nm, its dry glass transition temperature (Tg) is 28°C, and the initial solids content is 55 wt %.

Table 4.3 physical properties of latex (290 nm) provided by manufacturer

<table>
<thead>
<tr>
<th>Monomer Composition</th>
<th>Units</th>
<th>PW-1203A MAA/AAEM/MMA/BA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg (glass Transition Temperature)</td>
<td>°C</td>
<td>34</td>
</tr>
<tr>
<td>Solid Content</td>
<td>%</td>
<td>54.9</td>
</tr>
<tr>
<td>PS(pd)</td>
<td>nm</td>
<td>290(0.025)</td>
</tr>
</tbody>
</table>
To determine the periodicity on this latex polymer same AFM study has was carried out. Figure: 4.5 shows the same long range ordering, FCC packing, and measured interparticle was found to be \( \sim 287\pm3 \text{ nm} \).

![Figure: 4.5 AFM topography image of multilayers latex polymer (diameter- 290nm) deposited on the mica surface, taken in intermittent-contact mode (a) height image (scan size 5x5 um) (b) topographical cross-sectional line scan profile of height image (c) 3-D height image and the corresponding (d) 2D-FFT diagram showing the same particle size and almost perfect hexagonal, dense packing with only some minor defects visible, in the form of misalignment in the colloidal structure and empty lattice sites.]

4.2 Two dimensional Nano-Platelets: Preparation and Characterization

4.2.1 Graphene

Recently, efforts have been made to improve the liquid phase exfoliation process of graphite to produce graphene.\([222-225]\) This process of exfoliation can produce defect-free, monolayer graphene. These developments allow the production of graphene in large quantities, while maintaining low costs and a facile process. The main production method makes use of high surface tension solvents, such as N-Methyl-2-pyrrolidone (NMP). NMP is being one of the best solvent to exfoliate graphene as its surface energy matches very well with graphene but being very expensive and required careful handling and low yield are few drawbacks. In addition, due to their high boiling points, deposition of monolayers on surfaces is not easy, which means an alternative process is needed that results reasonably high yield of graphene from graphite. The most common solvent, water can be alternative solution being low boiling point, safe, and compatible, however high surface energy of water makes it inappropriate to work on its own. To
overcome this, graphite in surfactant-water solutions method has been used with the aid of ultrasound, similar to surfactant aided carbon nanotube dispersion process. Lotya et al.[224] reported large-scale exfoliation to give large quantities of few layers of (<5 layers) graphene and smaller quantities of monolayer graphene by this method and these nanoflakes are stabilized against restacking issue by a relatively large potential barrier, which originates in the Coulomb repulsion between surfactant-coated sheets.

In this study non anionic surfactant TritonX-100/water solutions with aid of ultrasound was used to exfoliate graphite to produce graphene and overcome the reaggregation. Graphene dispersions were prepared by our collaborator, Prof Coleman and research group in Trinity College Dublin and were used in our study as received. The procedure to obtained graphene nanoflakes has given below.

In typical procedure graphite powder was used purchased from Sigma-Aldrich (Product Number 332461) and to remover bigger particles sieved through a 0.5 mm mesh. Then the graphite powder was dispersed in water/TritonX-100 solution in cylindrical glass 25 ml vial at a concentration of 0.57 mg mL\(^{-1}\). This dispersion has been subjected to sonication in low power sonic bath for 30 minutes. One needs to be very careful with sonication time as excessive sonication may lead to damage the graphene sheets. Obtained dispersion after sonication was then centrifuged in Hettich Mikro 22R centrifuge for the duration of 90 minutes at the speed of 500 rpm. Later decantation was carried out in the dispersion by pipetting off the top half of the dispersion.

### 4.2.1.1 Optical Measurement

The absorption coefficient, \(\alpha\), is a key parameter in characterizing dispersion. It is related to the absorbance, \(A\), through the Lambert-Beer law as follows:\[226\]

\[
A = \alpha \cdot l \cdot c
\]

where \(c\) is the concentration and \(l\) is the path length of the cuvette. To measure it, the dispersion is then subjected to centrifugation for different centrifugation time at the fixed angular speed of rotation at 3000 rpm to obtain dispersion of different concentration to calculate optical constant. UV-vis absorption spectroscopy was employed using a Varian Cary 5000i with optiglass 1mm cuvettes to calculation absorption coefficient. Absorption spectra of the graphene dispersion with different concentrations measured and presented in the Figure: 4.6 (a), in each case, the absorbance spectra of the dispersions were flat and featureless as expected for a quasi-two-dimensional material.
The absorbance per cell length, $A/l$, versus concentration of these dispersions was measured at 660 nm as shown in Figure: 4.6 (b) A straight line fit showing Lambert – Beer behaviour and gives the absorption coefficient at 660 nm $\alpha = 1410 \text{ L g}^{-1}\text{m}^{-1}$ in reasonable agreement with the value measured for graphite/graphene in various solvents presented in literature.[224, 225] Inset of Figure: 4.6 (b) shows optical micrograph of graphene dispersion for two different concentration (a) 0.57mg/ml and (b) after centrifuge at 3000 rpm for 80 minute leads to decrease the concentration to 0.08 mg/ml thus increase in transparency.

Figure: 4.6 (a) Dispersions of graphene in water/ Tx-100, at a range of concentrations ranging from 0.57mg/ml to 0.08mg/ml after centrifugation at 300- rpm at 20, 40, 60, 80 minutes respectively. (b) Optical absorbance at 660 nm divided by cell length ($A/l$) as a function of concentration for showing Lambert–Beer behaviour with an average absorption coefficient of 1410 Lg$^{-1}$m$^{-1}$. Inset in Figure 5(b) shows optical photograph of graphene dispersion transparency after centrifugation (a) 0.57mg/ml and (b) 0.08 mg/ml.

4.2.1.2 Evidence of Exfoliation: TEM measurement

To further characterize and quantify state of dispersed graphene transmission electron microscopic study has been employed on graphene dispersion. This study is performed in our collaborators laboratory in Dublin. To perform TEM measurements, we drop cast
the graphene dispersion onto holey carbon grids (400 mesh size). Figure: 4.7 (a) represents optical image of the prepared Graphene dispersion after sonication.

TEM offers images Figure: 4.7(c) of these dispersions, which can be used to produce statistical data on the exfoliation state of the graphene in the dispersion. We measure the lateral dimensions of a large number of flakes ~ 256. In general, the graphene flakes are irregularly shaped. We chose to measure the dimension along the long axis and assign it as the length, L, and the dimension perpendicular to the long axis as the width, w. In addition, we estimate the number of layers per graphene flake, N, by inspecting the edges of the flakes. In TEM, edges of the individual flakes are almost always distinguishable in graphene multilayers. Figure: 4.7 (a) illustrated the optical micrograph of standard graphene dispersion 0.57 mg/ml in 20 ml glass vial. In the inset of Figure: 4.7 (c) shows TEM micrograph of the dispersed graphene flake. Measured flake length, L, with histogram shown in Figure: 4.7 (b). is $\langle L \rangle = 0.5 \mu m$.

![Figure 4.7 TEM analysis of dispersed (a) optical image of Graphene dispersion (b) Histogram analysis of the no. of flake Statistical analysis of TEM images showing histograms of the number of layers per flake. (C) A TEM image of grid coated a very thin flake.

4.2.1.3 Graphene Morphological Measurement: AFM

AFM is a versatile tool and employed here to demonstrate efficacy and degree of exfoliation and measure the physical dimensions such as thickness of graphene flakes after the preparing the dispersion. This AFM study was carried out on a NTMDT system in tapping mode after drop casting the dispersion (10μL) on a pre-heated
(150°C) Si/SiO$_2$ wafer with an oxide layer of 300 nm. Typical image sizes were 2.5-5 μm at scan rates of 0.4-0.6 Hz. The setpoint was chosen as high as possible.

During thickness measurements of graphene, only flakes were considered that were clearly not re-aggregated as evaluated from phase images, which were recorded in parallel. Height analysis of surfactant exfoliated graphene is always challenging to calculate number of layers in the flake as surfactant also contributes to flake height. To overcome this problem we have always chosen high set points (i.e. low interaction between tip and surface) in scanning measurement. To quantify the height of graphene sheet we count it as thickness because there are only few points on the substrate, where wrinkled graphene sheet come into close contact. The typical height profile of a graphene sheet, showing the method used to evaluate the diameter distribution, is given in Figure: 4.8 (a).

The inset of Figure: 4.8 (b) is a typical AFM topographic image showing a graphene sheet with the thickness of 2.45 nm. The thickness of graphene flakes varies between 1 to 5 nm as measured by AFM technique. Although large flakes are also present. Literature suggests that the apparent height of graphene monolayers as measured by AFM to be ∼1 nm. [227-229] This suggests the peak represents flakes with 2-3 layers.

![Graphene flake thickness histogram](image_url)

Figure: 4.8 (a) Graphene flake thickness histogram Inset: A representative zoomed image of graphene flakes and corresponding line scan taken horizontally through the image as marked with a white line from which the topographic height of the graphene flake is measured to be about 2.45 nm signifying the presence of only few layers of graphene sheets.
4.2.1.4 Kelvin Probe Force Microscopy

Along with AFM, Kelvin probe force microscopy (KPFM) is also a key characterization technique and very sensitive to local variations in the work function of materials. [230, 231] KPFM allows measuring strength of the electrostatic forces between a probe and the sample and providing surface potential maps of a sample. The work function varies for different materials, different layer thickness, surface dipole moments etc. Our liquid phase exfoliated graphene contains non-anionic surfactant Triton X-100. The graphene dispersion consists of flakes with lateral sizes ranging from ~100nm to ~ 500 nm. KPFM combined with AFM topography imaging was used shown in Figure: 4.9 (a-c) to create maps of contact potential differences that allowed to unambiguously distinguish between the substrate and the graphene area and to aid the visualization of graphene flakes covered with a layer of surfactant. This enables the careful determination of the thickness of the majority of flakes to be between 1 and 5 layers. Good quality dispersion is maintained despite its high-concentration of 0.57 mg mL\(^{-1}\).

Figure: 4.9 AFM (a) topography and (b) KPFM surface potential images of exfoliated graphene aqueous dispersion spin-coated onto a mica substrate. (c) The line profile showing the contrast in the surface potential changing in the (1.2 mV) – (1.8 mV) range where graphene is present.
4.2.1.5 Raman Spectroscopy

There are many methods available to characterize graphene such as AFM, TEM; however, precise measurement of graphene layers is always challenging. Although AFM has been proven to be one of the most direct and reliable methods to measure number of layers present in the graphene flake. However, this method also has some limitations, such as slow throughput and also can possibly damage crystal lattice during measurement.[232] In recent years, Raman spectroscopy has emerged as a powerful probing technique to characterize graphene and nowadays it is an integral part to analyse graphene.[233] Raman spectroscopy is a non-destructive technique and offers quick inspection about graphene sample quality and thickness and thus number of graphene layers.[225, 233] In graphene, Raman active modes arise from the Γ and K(K’) point of the Brillouin zone, providing key information on layer stacking and defects. Ferrari et al. reported Raman spectroscopy as a key tool to characterize monolayer graphene.[232] Their work reported two main features arise in Raman spectra and are related to graphite. The first is the G band (at ~1582 cm\(^{-1}\) for graphite) due to sp\(^2\) vibration of carbon atoms. This feature will be upshifted for monolayer graphene ~ 5cm\(^{-1}\). The intensity of G band increases almost in linearly with increasing number of graphene layer thus enabling to determine the graphene layer thickness. The second feature is the 2D band which appears at ~ 2700 cm\(^{-1}\) and occurs in second order Raman spectrum. This feature is extremely sensitive to the number of layers. The shape of 2D band, could determine the number of layers up to five layers. However, it is difficult to determine layer thickness that has more than five layers. For monolayer this feature is sharp, and highly symmetric; however, for bi and multilayer it becomes much broader due to change in electronic structure of graphene. Figure: 4.10 present the dependence of 2D band on number of layers. Figure (a) shows 2D band for monolayer graphene with intense Lorentzian peak. Figures (b) shows four Lorentzian peaks and is related to the four possible double resonance scattering process for double layer graphene. On increasing the layer number, the peak shape converges to that found for graphite where only two peaks were found.[234] Raman spectrum also possesses bands other than G and 2D. The presence of defects in graphene generates another band called D band and occurs at ~ 1350 cm\(^{-1}\) and usually expected at layers edge.[232] There is another band M at ~ 1750 cm\(^{-1}\), is strongly dependent on the number of graphene layers, only appears in bi and few layer graphene layer sample.[235]
Figure: 4.10 Dependence of 2D band on the number of layers (reprinted with the permission from [234]).

Raman measurements in graphene sample were obtained using an NT-MDT NTEGRA (Moscow, Russia) spectrometer fitted with an upright microscope and a 100x objective lens. Raman scattering was detected with a charge-coupled device (CCD) camera with a built-in thermoelectric cooling device. Samples were excited with the blue line - 473 nm (2.62 eV). The exposure time was 5 seconds and each spectrum was an average of 100 accumulations. For Raman spectroscopy studies, dispersion was drop-cast onto a glass substrate and dried for 24 hours at room temperature. Figure: 4.11 shows well defined Raman spectrum with characteristic 2D band (around 2700 cm$^{-1}$), G band (around 1600 cm$^{-1}$) and D band (around 1400 cm$^{-1}$) obtained from exfoliated graphene dispersion.

Figure: 4.11 Raman spectra of exfoliated graphene.
4.2.2 **Boron Nitride Nano platelets: Preparation and Characterization**

Hexagonal Boron Nitride some-times referred to white graphene and possesses a structure analogue to graphite. [158, 159] The structure of single sheet h-BN is the same as graphene. A bottom up approach, such as CVD growth has been widely used to synthesize this material but the high cost and tedious procedure makes this process unsuitable. The top-down approach provides an alternative way to synthesize these BN nanosheets (BNNs) in the same way as graphene but difficult in comparison due to “lip–lip interaction among the BN layers. This interaction arises from ionic character of the B–N bonding and is stronger than the weak Van der Waals force between graphene layers. Pacile et al. first reported mechanical exfoliation of BNNs but the low yield in the final product made it unsuitable.[173] Alternatively, Coleman et al. demonstrated liquid-phase exfoliation processes to produce BNNs, which has the advantages of simple processing and good yield.[223] BNNs, used in our study are also processed by the liquid exfoliation method and, as describe above for graphene, dispersed using the surfactant Triton X-100. This dispersion was also supplied by our same collaborators in Trinity and typical procedure is given below.

**Liquid Phase Exfoliation to obtain BNNs: Experimental Procedure**

Boron nitride was purchased from Sigma Aldrich (powder, 1 µm, 98 %) and used as received. The white powder was added to an aqueous solution of Triton X-100 (2 g/L, 80 mL) in an open top beaker to yield dispersion with solute concentration of 20 g/L. The beaker was connected to an external cooling system that allowed for cooled water (5°C) to flow around the dispersion during sonication. The dispersion was sonicated for 3 hours at 60% amplitude with a horn-probe sonic tip (VibraCell CVX, 750W). The sonication was pulsed for 6s on 2s off to avoid any damage to the processor and reduce solvent heating.

After sonication, the dispersion was centrifuged at 2.5 krpm (665 g) in 10 mL aliquots using a Hettich Mikro 220R centrifuge equipped with a A1016 fixed angle rotor. The sediment containing unexfoliated and very large BN nanosheets was discarded. The supematant was subjected to a second centrifugation step at 5 krpm (2660 g). The supematant after this centrifugation run (containing very small nanosheets) was discarded and the sediment was redispersed in 2 g/L Triton X-100. The volume was reduced to 1/3rd of the initial volume to yield a dispersion of exfoliated BN at higher concentration (typically 0.1 g/L).
Low resolution bright field transmission electron microscopy (JEOL 2100, operated at 200 kV) imaging was performed to confirm that the BN nanosheets are well-exfoliated (Figure: 4.12). Holey carbon grids (400 mesh) were purchased from Agar Scientific and prepared by diluting dispersion to a low concentration (factor 10) and drop casting onto a grid placed on a filter membrane. Statistical analysis was performed of the flake dimensions by measuring the longest axis of the nanosheet and assigning it as “length” (histogram figure *D). The mean nanosheet length $<L>$ was determined to be 410 nm.

![Representative Low resolution TEM images of the exfoliated BN in Triton-X100. D) Flake length histogram.](image)

Figure: 4.12. (a - c) Representative Low resolution TEM images of the exfoliated BN in Triton-X100. D) Flake length histogram.

UV-Vis spectroscopy is employed to determine the optical properties of BNNs with different concentration and results are presented in the Figure: 4.13 (a) shows measured absorbance spectra using 0.1mm quartz cuvette for three different BNNs concentration, which represents higher absorption for higher BNNs concentration. Figure: 4.13 (b) shows optical photographs of the BNNs dispersion of three different concentrations. All dispersion appearances and transparency are different. The milky appearance of BNNs is due to the size of dispersed BNNs, as they scattered the light in different manner. Figure (b) shows glass vials of 25ml volume, contains small, medium and large BNNs, which represent (0.1mg/ml), medium (0.6 mg/ml) and large (0.8 mg/ml) concentration respectively. Figure: 4.13 (c) shows plot of absorbance of the all three BNN’s plotted as a function concentration. The absorbance per cell length, A/l, versus concentration of these dispersions was measured at 300 nm as shown in Figure: 4.13 (c). A straight line
fit showing Lambert–Beer behaviour and gives the absorption coefficient at 300 nm $\alpha = 2683 \text{ mL mg}^{-1} \text{ m}^{-1}$ and is in reasonable agreement with the literature value.[164, 236, 237] The nanoparticles suspended in suspension scatters the incident laser light and the laser light path becomes visible in the suspension, this phenomenon is known as Tyndall effect. [174, 238] Similar results were observed for our small concentration (0.1mg/ml) of BNNs sample, on incident of scattering laser light. The Tyndall scattering is visible only when the particle size (~40-900 nm) is below or near the wavelength of light and such phenomenon will not occur for the small particle sizes (~1 nm). Figure: 4.13 (d) shows the glass vial (left) contains water/Tx-100 surfactant and the glass vial at right hand side is BNNs dispersion. It is evident from both the optical images that no scattering was observe in water/tx100 glass vial as laser light passes without being scattered, whereas scattered path in the BNNs suspension is clearly visible.

![Figure: 4.13 (a) Absorbance spectra of dispersions of BN nanosheets of various concentration (b) Photograph of three different concentration small (0.1mg/ml), medium (0.57mg/ml) and large (0.8mg/ml) boron nanosheets dispersions. (c) Lambert–beer plot of absorbance divided by the cell path length at 300 nm (d) Tyndall effect was visible when the laser light incident from the left in the images - DI water (left) and the BN nanosheets dispersion (right).](image)
To demonstrate the exfoliated state of the BNNs atomic force microscopy has been used. Similar process of preparing the specimen and similar AFM settings were used same as graphene dispersion measurement. The typical height profile of a BN nano sheet, showing the method used to evaluate the diameter distribution is given in Figure: 4.14 (f). The Figure: 4.14(a) and (c) are showing typical AFM topographic height image of BN sheet. The line scan profile of these corresponding height are presented in Figure: 4.14 (b) and (d), suggesting the BNN’s thickness of 12 and 20 nm respectively. The thickness of flakes varies between 5 to 25 nm as measured by AFM technique. Although large flakes are also present. As reported in the literature the apparent height of BN monolayer sheet as measured by AFM to be ~1 nm. This suggests that majority of BNN’s flakes consists ~ 12-20 layers. Figure (e) and (f) shows the histogram analysis on BNN’s lateral flake size distribution and thickness respectively. Statistical analysis shows lateral size distribution of BNN’s is ~ 412 nm, whereas average flakes thickness is ~ 20 nm.

Figure: 4.14 (a-d) Represents the AFM images of two different BNN’s and their corresponding line height profiles showing thickness variation in BNNs. Figure (e) and (f) represent the histogram for BNNs size and thickness respectively.
4.3 One Dimensional Nanotubes (Single walled carbon nanotubes): Preparation and Characterization

4.3.1 SWCNTs Dispersion

Carbon nanotubes are known for their unique properties and have shown potential in a range of applications. Their exceptional characteristics include tensile strength, elastic modulus, flexibility, outstanding thermal and electrical properties and high aspect ratio.[108, 109, 111-116, 118-120, 124] The main challenge to integrate them for any application is to prepare a uniform dispersion and produce them at low cost. Aggregation must be overcome before employing them in any specific application. There are two unique methodologies for dispersing carbon nanotubes: mechanical and chemical methods. Mechanical methods such as high shear mixing, ball milling or ultra-sonication have been used to disperse nanotubes, however the biggest disadvantage is they tend to break the nanotubes into shorter lengths, changing the aspect ratio and can also create undesirable structural defects.[239] In chemical methods, sometimes referred to as covalent methods, the surface energy is modified by using surface functionalization which enhances their chemical compatibility, this leads to a reduction in agglomeration. However, chemical functionalization can also result in modification of the nanotubes properties.[240] In the past few years chemical methods have been widely used to prepare isolated dispersions of nanotubes in both aqueous and organic solutions. Surfactant based solutions approach to modify the surface properties of the nanotubes were used in this report. The surfactant assisted procedure is an effective approach for spontaneous debundling of nanotubes, where surfactant induces steric repulsions, that counterbalance the van der Waals forces among nanotubes.

In a typical process, after adding the surfactant into the solution they tend to adsorb on the nanotube walls, ultra-sonication for a couple of minutes leads to debundling of the nanotubes. The combined approach of surfactant and sonication to debundling nanotubes was proposed by Smalley and workers. [241] The debundling mechanism is subdivided in three segments as shown in Figure: 4.15. Initially, (i) ultra-sonication provides the high local shear to nanotube bundles. (ii) It creates gaps where surfactant molecules can penetrate and surfactant adsorption will takes place (iii), eventually isolating the nanotubes from the bundles.
Various surfactants have been explored to prepare aqueous single-walled carbon nanotube dispersions, such as sodium 4-dodecylbenzenesulfonate (NaDDBS), hexadecyl (trimethyl) azanium bromide (CTAB, TritonX-100 and sodium dodecan-1-sulfonate (SDS) being the most pervasive. [242] Unfortunately, there is contradiction in the literature on which results in better dispersion of nanotubes. For example a report by Vaisman and workers suggested that non-ionic surfactants are better in organic solvents and ionic one are more suitable to aqueous dispersions.[242] Nevertheless, in another study, it was shown that the non-ionic surfactant Triton® X-100 was better than the anionic surfactant SDS. [243, 244] Later, it was demonstrated that nanotube diameter or side wall curvature is a key parameter in surfactant adsorption and it was demonstrated that long chains are preferable by showing surfactant adsorption on graphite. [245] Dispersions prepared in our study are based on non-ionic surfactant Triton-X 100. These surfactant molecules attaches to the nanotubes surface due to strong hydrophobic interaction.

4.3.2 Surfactant Characterization: Dynamic Light scattering (DLS)

On increasing surfactant concentration there is a point at which self-aggregation occurs, which leads to formation of the micelles. This particular concentration is called the critical micelle concentration (CMC). [246] Below the CMC, surfactant molecules are adsorbed at the water-air interface which leads to insufficient stabilization; whereas above the CMC, the depletion-induced aggregation occurs and micelles are formed. Thus, surfactant concentration is a key parameter to obtain homogeneous dispersions. The CMC was measured with Dynamic light scattering (DLS) using a model- ZetaSizer Nano S (Malvern Instrument, UK). The instrument contains 4mW Helium neon laser
with operating wavelength of 633nm and detects the scattered light at an angle of 173° with an avalanche photodiode detector, which increases the detection range. DLS measures the time dependent intensity fluctuations from the solution, which allows determination of diffusion coefficients. Later, utilizing the Stokes-Einstein equation yields the particle size. All measurements were performed at 25°C. Figure: 4.16 shows the variation in the scattered light intensity (in kilo counts per second) and hydrodynamic diameter (in nm) versus different concentrations of surfactant in DI water. The standard CMC value and hydrodynamic value for TritonX-100 are 0.3mm and 7.5nm respectively. It can be readily seen from the figure that the intensity below the CMC, which is (0.3mM) is very low. When the CMC concentration is reached, the scattering intensity shows a linear increase with concentration. The intersection point, at around 0.25mM concentration corresponds to the CMC of TritonX-100. Both values are in good agreement with literature values. It also confirms our dispersions were prepared well above the CMC concentration.

![Graph showing scattered light intensity and hydrodynamic diameter vs Triton X-100 concentration](image-url)

Figure: 4.16 A plot of scattered light intensity and hydrodynamic diameter for various concentrations of triton X-100 concentrations prepared in deionised water.

### 4.3.3 HiPCO SWCNTs Characterization

#### 4.3.3.1 Thermo Gravimetric Analysis (TGA)

Raw HiPCO SWCNTs (Lot no# PO312) were purchased from Unidym Company. They were produced by a gas process based on a CVD method. HiPCO SWCNTs have diameters in the range from 0.8 to 1.2 nm and the residue of iron catalysis in the raw HiPCO is less than 30% as per the manufacturer’s specifications. The main impurity in HiPCO SWCNTs is the metal catalyst.[247] They are enclosed in thin carbon shells and dispersed throughout the specimen as 3-5 nm particles. This impurity content in
samples can be measured using a TGA. TGA was performed on Q500 TA Instruments with a linear temperature ramp. Nanotube powder was placed in the TGA platinum pan, and heated in a temperature scan from RT to 800°C. The heating rate was selected at 10°C/min for better resolution of transition in the curve. Weight retention/temperature curves were recorded. The TGA curves were transformed into their first derivative (ΔWeight change/ΔTemperature).

Figure: 4.17 shows mass loss in nanotubes as function of temperature. The total obtained residual amount of iron catalyst in our lot of nanotube is 19.46%, which correspond to 0.3942 mg in contrast to 2mg. It was observed that ~2.2% mass was lost from room temperature (RT) to 50°C, corresponding to humidity. The % weight loss was then almost constant from RT to till ~ 300°C. The total loss in this range was ~2.3% and can be attributed to low burning of nanotubes and impurities. Later, from 350°C to 600°C, the main loss was observed and ~74.6%. It is due to carbon oxidation into gaseous carbonaceous species such as carbon monoxide and carbon dioxide. Finally, the total weight loss was ~80.5% and the total residue was ~ 19.46% corresponding to 0.3942 mg.

Figure: 4.17 TGA of as supplied HiPCO SWCNTs in air.

4.3.3.2 Raman Spectroscopy of HiPCO SWCNTs

Raman spectroscopy has been a key analytical technique to study the carbon nanotubes from the beginning. Raman spectroscopy offers a range of information in the materials such as crystallite size, chemical impurities, optical gap, doping, crystal disorder, strain, nanotube diameter, chirality, type of nanotubes etc. The details of Raman characterisation has already been discussed in the methodology chapter. Here, experimental Raman data and analysis will be presented for HiPCO SWCNTs. The
Raman measurement was performed on Renishaw system model no 2000 Raman Microscope. The laser beam was focused on the specimen with a 50X objective lens. It was calibrated with the Raman band of silicon positioned at 520 cm\(^{-1}\). A laser wavelength (514 nm) was generated by argon laser. Nanotube powder was sandwiched between two cover slips and sealed with scotch tape and Raman Spectra has been taken at room temperature. In Raman measurement, the parameters were used as follows: the detector time was ~ 1500 sec, accumulation 3, and objective lens was at 50X. Measurements were carried out at low laser energy to rule out heating effects. All the spectra were fitted by Fityk software. A Gaussian function was used for fitting the radial breathing modes and a voight function was used for the G peak. Figure: 4.18 show the Raman spectra of HiPCO SWCNTs.

![Raman Spectra](image)

Figure: 4.18 Raman spectra of HiPCO SWNTs excited with 2.4eV.

From the figure, one can observe the common feature for all sp\(^2\) hybridized carbon forms, the G band located ~ 1578.2 cm\(^{-1}\), the radial breathing mode (RBM) ~ 257.1 cm\(^{-1}\), which gives insight into the nanotube diameter and optical transitions, whereas D (1321.9 cm\(^{-1}\)) and G\(^\prime\) can be used to extract information about the electronic and geometrical structure.[234, 248-251]

**The G – Band**

The G band can be used to determine the structural changes in the nanotubes or graphene due to any strain or stretch. This band is extremely sensitive to modification in the tubes caused by interaction with different substrates, strain by forces, and change in nanotube side wall curvature, as these effects tend to change the bond length and
angles between the atoms. In SWCNTs curvature effects can be used to extract the information about tube diameter as it give rise to multiple peaks in the G band. However strain dependent G band is rich but still debatable. [251, 252]

**Radial Breathing Mode (RBM)**

The RBM is particularly essential in two ways:

1. To determine the nanotube diameter ($d_t$)
2. Relation between RBM frequency ($\omega_{RBM}$) and optical transition for a given nanotube

Nanotube diameter is dependent on frequency of radial breathing mode and experimental Raman data can be fit using the following equation:

$$\omega_{RBM} = \frac{A}{d_t} + B$$  \hspace{1cm} 4.2

**Disorder Induced Band (D-band)**

D band in Raman spectra reveals information about presence of disorder in the material. It can characterize disorder in many forms of the carbon such as nanotubes, nanotube fibres, amorphous carbon, diamond like carbon etc. In Graphene single layer the intensity ratio of D and G band can be used to quantify the disorder in the sheet. This ratio can also distinguish zigzag edge arrangements in contrast to the armchair by analysing the orientation of the carbon hexagons to define the crystallographic orientation of these edges. The armchair and zigzag structure can be distinguished by the presence or absence of the D-band respectively. [253]
Chapter 5  Self-assembled Colloidal Photonic Crystals: Fabrication and Results

In this chapter we will study the fabrication process of colloidal photonic crystals which are made by sedimentation method and grown along [111] crystallographic direction. Post-fabrication, the structural analysis will be presented by employing the means of scanning electron microscope and atomic force microscopy to probe the present defects in the system and to determine the interparticle distances between the latex spheres. This chapter introduces the theoretical approach exploited in this work to study the optical properties of photonic crystals (PhCs). The first section is devoted to the description of the crystallographic structure of photonic crystals. Subsequently an overview of both Transfer matrix method (TMM) and finite difference time domain (FDTD) methods is given. These techniques are used to derive the photonic band structure and the optical properties such as reflectance and transmittance. All results for reflection and transmission at normal incidence are presented: the calculated spectra will be compared with experimental measurements. The periodic modulation of the refractive index between particles and the air makes certain frequency bands are prohibited, giving rise to photonic gaps. Prohibit frequency range will depend on the opal lattice parameter, allowing us by suitable choice of particle size, tuning the photonic gap. In this chapter we will focus on the optical characterization of photonic crystals, constituted by latex polymer particles sizes of between 0.255 and 0.345 microns. This chapter also introduce the effect of disorder present in the system onto the optical properties of the crystals by measuring total intensity of light using diffuse reflectance measurement, which will be carried out using integrating sphere. Finally, this chapter is closed by detailed experimental optical study such as transmission and reflection studies of photonic crystals and setups that were used for characterization. Optical characterization of P-PhC discussed in this chapter, will be used in all other chapters in a common base.
5.1 Pristine Photonic Crystal (P-PhC)

P-PhC are closed packed structures of mono-dispersed latex spheres ranging in size from 100 to 1000 nm packed in a FCC or HCP Bravais lattices, which results in three dimensional periodic structures of the order of visible wavelengths, exhibiting bright colours. These periodic structures has a specific forbidden band of frequencies which is not allowed to propagate in the structure of any angle and polarization and is called a complete photonic bandgap, however generally 3-D dimensional PhC do not possess full photonic bandgap due to low index contrast and is called as pseudogap.[17, 254]

5.1.1 Important Parameters for Photonic Crystals

While working on photonic crystal there are some important parameters that must be taken into account when understanding the optical properties.

- Lattice parameter: The separation distance between the atoms. Pseudogap spectra are directly proportional to this parameter, usually denoted by (a).
- Filling fraction: Volume of a structure that is occupied by, or available to a specific constituent.
- Effective refractive index: The effective refractive index of a bulk material, sum of all the constituent refractive indices. It is denoted by (n<sub>eff</sub>).
- Refractive index contrast: Scattering strength of a photonic crystal is described by Refractive index contrast. It can be calculated by ratio of high and low dielectric constant of the material generally denoted by (δ).

5.1.2 Photonic Crystal: FCC Sphere Arrangement

A photonic crystal is usually made of dielectric spheres, which are arranged in FCC manner. Generally the (111) planes grow parallel to the substrate and can be visualized as stacking of (111) layers and every layer is perpendicular to the (111) growth direction, which is a triangular lattice. The periodicity can be calculated, which is equal to sphere diameter i.e. d = a/√2, where a is the FCC lattice constant. It forms the ABC, ABC sequence and has been shown in the following Figure: 5.1. The figure shows a top view of three (111) planes and each later is shifted along the y direction. It is shifted by the value of d/√3 in comparison to the previous layer. Photonic crystals grown and studied in this dissertation are oriented along the (111) direction. The distance d₁₁₁ between two consecutive layers is smaller than the sphere diameter and can be
calculated by $d_{111} = \sqrt{2/3}D = a/\sqrt{3}$ where $D$ is the sphere diameter and $a$ is the lattice constant.

Figure: 5.1 Close-packed fcc lattice schematic redrawn from [255].

### 5.2 Fabrication Procedure

To grow perfect three-dimensional photonic crystals is a challenge. In a typical specimen, the volume fraction occupied by spheres is $\sim 74\%$, and the rest of the volume is occupied by air.[17] Three dimensional photonic crystals are generally made of silica ($\text{SiO}_2$) or polystyrene spheres, with a typical refractive index of $\sim 1.5$. Photonic crystals operating in the visible range require spheres size in the range of hundreds of nanometres. Owing to the low refractive index ($\sim 1.5$) these materials cannot possess a complete photonic bandgap. To grow photonic crystals, the gravitational sedimentation approach was utilized in this study. This chapter will describe the properties of P-PhC for two different polymer sphere sizes 255 and 290 nm respectively.

Latex polymer of 255 nm sphere size was blended with TritonX-100 (0.01wt %) surfactant for the comparative study between P-PhC and infiltrated PhC. The surfactant concentration was kept 0.5 mg/ml for fabrication of photonic crystal with 255nm latex, due to the fact that as received graphene dispersions were stabilized in same amount of surfactant, which will be discussed in next chapter.

Latex polymer of 290 nm sphere size was blended with 1weight % (10 mg/ml) of Triton X-100 surfactant as fabrication of nanotubes infiltrated photonic crystals will made by using this latex polymer and stable nanotube dispersions were obtained at this
surfactant concentration, which is optimized concentration and has already been reported by many authors.[244, 256, 257]

Colloidal dispersions were prepared using latex polymer with Triton-x100 in glass vial of ~20 ml volume. This dispersion was then subjected to magnetic stirring for better mixing of surfactant molecules with the latex polymer. To fabricate a photonic crystal, typically 2.5 mL of dispersion was transferred to a smaller glass vial (~12 ml volume) and kept for natural sedimentation at room temperature (RT 22°C) with an open lid to induce the self-assembly of the particles combined with drying of the suspension from above. After ~2 weeks, a ~1 mm thick bright, green colloidal crystal was obtained in the glass vial. Later, carefully, the glass vial was broken to remove the crystal from it. The crystals were formed under a relative humidity of ~65% via gravitational force and capillary forces between the particles. As a result, the particles go through sedimentation and self-assemble into an ordered structure. Figure: 5.2 (a) shows the schematic of fabrication process under sedimentation, whereas in figure (b) latex polymer in the glass vial has been shown. The glass vial shows three different phases, water, suspension, and sediment. Once the water evaporated, a thick crystal has been obtained in the bottle, which can be observed in figure (c). The thickness of the crystal was ~1 mm. Pristine photonic crystal made with both polymer diameters were similar in appearance, so images shown below are for only for 290 nm diameter photonic crystal.
Figure: 5.2 (a) Schematic shows P-PhC fabrication process. (b) latex polymer dispersion under sedimentation. (c) Represent optical images of pristine photonic crystal (whitish and opaque crystal), normal and tilted at angle of ~ 10°.

The sedimentation process can be described by Stokes law [258] and given by the equation (2.8) as discussed in the literature review chapter. The table given below shows calculations of sedimentation velocity to estimate the average sedimentation time of crystals, which is ~ 2 weeks for both the sphere sizes. The suspension height was ~2.5 mm.

Table 5.1 estimated sedimentation time for two different size photonic crystals

<table>
<thead>
<tr>
<th></th>
<th>255 nm</th>
<th>290 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ_{sphere} [gm/cm³]</td>
<td>1.18</td>
<td>1.18</td>
</tr>
<tr>
<td>D_{sphere} [nm]</td>
<td>255</td>
<td>290</td>
</tr>
<tr>
<td>V_{sed} [mm/hr]</td>
<td>0.00296</td>
<td>0.00297</td>
</tr>
<tr>
<td>T_{sed} [weeks]</td>
<td>~ 2 weeks</td>
<td>~ 2 weeks</td>
</tr>
</tbody>
</table>

5.2.1 Structural Analysis: Investigation on the Formation of Micro-Structural Domains and Cracks

Photonic crystals show iridescence under incident white light, whereas it looks opaque in transmission. This iridescence arises from combination of diffraction and scattering that is generated by defects, which is responsible for a milky or opaque appearance. The less the defects, the brighter the iridescence will be from the photonic crystals. Mainly, reflected colours depend upon the particle size and observing angle and the colour changes with the viewing angle. Regardless of their fabrication process and controlled parameters, photonic crystals tend to form different domains (packed, segregated volumes), which have different brightness at different positions under the microscope. These domains are oriented slightly differently with respect to the incident light, and so can be seen to show slight differences in their reflectance. During the growth in photonic crystals, domain formation leads to macroscopic-size cracks. Generally, cracks originate in a random fashion, at various sites and are misaligned. Large cracks developed due to originated stress in the lattice during shrinkage of the polymer spheres in the drying process. These domains and cracks can be counted as disturbed portions in the system which can alter the optical properties of the photonic crystals. These defects can create new photonic states, which in turn leads to incoherent scattering of light. However, cracks formation cannot be fully avoided and - they allow
incident light to penetrate, which can reduce the height of the measured spectra. Domains and cracks have been observed and reported for almost every fabrication procedure. However, separation between cracks can be controlled by the thickness and their preparation method.[94] A table given below shows the average domain size for different fabrication methods.[19]

Table 5.2 literature survey of domain size formation via different fabrication process

<table>
<thead>
<tr>
<th>Photonic crystal Fabrication Method</th>
<th>Domain Size (μm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Sedimentation Process</td>
<td>(100-250)²</td>
</tr>
<tr>
<td>Horizontal Deposition Method</td>
<td>(25-50)², (100-170)²</td>
</tr>
<tr>
<td>Vertical deposition Method</td>
<td>(10-100)², (50-150)²</td>
</tr>
<tr>
<td>Cell confinement method</td>
<td>(100)²</td>
</tr>
<tr>
<td>Capillary Deposition method</td>
<td>(50-500)²</td>
</tr>
</tbody>
</table>

There are two different models to understand crack formation: elasticity and the capillary pressure model. The first models explains it in terms of volume shrinkage, which creates mechanical stress during the drying of the crystal; whereas the second model is based on the pressure difference between wet and dry areas in the film.[259, 260] This study uses the sedimentation process to make photonic crystals and is also not free from cracks and domains. To quantify the average sizes of these domains, optical and electron microscopy at lower resolution has been employed.

We measured the domain dimensions formed in our P-PhC for both particle diameter crystals and due to similar findings; results are shown only for 290 nm diameter crystal in Figure: 5.3. Figure (a) shows the SEM image of the photonic crystal surface captured at lower resolution ~ 70x. Image shows various domains have develops with distinct boundaries among them. Figure (b) and (c) shows the statistical analysis on the length and width size of domains respectively. The observed average length of a domain was ~ 127±4 μm and width ~ 91±3 μm. Larger domains are favourable with controlled thickness, as they decreases the number of grain boundaries, which contribute to increase in the extinction of light due to scattering.[94] Increasing the photonic crystals thickness will increase lateral domain sizes, therefore, the scattering from grain boundaries will be decreased for thick, in contrast to thin, crystals.
Figure: 5.3. SEM micrograph shows surface picture of photonic crystal surface. Micrograph shows single-crystal domains that are separated by boundaries or cracks. Arrows indicates the domains widths and lengths. The average domain length $\langle L \rangle$ for this picture is $\sim 127 \pm 4 \ \mu m$ and width $\sim 91 \pm 3 \ \mu m$.

5.2.2 Morphological Studies: Pristine Photonic Crystal (290 nm)

5.2.2.1 Scanning Electron Microscopy Analysis

Self-assembly of colloidal structure has pulled in a lot of consideration from both theoretical and experimental communities. Numerous hypothetical studies have been performed keeping in mind the end goal to find out which of the possible phases, fcc, hcp, combination of these, and random stacking are favourable for closed packed structure formation. Woodcock et al theoretically suggested fcc arrangement is the most stable one, and Pusey et al experimentally shows same arrangement of PMMA spheres.[78, 83]

SEM is used to study P-PhC and long range ordering of FCC packing was observed. Details on structure hierarchy of the photonic crystal made by 290 nm diameter were studied by utilizing Field enhanced Scanning Electron Microscope (FESEM). SEM images were obtained by Hitachi S4000, JSM-7100F operating at 3keV. A broken piece
of photonic crystals was then fixed to a metal holder and was sputter coated with gold of thickness ~ 1nm (to avoid charging from the sample) using an Emitach K575X. SEM images were taken from cross-sectional view of photonic crystals by cleaving one side of it from the central portion of the crystals. This is due to nonhomogeneous thickness of the crystal. The crystal is thicker (~2 mm) at the edge in contrast to center due to changes in the suspension concentration and meniscus during crystallization or drying. This cleaved edge offers the opportunity to observe well-ordered lattice planes in the crystal. Figure: 5.4 shows SEM images at different resolution and spot of P-PhC, which shows clearly the well-ordered polymer latex spheres corresponding to the (111) plane of a FCC lattice. To separate between the diverse phases, it is key to study the internal ordering through characterization of different facets, which can be obtained by cleavage of the sample. Figure: 5.4 reveals SEM images and shows typical FCC planes. Image (b) and (d) and (e) correspond to a (111) plane of an FCC structure, oriented in different directions, while Image (a) presents different lattice arrangements and also shows the interface where different lattice ordering took place. This figure (a) also shows an example of a (110) type surface. This type of a rectangular lattice of sphere ordering or arrangement in the particles is due to spheres arrayed at different distances. This type of ordering also exists in HCP structure. SEM result gives clear evidence that mostly latex spheres in pristine photonic crystals are arranged in an FCC manner through sedimentation.

Figure: 5.4 SEM micrograph of a cleaved edge of a pristine photonic crystals made of a 290 nm diameter sphere. Images indicate long range ordering is observed in lateral surfaces.
5.2.2.2 Atomic Force Microscopy Analysis

This section will describe surface examination of pristine photonic crystal (290 nm) by atomic force microscopy. AFM offers high resolution three dimensional images of the photonic crystal surface. The advantage of using AFM is as there is no pre-treatment required to the specimen and it is a non-destructive approach. Figure: 5.5 (a) shows the AFM topographic surface image of the crystal. It shows a close packed structure with hexagonal ordering. A careful observation shows vacancy defects present in the crystal. Vacancy changes the co-ordination of spheres around the defect; they also create lattice distortions in the crystals. A micron size crack is also visible, formed during crystal growth and hampers the homogenous growth of the crystal, which creates different lattice orientation and ordering in the crystals. The most common planes are (111), (100) and (110), - especially in the valley portion of the crack they can be readily seen. Inset of the figures shows Fast Fourier transform analysis on hexagonal portion of the image, revealing long range ordering of the spheres. Figure (b) shows the line scan profile of the crystal and suggests interparticle distance is ~ 270 nm. Figure (c) shows the zoomed in clear image of a vacancy defect, where the center sphere is missing creating distortion.

The morphological analysis on P-PhC with diameter 255 nm has shown similar results so they haven’t been included here.

Figure: 5.5 (a) shows AFM analysis of the surface of the pristine photonic crystal (290 nm). (a) depicts well fcc ordered packing of the spheres with cracks and defects. The inset in figure (a) corresponds to Fast Fourier transform (FFT) analysis representing the long range ordering in the photonic crystal. Figure (b) represents line scan profile of crystal, to measure interparticle distance. Figure(c) shows vacancy defect in ordered crystal.
5.3 Optical Characterization: Photonic Crystals

Interference of light in the photonic crystal is the fundamental mechanism of Bragg Diffraction of light.[16, 261, 262] Bragg reflection of electromagnetic radiation was first studied for X-rays that are diffracted by crystals planes and later for optical waves diffracted in layered mediums and gratings. A set of crystal planes acts like a mirror if the Bragg condition:

\[ m\lambda_{\text{Bragg}} = 2dsin\theta \]  \hspace{1cm} (5.1)

is met, where d is the distance between the lattice planes. Figure: 5.6 (b) illustrates the diffraction geometry. When the path difference of light of these reflected waves is equal to an integer number of wavelengths, n, the waves constructively interfere and the wave with that certain wavelength is amplified. This reflection, which depends on the wavelength, causes the distinct optical appearance of photonic crystals, which is often referred to as iridescence or opalescence.

![Figure: 5.6 (a) Snell’s law (b) Bragg’s law.](image)

Due to refraction in photonic crystals i.e. reduced angle with respect to the normal, it is required to take Snell’s law into account. This law of refraction as shown in figure (a)

\[ n_1sin\theta = n_2sin\phi \]  \hspace{1cm} (5.2)
where \( n_1 \) and \( n_2 \) are the refractive index of the incoming wave medium (air) and material respectively. In our case \( n_1 < n_2 \), \( \Theta \) is the angle between the incoming wave and the surface normal whereas \( \Phi \) is angle between higher index material and the normal.

As per schematic (b) the Bragg equation becomes:

\[
m\lambda_2 = 2d\cos\Phi
\]

5.3

On combining Bragg’s and Snell’s law:

\[
\frac{\lambda_{Bragg}}{\lambda_2} = \frac{\sin\theta}{\sin\Phi} = \frac{n_{eff}}{n_{air}}
\]

5.4

\[
m\lambda_{Bragg} = 2d_{hkl}n_{eff}\cos\Phi
\]

5.5

Whereas Snell’s law yield the relationship:

\[
\sin\Phi = \frac{1}{n_{eff}} \sin\theta
\]

5.6

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

5.7

After rearranging the modified Bragg’s equation:

\[
\lambda_{Bragg} = \frac{2d_{hkl}}{m} \sqrt{n_{eff}^2 - \sin^2\theta}
\]

5.8

The \( n_{eff} \) is the effective refractive index of the system. It can be determine by various approaches, one of them is the effective medium approach:

\[
n_{eff}^2 = \sum n_i^2 \Phi_i
\]

5.9

Where \( n_i \) and \( \Phi_i \) are the refractive index and the volume fraction of each portion, respectively.
Alternatively, $n_{ef}$ can also be extracted by the Maxwell Garnett approach [263]:

$$n = n_{med} \frac{2n_{med}^2 + n_{sph}^2 + 2\phi(n_{sph}^2 - n_{med}^2)}{\sqrt{2n_{med}^2 + n_{sph}^2 - \phi(n_{sph}^2 - n_{med}^2)}}$$  \hspace{1cm} (5.10)

Where $n_{med}$ and $n_{sph}$ is the refractive index of surrounding medium and polymer spheres. $\Phi$ is the volume fraction of polymer spheres.

The inter-planer spacing $d_{111}$ can be calculated using:

$$d_{111} = \frac{a}{\sqrt{3}}$$  \hspace{1cm} (5.11)

Where

$$a = \frac{2D}{\sqrt{2}}$$  \hspace{1cm} (5.12)

where $D$ is center to center distance between the polymer particles or spheres and $a$ is lattice constant. The Bragg diffraction causes the well-known iridescence of 3D photonic crystals. Changing the angle of incidence, we simply change the wavelength of the reflected radiation. Natural examples of colours due to interference occur in minerals, insects, birds, gemstone opal, mother of pearl, butterfly wings, feathers of peacocks and hummingbirds etc. [264]

**5.3.1 Visualization of Band structure and First Brillouin Zone in 3D Photonic Crystals**

The bandstructure diagram of photonic crystals allows us to calculate the optical characteristics of the entire photonic crystal due to the periodicity. Brillouin zone a characteristic feature is used to characterize the solutions for the wave propagating in the photonic crystal in reciprocal space and defines the areas and boundaries that affect the movement of a propagating wave. In Brillouin zone defining the critical points is correspond to plot the frequencies allowed in each direction and the band structure of the crystal. Figure: 5.7 (a) shows the 3 dimensional close packed structure and a cubic lattice is represented by a red box. Figure (b) represents the first Brillouin zone of the fcc with high symmetry points: the point L corresponds to the (111), the point X to the
address (100) and the point K (110). The angle of incidence with respect the Γ-L direction, θ, is the experimental parameter to perform spectroscopy. Given the way in which the samples grow, varying the θ sweeps different high symmetry points of the Brillouin zone from point L to the U, W and K points, as shown in the figure. Photonic crystals fabricated and studied in this dissertation are grown in the (111) direction, which corresponds to Γ-L direction in reciprocal notation. It is observed in the figure that any deviation from the symmetry point L will correspond to moving away from (111) direction.

Figure (c) shows the band structure of silicon (n=3.5) [265] where k is plotted on the x axis which is the modulus of the wave vector and describes an address within the crystal, whereas the y axis represents the energy in reduced frequency ωa/2πc, where a is the lattice parameter of the fcc lattice (a = √2d) and frequency ω, c is the speed of light in vacuum. Various bands represent the allowed states for photons inside the photonic crystal. Photonic band structure shows directions determined by high symmetry points, which observed on the edges of gaps as open photonic gap. The photons, whose energy is located within one of these gaps will not able to propagate in certain directions in the crystal. For example, a gap opens at the point L between the first and second bands, and is responsible for the observed strongly attenuated peak obtained at normal incidence transmission (θ = 0°) with respect to the planes (111). The wave vector of the incident radiation is located, then, in the Γ-L direction. When for a specific frequency, the wave vector reaches the edge zone (point L), there opens a range of energies for which photonic density of states is zero, whereby the incident radiation cannot propagate through the material and is reflected. This occurs for a value of the vector incident wave, k_i that satisfies:

\[
\overline{k_i} = \frac{G_{111}}{2} = \frac{2\pi n_{av}}{\lambda}
\]

k_i being the incident wave vector, whose modulus is \(k_i = 2\pi n_{av}/\lambda\), where \(n_{av}\) is the average refractive index of the photonic crystal and \(G_{111}\) vector is reciprocal lattice of module \(G_{(111)} = 2\pi/d_{(111)}\). The above equation allows one to calculate the center frequency position of the pseudogap under normal incidence.
Figure: 5.7 (a) A 3D close packed opal structure with a cubic lattice is represented by a red box. (b) Wigner-Seitz cell of the fcc lattice with two different wave vectors shown in red and blue lines. (c) Photonic band diagram of the silicon (n =3.5). The pseudogap along [111] direction (Γ-L) is represented in a red colour. Reprinted with permission from [265].

5.3.2 Simulated Reflectance Spectrum in Photonic crystals: Transfer Matrix Method

From the beginning, photonic crystals have been using reflectance and transmittance spectroscopy to characterize the forbidden frequency or psuedogap in the photonic crystals. Experimentally, the spectral position of the pseudogap has been calculated by using the modified Bragg equation, taking refraction into account, which in turn gives the lattice parameter, sphere size, total effective refractive index, deformation etc. There are various numerical approaches to analyse the multilayer system such as Transfer Matrix Method, Plane Wave Method, and Finite Difference Time Domain.[266-269]. We have used Transfer Matrix Method (TMM) for simulation of reflectivity and transmission. Flexibility of manipulating layer and the refractive index of each layer makes TMM most suitable for simulating structures formed by different periodic multi-layers stacked together. Theoretically, reflection and transmission spectrum of periodic structures can be simulated by transfer matrix method (TMM).[268-270] TMM is assumed to be periodic in x-y planes, whereas along the z direction, which is propagation of incident light it assumed finite thickness. In TMM, at the interface of two different materials and the filed corresponding to incident, reflected and transmitted light are arranged in such manner that left and right side boundary can be related by matric manipulation and the metrics called is transfer matrix. The matrix
transfer the field value from one plane to corresponding filed in next plane. The multiplication of all transfer matrices at each interface in z direction gives total response of the structure. The derivation of TMM is straightforward and details can be found in literature. Four our study, we refer a recent study based on standard matrix formalism reported by Daniel Bloch et al group.[271-273] This standard matrix formalism for a stratified medium made of successive parallel layers has been used to calculate the reflection and transmission coefficients. It considers incident light irradiation defined by its electric field with a frequency \( \omega \) in the region of index \( n \), incident under an angle \( \theta \) on a medium composed of \( N \) finite parallel layers and ended by a region of index \( N + 1 \). This formalism allows going from one layer to another layer with limiting boundary conditions and takes into account propagation in each layer, for the forward and backward component resulting from successive transmission and reflection and propagate under an angle which satisfies the Snell’s law of refraction at the successive interfaces. The detailed matrix formalism is given in the appendix A1. It also assumed that the photonic crystal crystals have a face-centered cubic structure, so that a simple periodic dielectric layers could be implemented. To calculate reflectance spectrum, the crystals was assumed to perfect and defect free. We then, calculated reflectance spectrum for different number of layers assuming sphere parameters (diameter - 255 nm, refractive index – 1.49) and water as the surrounding medium with refractive index of 1.33.

In the Figure: 5.8 a comparison of the simulated reflection by TMM in [111] direction of photonic crystal with different number of layers [from 1 layer figure a) to 30 layers (figure (f))] is presented and is directly related to photonic bandgap in \( \Gamma - L \) direction. It is evident from the figure (g) and (h) that the Bragg peak increases in intensity and its full width half maximum decreases with increasing number of layers. The period of Fabry-Perot oscillations, also decreases with number of layers. It can be seen from the figure calculated reflectivity approaches the theoretically expected value of 100% for \( \approx 20 \) layers and above this thickness \( \sim 99\% \) of light will be reflected in the vicinity of photonic band gap frequency range. The width of photonic bandgap is characterised by full width half maximum and narrowing of photonic band gap peak was observed with increasing number of layers. For the thickness of layers above \( \approx 20 \) monolayers the difference to crystals with infinite number of layers is negligible.
Figure: 5.8 (a) to (f) the evolution of reflectance spectrum in [111] direction with increasing number of layers for a bare photonic crystals. (g) Peak position and FWHM variation (h) vs number of layers in photonic crystals.
Theoretical presumptions are based on perfect and infinite periodic lattices, whereas real photonic crystals are not free from defect and are finite in size. It is interesting to see comparison of theoretically predicted reflectance/transmission by using TMM vs experimentally measured spectrum.

5.3.3 Reflectance and Transmission Studies on Pristine Photonic Crystal: Experimental and Simulation Results

Figure: 5.9 (a) and (b) shows the simulated and experimentally measured diffuse reflection and transmission spectrum of photonic crystals made of 290 nm diameter. The reflectance spectrum simulated by TMM was assumed to be ~ 20 layers in thickness, whereas fabricated photonic crystal is ~ 1mm (~3500 layers). The spectral region where pseudogap lies is ~ 500 – 700 nm with the central frequency located ~585 nm. It is evident from the figure that in terms of peak position our experimentally measured reflection/transmission spectrum is in excellent agreement. In the absence any material absorption or disorder, reflection and transmission spectra should provide the same information, i.e. the light which is has not been reflected is transmitted. In the vicinity of the pseudogap there is high reflectance and low transmittance. There are couple of important features that can be observed and calculated from the spectrum including; - center of the peak, called the called Bragg resonance peak, is the center frequency of the pseudogap \( \lambda_B \), peak height, and Full width half maximum of the peak. Using these parameters relative bandwidth \( \Delta\lambda/\lambda_B \) can be measured for comparative studies of different photonic crystals. Using equation 5.8 and these parameters, interparticle spacing and effective refractive index can also be calculated. As described in the morphological section, these crystals are not free from disorder. Disorder or imperfection in the crystal can hamper optical properties of the crystals as propagating light will be scattered, and attenuated. In results it reduces peak intensity, generates an asymmetric profile, and can induce broadening of the features. It is also evident from the figure that there is no Fabry-Perot oscillations observed and it is due to extinction by scattering in thick photonic crystal. The FWHM is also significantly reduced for such a large thickness photonic crystal compare to 20 layer thick crystal.
Figure: 5.9 (a) simulated reflectance and transmission spectra for 5 layers and (b) experimentally measured reflectance and transmission spectra measurement of pristine photonic crystal made of 290 sphere diameter at normal incidence on the (111) planes or in reciprocal space in Γ-L direction.

Here we will present analysis of L pseudogap with respect to (111) planes for pristine photonic crystals made of 255 nm diameter of spheres. The spectroscopy will be carried out along the Γ-L direction in reciprocal space, which is normal incidence to (111) planes.

### 5.3.4 Pristine Photonic Crystal (D = 255 nm): Propagation in Γ-L Direction

At low frequencies $a/\lambda < 1$, the pseudogap in photonic crystals will arise along various crystallographic planes or directions, where $a$ is the lattice parameter and $\lambda$ is the wavelength of light in a vacuum. Here we demonstrate pseudogap formation along the Γ-L highest-symmetry point, which corresponds to crystallographic orientations (111). In Figure: 5.10 we compare the theoretically calculated bandstructure along Γ-L point and reflection spectra by using Finite-difference time-domain (FDTD) numerical analysis technique, which has been performed by our collaborator Florescu group et al. in Surrey university. Crystal was assumed of a 100-layers thick of made by 255 nm sphere size and reflection spectra was calculated along Γ-L symmetry point. The experimental reflection spectra were measured using a Diffuse Reflectance accessory (DRA) and background has been subtracted for clarity. The FDTD simulated reflection spectra is shown in figure (a) with peak position ~505nm, and figure (b) represent the simulated pseudogap in the bandstructure originates along the Γ -L direction. The bandstructure in this spectral region is linear in behaviour and will be divided at the
edges of the Brillouin zone due to Bragg diffraction from (111) planes. Figure (c) shows experimentally measured reflection spectrum having peak position at ~ 505 nm and is in excellent agreement between simulated spectrums at point L. In figure (a) simulated reflection spectrum shows secondary oscillations outside the psuedogap. These oscillations are Fabry–Perot resonances (FPR), which are due to interference of light reflected at both interfaces of the specimens. [274] These oscillations are decreased as film thickness increases and with increasing disorder in the sample. The simulated spectra doesn’t take into account any disorder so FPR are visible, whereas they are absent in experimental reflection spectrum due to the large thickness and defects.

Figure: 5.10 Reflectance spectrum of a sample of 255 nm in diameter (panel right) compared to the band structure in the Γ -L direction. The agreement between theories (left panel) an experiment is very good for the First pseudogap.

5.3.5 Tuning the Pseudogap by varying the Lattice Constant

The psuedogap position scales remarkably well with the size of the sphere. In addition to the effective refractive index parameter in Bragg’s law, sphere diameter tuning offers the possibility to tune the psuedogap in the spectrum. Four different photonic crystals were fabricated with different sphere size to verify it. Figure: 5.11 show the transmission spectra for photonic crystals made from different sizes of latex polymer. It is observed that the psuedogap peak position shifts towards longer wavelengths, obeying Bragg’s law. Photonic band gap spectral position scales extremely well with the size of the latex sphere, demonstrating it is an intrinsic signature of the stacking structure.

The graph has been plotted with an offset for the sake of clarity. Graph (b) shows the linear regression analysis on peak position as function of interparticle spacing with
change in diameter. The position of the diffraction peaks of the sphere prepared from 262 nm spheres deviates from the position, which may be due to dispersion of the refractive index. The scaling law applies for systems retaining the same refractive index. Dispersion of the refractive index makes this is not valid. However, the change in refractive index is small and doesn’t affect the linear relationship. The calculated refractive index by linear regression is ~1.44.

Figure: 5.11 (a) shows measured psuedogap position as a function of varying latex particle diameter in photonic crystals normal to the (111) plane. (b) Shows Bragg’s law fit to peak positions with different diameter of sphere.

5.3.6 Angular Dispersion Spectroscopy of Photonic Crystals

The psuedogap position is strongly dependent upon the propagation of incident waves in relation to the axes of the photonic crystals. An incident wave can couple only those eigen modes of the photonic crystals which possess the same vector k. In this situation, changes in the psuedogap position with the angle of incidence are equivalent to probing different directions in the FCC BZ or scanning the BZ from L point towards different symmetry points such as W, U, K and edge of the BZ. If the photonic crystal is rotated around its growth direction the diffraction will takes place from the Γ, L, and U symmetry points in the Brillouin zone, where as it will be Γ, L, and W for rotation.
perpendicular to the growth direction. Herein, we employed the angle resolve transmission spectroscopy to study this behaviour and experimental dependence of the obtained pseudogap positions for higher angles, the spot size of the incident beam on the sample also increases and alters its shape from circular to elliptical. It can be ruled out for our discussions as our measurement were restricted to 25°, up to which, spot size doesn’t change significantly.

Figure: 5.12. (a) and (b) presents the angle dependent transmission spectra showing change in the pseudogap position as a function of increasing incident scanning angle for two different 255 and 290 nm diameter PhCs respectively. Both the figures have been plotted with offset in the y axis for the sake of clarity. As incident angle increases or moving away from the (111) direction, the pseudogap shifts its spectral position to higher energy and gradually becomes less pronounced which confirms most of the efficient Bragg reflections are originating from either all odd or even miller indices. For the photonic crystals with 290 nm diameter, there was an additional peak also observed ~ 20 degree, and moving towards longer wavelength on increasing the incident angle, which is attributed to simultaneous diffraction from other planes and can be understood by Laue diffraction.[275] The appearance of photonic band gap is due to Bragg diffraction of light, which occurs when the Laue conditions are satisfied: k’ = k + b(hkl), where k and k’ are the wave vectors of the incident and scattered light waves, and b(hkl) is the reciprocal lattice vector. If the Laue condition occurs simultaneously for two or more planes with different Miller indices, the photonic bandgap shows doublet in optical spectra due to multiple Bragg diffraction of light and has been reported by other studies in literature.[276, 277] The doublet in photonic bandgap peak can be decomposed into its components for 25 and 30 degree respectively by Gaussian fit and presented in appendix section. Bragg’s law doesn’t take into account any deformation in the calculation which alters the optical parameters. As polymer latex tends to deform with water evaporation, it is not an easy situation to calculate filling fraction of the lattice and thus it is hard to calculate n_eff and d(hkl). The inter-planer spacing and effective refractive index can be estimated by fitting the angular behaviour of the pseudogap positions using the modified Bragg’s law equation. In Bragg’s law equation, using n_eff and D as fitting parameters to adjust the theoretical expression on the values λ_B corresponding to center of the photonic band gap position in the transmission spectra. Figure (c) and (d) show the processed experimental psuedogap position of the stop band minima from the angular transmission spectra. The figure shows plots of peak

120
wavelengths of the (111) plane against various $\theta^o$ for both pristine photonic crystal with diameter 255 and 290 nm. The following equation has been used to fit the experimental data. Refraction in the photonic crystals has been taken into account:

$$\lambda^2_{hkl} = 4 d^2_{hkl} \left[ n^2_{\text{eff}} - \sin^2 \left( \arcsin \left( \frac{\sin \theta_{\text{int}}}{n_{\text{eff}}} \right) \right) \right]$$  \hspace{1cm} 5.14

Where

$$\theta_{\text{int}} = \sin^{-1} \left( \frac{\sin \theta_{\text{ext}}}{n_{\text{eff}}} \right)$$  \hspace{1cm} 5.15

is the internal angle and has been calculated using Snell’s law. The data clearly suggests a good fit and obeys the modified Bragg’s law. The fitted approximation for the photonic crystal made of 255 nm particles, gives the sphere diameter ~238 nm, and, effective refractive index of 1.29. This indicates that the structure has shrunk ~ 7% in the direction perpendicular to the sample surface, which corresponds to a reduction in interparticle distance ~ 15 nm. The comparison was carried out with respect to the latex polymer particle size measured by AFM. Literature suggests upto 26-34% of shrinkage has been observed for air - sphere photonic crystals.[278] This reduction is attributed to the shrinkage of latex polymer spheres during drying. The effective refractive index calculated by the effective medium approach and Maxwell Garnett approach gives $n_{\text{eff}}$ 1.448 and 1.447 respectively where water was taken into account as the medium. While Bragg’s fit gives $n_{\text{eff}}$ ~ 1.29, which is quite far from the other calculated ones, indicating the limitations of the Bragg one-dimensional model. The diameter calculation by the Bragg approximation is ~ 240 nm, which is in agreement with AFM results, giving the diameter ~ 240 nm and also with coherent small angle scattering (C-SAXS) experiments which gives diameter 239±2 nm. C-SAXS results will be presented in the next chapter.

Photonic crystals made of 290 nm spheres have a diameter ~250 nm in contrast to ~270 nm calculated by AFM and SEM methods. From AFM and SEM measurements the calculated shrinkage in the lattice is ~ 6.8%, which is close to the value of photonic crystals made of 255 nm. It shows around ~ 20 nm reduction in interparticle separation.
in contrast to the standard polymer diameter ~ 290 nm, provided by the manufactures. Bragg’s fit gives \( n_{\text{eff}} \sim 1.28 \).

Figure: 5.12 (a) and (b) shows angular dependence transmission spectra of two different 255 and 290 nm diameter of photonic crystals ranging from 0° to 25° at 5° interval. Figure (c) & (d) shows experimentally observed pseudogap peak positions for various incident angles for 255 and 290 nm diameter sphere photonic crystals. Dash lines are modified Bragg’s law fitting.

5.3.7 Effect of Disorder

All types of photonic crystals contain certain amounts of structural disorder, which tends to change the optical properties of the crystals. As we have already observed in the section of morphological study, there are different structural imperfections such as vacancies and distortions in the lattice. These defects generates scattering in the crystals and also large disoriented domains can lead to inhomogeneous broadening in the pseudogap spectrum. 3-D photonic crystals also undergo attenuation of the incident light, which in turn generates diffuse intensity. Here we have measured diffuse intensity in terms of reduced frequency. The latex polymer does not absorb in the region of interest so it can be calculated by measuring the total reflectance and transmittance. This means measuring the light, which is either not transmitted or reflected in the incident direction.

A quantitative comparison has been estimated and shown in the Figure: 5.13 for photonic crystals made of 290 nm diameter particles. Figure (a) shows the total
reflectance, (b) total transmittance and (c) shows the total intensity, which has been calculated by the sum of total reflection and transmission. Measurements were carried out using the Diffuse Reflectance accessory with 110 mm diameter (integrating sphere). To measure total transmission, the zero order incident light beam was blocked to estimate the contribution of the diffuse part. It has been shown by the schematic diagram in the respective figures.

There are number of things that can be observed from the figure. Figure (a) shows diffuse reflectance spectrum, very small background was observed outside the pseudogap frequencies and an enhancement in the frequencies, which are in the pseudogap. Figure (b) shows the total transmission which shows higher background and lower intensity in contrast to the reflection spectra. Figure (c) shows the total intensity of scattered light in the photonic crystals, determined by summing the reflection and transmission. Total scattered intensity shows a monotonic increase for the frequencies outside the pseudogap; whereas decreased intensity was observed in transmission intensity. An interesting feature was observed at the low frequency edge, where a sudden increase was observed (grey dashed line) and later a rapid decrease for frequencies within it. This can be explained by considering, how incident light propagates inside the crystal in this spectral range. [279-281]

As described earlier, disorder in the system makes light to scatter elastically, which will alter its propagation direction in the crystal, which means its wave vector will change by δk. Frequencies at the pseudogap edges, will be flattened and incident light will spend more time inside the crystals, which will increase the probability of scattering events. In results the enhancement in the diffuse intensity is expected. However for frequencies in the pseudogap light is attenuated exponentially, which will decrease the scattering events and will be less than the out of pseudogap or at its edges. So there will be small contribution of scattered light for frequencies close to the center of the pseudogap as penetration length of incident light will be smaller in this range. Observed asymmetry on the spectrum is due to different directions where scattered intensity will propagate, adjacent to incident direction in the bandstructure.[281]
Figure: 5.13 Total diffuse reflectance (a), transmittance (b) and their sum (c) for pristine photonic crystal, collected with an integrating sphere. Insets show the integrating sphere configuration used for different measurement.
5.4 Summary

In this chapter we have presented in depth study fabrication procedure of colloidal photonic crystals made of two different sphere diameters. Later, in depth optical spectroscopy and morphological property has been discussed.

The colloidal photonic crystals were made with sedimentation method and took time ~2 weeks and estimated sedimentation time based on Stokes law was also found to be ~ 2 weeks. Our photonic crystals show different iridescence at different spots due to presence of large domains. The large the dimension of domains, reduce the number of domains and in turn will give better optical properties. The estimated average domain length (L) for our colloidal photonic crystals is ~ 127±4 μm and width is ~ 91 ±3 μm, SEM studies shows different stacking orders, vacancy and orientation of planes and ordering was dominating by (111) planes and (100) planes. The center pseudogap frequency was observed ~ 505 and 585 nm for 255 and 290 nm sphere diameter respectively and is in agreement with theoretically simulated reflection calculated by FDTD and TMM approaches. TMM was used to simulate the reflection spectrum of the photonic crystals with varying number of layers which explain and establish the relationship between the peak reflectance and full width half maximum. The experimental angular dispersive optical data has been fitted by using modified Bragg’ law to calculate interparticle spacing and effective refractive index and is in excellent agreement with the theory. Tuning of pseudogap position has been achieved by changing the sphere size and shows linear behaviour and is in excellent agreement with Bragg’s law.
Chapter 6  Self-Assembled Photonic Crystals Infiltrated with Two Dimensional Nano-Platelets

In this paper, we present fabrication and analysis of infiltrated 3-dimensional photonic crystals using facile sedimentation method. These photonic crystals are made up of highly ordered colloidal polymer particles and infiltrated with 2-dimensional layered nanofillers such as graphene and boron nitride. This chapter introduce how the infiltration of a different refractive index material refractive drastically changes the optical properties of the base material.

The morphological studies of the base and nanofillers incorporated 3-D photonic crystals will be demonstrated to measure the interparticle separation and change in ordering if any, causing by these nanofillers infusion. The photonic bandgap study of the base crystal which is modified by the inclusion of graphene and boron nitride nanomaterial due to their different refractive index will be presented by using optical spectroscopy (transmission and reflection) and will be compared by simulated reflection spectrum by employing FDTD method. Effect of nanomaterial inclusion on progress towards a full band gap by measuring much wider angular range will be described. The small angle x-ray (C-SAXS) offers much better explanation in terms of measuring the ordering and interparticle separation ion colloidal crystals. In this chapter the interparticle separation measurement done by C-SAXS will be presented to compare with the resultant values of scanning electron microscopy and atomic force microscopy. In this chapter, brief results of mechanical properties of graphene incorporated photonic crystals will also be presented. In this chapter, I show how how different material owing different refractive index can tune the optical and mechanical properties of the whole system.

Tuning the optical properties of pristine photonic crystals opens up and extends the range of application for these materials. Fabrication of inverse opals offers larger index contrast compered to direct photonic crystals, infiltration is another way, in which one fills the interstitial sites in a photonic crystal with high refractive index materials. Minimum index contrast ~ 2.8 is the theoretically predicted value to achieve a complete photonic bandgap.[11] Luminescent emitters with large indices were the first materials,
to be incorporated into photonic crystals. This altered the density of states and therefore modified the emission spectra.[282-284] All these efforts were employed to localize and trap the light in all spatial directions and provide control over the complete inhibition of spontaneous emission, over a broad frequency range. There are also experimental reports of organic dye and quantum dot incorporation, however doping with these leads to broad emission spectra, which may overlap with the photonic bandgap.[285] Infiltrating with the size selected nanomaterials, with varying refractive indices can allow for tuning of the photonic bandgap of a crystal. Infiltration of photonic crystals can be achieved by generally by two different methods, chemical infiltration and physical infiltration. In our study we used the physical method (wet chemistry), as in this method infiltration of the material is done in the precursor solution. In principle, it can be presumed that the whole photonic crystal will be homogeneously infiltrated with the material.

To the best of our knowledge there are no reports of photonic crystals infiltrated with two dimensional nanoplatelets materials, such as Graphene (GR), Boron nitride (BN), or one dimensional nanotubes such as single walled carbon nanotubes (SWCNTs) into the PhCs. This chapter is divided into main segments; in first section infiltration with graphene will be discussed and in the second section infiltration with boron nitride will be discussed.

### 6.1 Self-Assembled Photonic Crystal Infiltrated with Graphene

#### 6.1.1 Fabrication of Photonic Crystals Infiltrated with Graphene

To fabricate graphene infiltrated photonic crystal, 0.01wt% of graphene has been used from the graphene dispersion. The graphene dispersion as discussed above in materials methods chapter was blended with latex polymer (particle size of 255 nm). The latex polymer-graphene dispersion was then tip sonicated in an ice-cold water bath with cold ice around for 10 minutes at a power level of 10 Watts using the discontinuous mode to ensure a better mixing. Graphene amount in weight percent was based on the postulation that all graphene is in solution and on the basis of the weight of the latex solids content. For the comparison, P-PhC sample containing the same amount of Triton–X 100 was also prepared.

In a typical procedure to fabricate a photonic crystal, the dispersion containing 0.01wt% (typically 2.5 mL) graphene was transferred to a glass vial and kept for natural sedimentation with the open lid at room temperature (RT 22°C) to induce the
self-assembly of the particles combined with drying of the suspension from above. After 14 days a ~1 mm thick bright green colloidal crystal was obtained in glass vial. Later carefully, the glass vial was broken to remove the crystals from it. As a result the particles go through the fan into sediment and self-assemble into an ordered structure. After 1 week, majority of water in the colloidal dispersion evaporated to leave well-ordered graphene based latex photonic crystals. The crystals were formed under a relative humidity of ~ 65 % via gravitational force and capillary forces between the particles.

Figure: 6.1 illustrates the fabrication process of making the photonic crystals and final product under the natural gravitational sedimentation process. Figure: 6.1 (a) shows three different dispersions in three different glass vials, (I), (II) and (III) are pristine dispersion, latex polymer blended with graphene and latex-graphene dispersion after 5 days of sedimentation respectively. In glass vial (III), three different phases were observed; firstly a suspension with uniform dispersion, second is a fan layer which forms due to the constant decrease in volume fraction of particles due to water evaporation and the third phase at the bottom of the glass vial is where formation of the photonic crystals has started and bright green iridescent colour was observed.

The crystal typically forms as a result of several processes, driven initially by the Brownian motion of particles, which eventually leads to the nucleation and growth of a majority FCC crystals with long range ordering. During the formation of the graphene incorporated photonic crystals, a sub-lattice of interconnected pores, filled with water and graphene, exists in the space between the deformed latex spheres. According to the Bragg equation, the wavelength of the reflected light depends on the observation angle. In the presence of only 0.01 wt. % of graphene within the lattice structure the crystal appears as an intense iridescent green [(Figure: 6.1 (c)], gradually changing to a dark blue [(Figure: 6.1 (d)] as the viewing angle (~ 20°) is modified under natural lightning conditions. Photonic crystals infiltrated with graphene reflect a more prominent green colour, which is present at all angles to the illumination.

When graphene is not present at the interstitial sites, the photonic crystal (PC) is milky white in colour with a slight tint of green Figure: 6.1 (b). Under visual appearance it is very apparent that photonic crystals with graphene have improved clarity compared to the pristine latex crystal. To estimate the periodicity of the infilled photonic crystals AFM has been employed. The piece of photonic crystal was fixed on a metal circular
disc with the help of double side tape and glutax to avoid any vibration generated by sample movement, as the specimen was not in a symmetrical shape. AFM images were scanned in the tapping mode from the cross-section area of the crystal. Figure (e) and (f) are AFM height images of the graphene incorporated photonic crystals. AFM shows well-defined fractured planes. AFM also indicates that the presence of graphene at interstitial sites does not affect the structural periodicity of the crystal.

Figure: 6.1. (a) Photonic crystal fabrication process is in three different glass vials named as (I), (II) and (III) are pristine dispersion, latex polymer with graphene and latex graphene after three days respectively. Figure (b) represent optical images of pristine photonic crystal (whitish and opaque crystal), and (c) with incorporated graphene photonic crystals at normal incidence and (d) tilted at angle of ~ 20°. Fig (e) and (f) represent AFM topographic images of graphene photonic crystal cross-section.

6.1.2 Effect of Graphene Incorporation on Pseudogap: Optical Spectroscopy

Infiltration of bare photonic crystals with other materials can alter the optical properties of the crystals by changing either the effective refractive index or the interparticle spacing, which largely depends upon the doping material properties. Graphene has a large refractive index materials (~ 2.65). [286] In the following section, we will determine how graphene changes the optical properties of the pristine crystal. To do this, transmission spectroscopy, a conventional approach to measure psuedogaps in photonic crystals was employed. Dimensions of our specimen were as follows – diameter ~ 20 mm, thickness ~ 1 mm.
Figure: 6.2 presents the theoretically simulated transmission spectra fig (a) of graphene infilled voids using FDTD approach calculated by Marian et al group and experimentally measured transmission spectra at normal incidence for pristine, (c) and graphene incorporated, photonic crystals (b) with unpolarised, white light. These spectra were recorded with the light incident normal to the sample surface (i.e. in the Γ→ L direction from the Γ to the L point of Brillouin zone of FCC lattice). It is evident from the figure that the characteristic psuedogap lies in the visible region due to Bragg diffraction in this region arising from (111) planes. Pristine photonic crystal shows a transmission dip ~505 nm, which is the pseudogap of this crystal; whereas pseudogap for the graphene incorporated photonic crystal is present ~520 nm. The -15 nm shift is due to either a change in the particle spacing, or the effective refractive index of the system. Atomic force microscopy data suggests the interparticle spacing for the pristine latex crystal (238±1 nm) and infiltrated crystal (239±2 nm) remains almost the same. In the material and methods chapter, TEM statistical analysis on the graphene dispersion suggests the majority of flakes are mono or bilayer. The thickness for graphene monolayer is 1 nm, suggesting graphene incorporation shouldn’t affect the interparticle separation significantly. If the interparticle spacing hasn’t changed then the shift in pseudogap position can only be attributed to changes in the effective refractive index ($n_{\text{eff}}$). The calculation of $n_{\text{eff}}$ is not easy as it requires estimation of the precise filling fraction of the materials and also the latex polymer undergoes structural deformation on drying, which changes the volume fraction of the system. Alternatively, it is possible to calculate $n_{\text{eff}}$ by fitting the angular dispersion behaviour of stop band positions, which will be discussed in the section. Both crystals do not exhibit a complete photonic band gap (PBG) due to the low index contrast and presence of lattice defects. The stop band position calculated by FDTD and experimentally measured are in excellent agreement, assuming graphene sheets size ~25 nm.
Infiltration in photonic crystals can significantly modify the optical properties of the photonic crystals, thus estimation of quantity plays an important role. Here we have estimated the filling fraction based on two different approaches; effective medium and Maxwell Garnett approximation.

### 6.1.3.1 Refractive Index based on Effective Medium Approximation

In effective medium approximation the effective refractive index can be described as a weighted sum of indices of refraction $n_1$, $n_2$, and $n_3$ for spheres, infiltrated material and air/water, respectively. For the pristine and infiltrated photonic crystals the effective refractive indices accordingly are:

$$ n_{\text{eff}} = n_1 0.74 + n_3 0.26 $$

And
\[ n_{\text{eff}2} = n_1 0.74 + n_2 f + n_3 (0.26 - f), \]  

where \( f \) is the filling factor for infiltrated material, whereas 0.74 and 0.26 are the filling factors for the spheres and water/air, respectively. Substitution of equation (7.1 and 7.2) in equation yields (6.8) Bragg wavelengths \( \lambda_1, \lambda_2 \) for pristine and infiltrated photonic crystal. The shift in the spectra due to infiltration can be estimated as

\[ \Delta \lambda = \lambda_2 - \lambda_1 = 2d_{hkl}(n_{\text{eff}2} - n_{\text{eff}1}) \]  

Substituting definitions (7.1 & 7.2) into (3) yields the relation for the filling factor

\[ f = \frac{\Delta \lambda}{2d_{hkl}} \cdot \frac{n_2 (\lambda_2) - (n_1(\lambda_2))0.74}{n_2(\lambda_2) - n_3} \]  

The calculated filling fraction of graphene in this case is \( \sim 1.5\% \)

### 6.1.3.2 Effective Refractive Index based on Maxwell-Garnett Approximation

Maxwell-Garnett approximation is another widely used method to estimate effective refractive indices. Effective refractive indices for the pristine and infiltrated opals can be determined as a weighted sum of the squared refractive indices

\[ n_{\text{eff}1}^2 = n_1^2 0.74 + n_3^2 0.26 \]  
\[ n_{\text{eff}2}^2 = n_2^2 f + n_3^2 (0.26 - f) \]

Substitution of definitions (7.7, 7.8) into (6.8) gives two squared wavelengths and corresponding to the pristine and infiltrated photonic crystal, respectively. The difference between them is

\[ \lambda_2^2 - \lambda_1^2 = (2d_{hkl})^2 (n_{\text{eff}2}^2 - n_{\text{eff}1}^2) \]

From (7.7) (7.8) and (7.9) the filling factor can be estimated as

\[ f = \frac{\lambda_2^2 - \lambda_1^2}{(2d_{hkl})^2 n_2^2 - n_3^2} \]
The calculated filling fraction of graphene by this approximation is ~ 1.6%

The comparison between effective medium and Maxwell Garnett approximation shows that both approaches can be used to quantify the infiltrated nanomaterials inside the photonic crystals.

6.1.4 Effect of Graphene on total Transmission

Graphene, only one atomic thick layer absorbs ~2.3 % of incident light in the visible region. [141] Graphene transparency depends upon the layers and decreases almost linearly up to 20 layers. [287] The graphene dispersion used for our study has the majority of mono and bi layers but also contains few multilayer graphene flakes. To determine, the effect of graphene on transmission, we have measured total transmission on pristine and graphene incorporated photonic crystals, and the results are presented in Figure: 6.3. Figure (a) is adopted from literature, which is measured on graphene layer deposited on substrate to give an idea of how the number of layers affects the transmission spectrum.[287] Figure (b) shows the overlay of the total transmission spectra of pristine and graphene photonic crystal. The graphene photonic crystal shows a significant decrease in transmission in contrast to pristine photonic crystal, which suggests that graphene presence, will decrease the transmission by absorbing the light.

Figure: 6.3 (a) Optical transmittance of CVD grown graphene as a function of the number of layers, adopted from [287] (b) shows total transmittance of pristine and graphene infiltrated photonic crystals exhibiting reduction in transmittance.
6.1.5 Effect of Incident Angle on Pseudogap Centre Frequency: Angular Dispersion Spectroscopic Analysis

The optical properties of a photonic crystal are strongly dependent upon the incident angle and axes of light. The pseudogap position will vary as the angle of incidence is varied, as varying the angle is equivalent to probing different planes in the crystal, which corresponds to different symmetry points in reciprocal space.[254] The reciprocal space describes how the incident light will see the material and also explains how propagation of light will be affected by its boundaries. This section describes the angle resolved transmission spectroscopy of both pristine and graphene infiltrated PhC and will determine the angular behaviour of pseudogap positions. The region of the sample probed was fixed at the center of the crystals in order to avoid the edges, where the crystal thickness is different due to meniscus shape.

The transmission measurements were carried out using a Cary 5G UV/vis-NIR spectrometer (Varian). Angular dependent spectroscopy (ADS) allows us to measure the change in stop band position as a function of angle. It was measured with the respect to photonic crystal growth direction. A rotating stage was positioned in the middle of the sample holder space of the spectrometer. The photonic crystal was positioned and fixed on top of the rotating stage at a distance of about ~10 cm from the incoming light entrance. The beam spot size was approximately $15 \times 3$ mm$^2$. The measurements were carried out by synchronizing both the spectrum measurement and the stage rotation. After every scanning measurement at a certain incident angle, the photonic crystal was rotated to the next planned angle. All peak positions and widths were determined by standard software (Origin).

Figure: 6.4 shows the transmission spectra for graphene incorporated photonic crystals as a function of scanning angle. The transmission spectra were acquired at $5^\circ$ intervals from the normal to the incident light beam, but for the sake of clarity only a few selected angles have been included. The pseudogap shifts substantially towards shorter wavelengths and broadens with increasing scanning angle. It is also observed that increasing the scanning angle means moving away from (111) planes, and the pseudogap becomes less pronounced. This agrees well with the fact that the most efficient Bragg resonance in FCC lattices is for planes with either all even or all odd miller indices.
Figure: 6.4 Angular dependence transmission spectra of graphene infiltrated photonic crystals ranging from 0 to 50° at 10° interval.

6.1.6 Optical Parameters Estimation

Optical properties of photonic crystals can be expressed by Bragg’s equation taking Snell’s law into account. The effective refractive index of the photonic crystals is often calculated by the volume-averaged refractive index of constituent materials. To calculate $n_{\text{eff}}$ and $d_{\text{hkl}}$, the filling fraction must be known very precisely. It is non-trivial to calculate the filling fraction for self-assembled photonic crystals as the lattice undergoes structural changes due to particle deformation and sintering during formation. The inter-planer spacing and effective refractive index can be determined by fitting the angular behaviour of pseudogap positions. Figure: 6.5 shows a plot of the peak wavelength of the (111) plane against various $\theta^\circ$ for pristine and graphene incorporated photonic crystals. The modified Bragg’s law, equation (5.14) discussed in the previous chapter, was used to fit the experimental data taking refraction into account.

The data clearly suggests a good fit to the modified Bragg’s law. Fitted parameters gives the sphere diameter as 235 nm, the effective refractive index as 1.27 for the pristine and 238.2 nm and 1.34 for the graphene incorporated photonic crystals respectively. Fitted results for pristine crystals estimate that the structure has shrunk ~7% in the direction perpendicular to the sample surface, which corresponds to a reduction in interparticle distance ~ 20 nm and also lowers the effective refractive
index. The comparison was carried out with respect to the latex polymer particle size as specified by the manufacturer. The reason of this reduction in interparticle spacing is due to the shrinkage of latex polymer spheres during drying.

The fitted interparticle spacing for graphene infilled crystal suggests ~ 6.58% shrinkage, which is also due to drying and shrinkage of the latex polymer. The increased $n_{\text{eff}}$ was expected compared to pristine crystals due to graphene higher index. Calculating Bragg’s peak using these parameters, gives the position of the pseudogap as ~ 520.91 nm, which matches well with our experimentally observed value ~520nm.

This indicates that the inclusion of graphene has barely any effect on the interparticle spacing, and that therefore the changes in the pseudogap position are due to the changes in the refractive index due to the contribution form graphene. As per the Bragg’s law, a higher the effective refractive index shift the pseudogap to longer wavelengths. There is ~15nm shift observed in the pseudogap for the graphene infiltrated crystal compared to the pristine, for normal incidence angle. Our experimental results agree well with Bragg’s theory.

Figure: 6.5 Observed experimental psuedogap peak positions for various incident angles for pristine and graphene incorporated photonic crystals. Solid lines show Bragg law fitting which agrees well with the theoretical prediction.

6.1.7 **Approach to Full Photonic Bandgap**

A full photonic bandgap is desirable because it allows complete control of the photonic states. Figure: 6.6 depicts the relation of photonic stop band width of $(\Delta \lambda / \lambda_B)$ (calculated from full width half maximum (FWHM) of the photonic bandgap peak)
with varying angle of incidence. It can be readily observe from the figure (a) that the FWHM is greater for the pristine photonic crystal compared to the graphene crystal. This is expected as a larger index contrast corresponds to greater bandwidth or FWHM, which is valid for our pristine crystal. A larger FWHM leads to a greater extent of overlap in the Bragg peak, which leads to a fractional increase in the space for light propagation. In addition, the forbidden light region/space can also be quantified by measuring the relative shift of the pseudogap with varying angle of incidence ($\lambda_{shift}/\Delta\lambda$) that determines the rate of approach to complete band gap ($\lambda_{shift}/\Delta\lambda<1$).[288] Figure: 6.6 (b) depicts that for both the photonic crystals the relative shift is less than 1 at all the scanning angles. When compared to graphene the relative shift for pristine photonic crystals is lower than graphene by up-to 30 degrees, which indicates a nondispersive pseudogap in pristine photonic crystals.

![Figure: 6.6 Angular dependence of (a) pseudogap FWHM and (b) relative stop band shift for both pristine and graphene infilled photonic crystal.](image)

To demonstrate further enhanced photonic behaviour in pristine photonic crystal, Figure: 6.7 shows the comparative pseudogap dispersion diagram near the L point of the fcc Brillouin zone and plotted based on the data in Figure: 6.6. The pseudogap in pristine photonic crystals is wider due to a larger index contrast in the pristine photonic crystal. Our results are consistent with other work published elsewhere. [288]
Figure: 6.7 Photonic pseudogap diagram from 0° to 30° in the vicinity of the L point of the fcc Brillouin zone.

We only see a superposition of our psuedogap from 3.7 – 25 degrees, Figure: 6.8(a) and (b), which again confirms that we only have a pseudogap rather than a full photonic bandgap.

![Graphene -PhC](image1)

![Pristine -PhC](image2)

Figure: 6.8 (a) and (b) Stop band position (dots) and FWHM (triangles) for the pristine and graphene infilled photonic crystals respectively in function of the refractive angle. Beyond 20° the superposition of stop band peaks disappears, representing no complete photonic band gap. The black straight line indicates the wavelength region in which the stop band would remain for complete photonic gap case.
Small Angle X-ray Scattering studies on Pristine and Graphene Infiltrated Photonic Crystal

Small Angle X-ray Scattering (SAXS) is an important tool to determine size, shape, colloidal particles interaction and internal structure of polymer particles.[289-292] SAXS can detect large lattice spacings, of the order of hundreds of interatomic lattice distances, in contrast to X-rays. This technique has also been used to probe the structural information inside colloidal crystals and can be used for submicron size particles too. SAXS measures wide ranges of scattering vector values, so specimens with small periodicities can also be probed.

We used the c-SAXS method to probe the structural information of pristine and graphene infiltrated photonic crystals. The c-SAXS was performed at the Swiss Light Source (SLS) and Paul Scherer Institute (PSI) based at Geneva Switzerland. It is used for small angle scattering and coherent imaging measurements. Figure: 6.9 shows the Debye-Scherrer rings pattern of Pristine and graphene infiltrated photonic crystals. The well-defined rings in both crystals exhibit the polycrystalline structure of both the photonic crystals.

Figure: 6.9 (a) and (b) shows Debye-Scherrer rings in pristine and graphene infiltrated photonic crystals due to polycrystalline structure.

Figure: 6.10 show the azimuthally averaged c-SAXS intensity distribution in the pristine and graphene infiltrated photonic crystals, which exhibits the changes in q values at diffraction positions quantitatively. There are five different peaks that can be observed from the spectra for both photonic crystals. The Miller Indices of every peak has been shown on the graph, which corresponds to an FCC crystalline structure.
Figure: 6.10 shows integrated small-angle X-ray scattering intensity distribution in pristine and graphene infiltrated photonic crystal.

Effective scattering vector intensity (q) and corresponding wavelength (λ) has been measured from C-SAXS measurement for both crystals and used to calculate the interparticle spacing of the crystals. The following equation has been used to calculate the interparticle spacing from q and λ values.

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{2\pi}{q} \]  

6.9

\[ d_{\text{particle}} = \frac{a}{\sqrt{2}} \text{ for FCC} \]  

6.10

\[ d_{\text{particle}} = \frac{\pi\sqrt{2(h^2 + k^2 + l^2)}}{q} \]  

6.11

Table 6.1 Table of calculated parameters (q and λ) from c-SAXS measurement

<table>
<thead>
<tr>
<th>Peak</th>
<th>Pristine PhC</th>
<th></th>
<th>Graphene PhC</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q</td>
<td>λ</td>
<td>d_{\text{particle}} /nm</td>
<td>q</td>
</tr>
<tr>
<td>111</td>
<td>0.003210</td>
<td>215.3116</td>
<td>239.7</td>
<td>0.003155</td>
</tr>
<tr>
<td>220</td>
<td>0.005413</td>
<td>127.6834</td>
<td>232.2</td>
<td>0.005358</td>
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<tr>
<td>222</td>
<td>0.006260</td>
<td>110.4074</td>
<td>245.9</td>
<td>0.006287</td>
</tr>
<tr>
<td>331</td>
<td>0.008091</td>
<td>85.42212</td>
<td>239.4</td>
<td>0.008243</td>
</tr>
<tr>
<td></td>
<td>Mean = 239±2</td>
<td></td>
<td>Mean=240±2</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.1 displays all the calculated parameters for different miller indices. The calculated interparticle spacing for the pristine crystal is 239±2 nm, whereas for the graphene infiltrated photonic crystals it is 240±2 nm. These interparticle spacing values are in excellent agreement with the values calculated from Bragg fitting and from AFM values and therefore add to the conclusion the presence of graphene doesn’t change the interparticle spacing between the polymer spheres. It can be concluded that the ~15 nm shift in the pseudogap position of graphene infiltrated photonic crystals from the pristine photonic crystal is due to changes in effective refractive index, as a result of graphene properties.

**6.1.9 Anomalous Reflection from Graphene Infiltrated Photonic Crystal**

Qualitatively by introducing just 0.01% (by weight) of graphene the photonic crystals appearance changes remarkably from milky white to a spectacular, homogenous green. To determine this unusual behaviour, we employed diffuse reflectance studies to determine the total diffuse reflectance using an integrating sphere. Figure: 6.11 shows the overlay of the diffuse reflectance measurement of pristine and graphene incorporated photonic crystal. This measurement is not selective with respect to planes, as reflected light is collected irrespective of direction and reflectance is checked against a standard. In a typical experiment photonic crystal were measured at an angle of 3° with respect to the (111) surface. A few interesting features can be extracted from this spectra. It is observed that, on incorporating graphene into photonic crystals reduces the background diffuse reflectance significantly compared to pristine photonic crystal. The reduction in the background can be explained by the graphene absorption in the visible range, which reduces the background scattering of the light in the photonic crystals outside the pseudogap region. A careful inspection also reveals that, relative widths are larger in pristine photonic crystals (~9%) compared to graphene infiltrated crystals (~5.7%). Finally, the intensities (percentage reflectance above background) coming from the graphene infiltrated photonic crystals are between ~3 times larger than those coming from pristine photonic crystals. To explain this behaviour additional consideration is required.

In addition to effective refractive index, refractive index contrast is also one of the key parameter to achieve compete photonic bandgap. Generally, complete photonic bandgap appears for high index contrast structures, which means more significant the scattering of light, more likely a complete photonic bandgap will appear. It can be quantified by either estimating ratio, bandwidth over stop band position (Δλ/λ₅₀) vs the
filling factor, $(\beta)$, of the scattering material or alternatively index contrast. It has been theoretically predicted that low infiltration of high index material can cause the large scattering strength $\varepsilon_r$ in the composite/material.[66, 293, 294] For two component dielectric medium with $\varepsilon_a$ being dielectric constant for infiltrated material and $\varepsilon_b$ for host matrix, the scattering strength can be written as a function of dielectric constant of each medium and filling factor:

$$||\varepsilon_r||^2 = \frac{\beta \varepsilon_a^2 + (1 - \beta) \varepsilon_b^2}{\beta [\beta \varepsilon_a + (1 - \beta) \varepsilon_b]^2} - 1$$  \hspace{1cm} 6.12

This equation is a consequence of the general concept of effective medium approximation and can be generalized to a system with random infiltration of different dielectric constant. The scattering strength from this expression was obtained $\varepsilon_r = 0.09$ for the pristine crystal and $\varepsilon_r = 0.32$ for graphene infiltrated photonic crystal. The ratio of this scattering strength is $\sim 3.5$, which is reasonably in agreement with the measured reflectivity. Since graphene is a high index material, even low infiltration (0.01 by weight %) yields a significant increase in scattering strength.

Figure: 6.11 Overlay of Diffuse reflectance spectra of pristine and graphene infiltrated photonic crystals.
6.1.10 Effect of Graphene Infiltration on Mechanical Properties of the Photonic Crystals

Among all the carbon based nano fillers, graphene has pulled in significant consideration recently owing to its intrinsic mechanical properties.\[136\] Graphene has a Young's modulus of \(~ 1\) TPa and intrinsic strength of \(\sim 130\) GPa, giving it the potential to improve the mechanical properties of the materials by adding it to the host matrix.\[295-298\] Photonic crystals have important applications in sensing, energy conversion, photonics etc. and for some applications their good mechanical properties are mandatory to address the issues like stability against the deformation. Here we have investigated the effect of graphene in enhancing the mechanical property of the photonic crystals by using indentation technique. There are very few reports available to describe or mechanical property of pristine colloidal crystal and inorganic nanocrystals using this technique, \[299-305\] however, to date there are no reports of describing improved mechanical properties of photonic crystal with graphene inclusion. Indentation is a powerful tool for measuring the mechanical properties, such as the Young's modulus and hardness, of various types of materials. To investigate the mechanical properties of photonic crystals indentation has been employed on pristine and Graphene infiltrated photonic crystals.

Figure: 6.12 (a) shows the load – displacement curve during indentation on pristine and graphene photonic crystal with \(2N\) as the applied force. The figure (b) shows calculated parameters for both the photonic crystals. Test speed was fixed to \(0.01\)mm/sec for the indentation. 20 sets of experiment have been performed on each crystal at different positions and the average value has been taken. The Young’s modulus and Hardness for both pristine and graphene infiltrated has been calculated from Oliver and Pharr method described in the materials and methods chapter.\[207, 210, 211\] The estimated Young’s modulus and hardness for pristine photonic crystal is \(\sim 66.49\) MPa and \(6.52\) MPa respectively, whereas, for graphene infiltrated crystal it gives modulus and hardness \(105.98\) and \(411.69\) MPa respectively. Compared to a pristine PC, the inclusion of only \(0.01\) weight\% of graphene substantially enhances the crystal’s hardness by over \(800\)% with a Young’s modulus increase of almost \(240\)%.
Figure: 6.12 (a) shows the load vs displacement curve for pristine and graphene infiltrated photonic crystal and (b) shows the estimated young modulus and hardness of comparison of pristine vs graphene crystal.

6.1.11 Raman Fingerprint in Graphene Infiltrated Crystal

It is difficult to obtain information about graphene, when infiltrated with such a low weight fraction (0.01 wt%) in photonic crystals by using techniques such as AFM and SEM. Raman spectroscopy is potential non-destructive characterization technique that can be used to probe the photonic crystals to study graphene. Raman measurements were carried out on graphene infiltrated photonic crystals and results are shown in the Figure: 6.13. Figure (a) shows all the characteristic Raman features D, G and 2D bands appeared in the spectrum, which confirms graphene presence in the photonic crystal. Two peaks arise at 1450 cm\(^{-1}\) and 1728 cm\(^{-1}\) correspond to polymer matrix. The peak positions for D band (~1327 cm\(^{-1}\)), G band (1577 cm\(^{-1}\)), D' (around 1610 cm\(^{-1}\)) and 2D band (~2675 cm\(^{-1}\)) were obtained. Raman spectra exhibits strong D band, and is associated to the presence of disorder in the graphene layers.[306] Eckmann et al reported that ratio of intensities of the D and D' bands can be used to probe the nature of defects present in the graphene that the nature of defects in graphene can be probed by the ratio of intensities of the D and D' (D' band is a correspond to defects and appears as a shoulder on the right side of the G band).[307] They showed intensity ratio for ID/ID' is ~3.5 correspond to edge or boundary defects, ~7 for vacancy basal plane point defects and ~13 for sp\(^{3}\) defects.[307] Measured ID/ID' from our Raman spectrum shows ~3.17, thus our data is consistent with the hypothesis that origin of D peak is due to edge or boundary disorder and no basal plane defects are introduced after making photonic crystals. However, Eckmann study contains no error range, taking into
account, another study by Coleman et al proposed the more appropriate value for edge defects are in the range of \(3 \leq I_D/I_D' \leq 4.5\) is more appropriate.[152] Figure (b) shows the fit of G band and the D' band which originates at shoulder of G band due to disorder and observed at 1610 cm\(^{-1}\). Due to interparticle spacing importance in Bragg’s law, it is necessary to measure accurately thickness of the graphene flakes present in crystal. Flake thickness estimated by AFM and graphene already described in materials and method chapter shows exfoliated graphene is in few layer, typically 2~5 layers. However, post photonic crystal fabrication, the measurement of flake thickness is not possible. Although by measuring the interparticle spacing of polymer can describe; if there any changes occurred due to graphene incorporation. In an alternative way, the 2D Raman band and its shape can also reflects quantitatively thickness of graphene nanoflakes, which originates from the double resonance Raman process.[306, 308] Figure (c) shows the 2D band observed in our spectrum is \(\sim 2675\) cm\(^{-1}\) and shows asymmetric shape, however 2D band for monolayer flake has been shown to have single symmetric peak and fit a single Lorentzian perfectly. We fitted our Raman spectra with four Voigt (mixture of Lorentzian and Gaussian) peaks, which suggest 3 layers of graphene, and is consistent with our AFM results. In photonic crystal fabrication process, due to the evaporation of water, generated capillary forces trigger graphene assembly to take place at the interstitial sites between the polymer particles. Figure (d) shows the Raman map of the 2D band position verifies that the graphene is only positioned at the interstitial sites between latex polymer particles.

Figure: 6.13 (a) Raman spectra of graphene infiltrated photonic crystals showing characteristic D, G, D' and 2D bands. (b) shows the G band and D' band originated at shoulder of G band due to disorder. (c) shows 2D band and fitting components, suggesting four layers of graphene. (d) Raman map of photonic crystal at 2D band frequency, graphene can be observed in the void space between the polymers.
6.2 Boron Nitride Infiltrated Photonic Crystals

In addition to graphene Boron nitride (BN) was incorporated into pristine photonic crystals. The fabrication procedure to make photonic crystal with BN remains the same as graphene. Figure: 6.14 (a) and (b) shows the optical photograph of fabricated BN photonic crystal taken under an optical microscope at ~ 40 degree. The crystal exhibits bright, bluish-green iridescence and some small domains can also be seen.

Figure: 6.14 (a) BN infilled fabricated photonic crystal (b) optical image taken under the optical microscope of the same crystal reflecting bright bluish green light at ~ 40 degree.

6.2.1 Ordering of Spheres in (111) Growth Plane

The packing structure, ordering and homogeneity of the sample is identical to that observed for the graphene crystals. AFM confirms this is as shown in Figure: 6.15. with only the occasional lattice vacancy etc. One key difference between the BN and graphene crystals is that the BN tends to form crystals with more separated domains. It is seen from the Figure: 6.15 (a) (b) and (c) that it is most common occurred imperfection in our crystal. At some locations near to interface the grain boundaries was also observed. The interfaces which separate domains called as grain boundaries. The structure of grain boundaries depends on the misorientation of the spheres that it separates. When the misorientation is small it’s called as planar array of dislocations, while for larger misorientation it is defined as region of disorder. Inset in figure (b) correspond to FFT analysis representing the long range ordering in the photonic crystal.

Another important parameter can be extracted from AFM analysis is inter particle distance, which directly influence the optical properties of the photonic crystals. A line scan through the surface of photonic crystal was performed and area was chosen such as where a vacancy can also be included. Figure: 6.15 (d) show the line scan profile of photonic crystal surface and its corresponding scanning area was also mentioned by blue line in figure (c). It was observed that there is a significant dip in the scanning profile after scanning initial sphere, which corresponds to the missing sphere creating a
vacancy defect. The calculated Interparticle spacing from the AFM micrograph is ~ 268±2 nm.

Figure: 6.15 (a) (b) (c) shows AFM images of the bottom surface of the BN infilled photonic crystal depicts well fcc ordered packing of the spheres. The inset in figure (b) corresponds to FFT analysis representing the long range ordering in the photonic crystal. Figure (d) represent line scan profile of crystal, to measure Interparticle distance.

**6.2.2 Pseudogap Measurement in Γ- L Direction Propagation**

Optical analysis was carried out in same instrument with similar settings and condition was employed as used for graphene crystal. Transmission spectra were measured over the visible range. A representative transmission spectrum measured along Γ-L direction in reciprocal space or normal to (111) plane is shown in the Figure: 6.16(a). It shows sharp transmittance minimum or pseudogap ~ 522 nm, indicating Bragg diffraction in this spectral range, shown in the grey shaded region. In order to determine the correct position of the pseudogap center frequency the background was subtracted from the experimental spectra. As already described the pseudogap centre frequency for pristine was observed at ~505 nm, thus there is ~17 nm shift is observed in BN infilled crystals in contrast to pristine ones.

**6.2.3 Pseudogap Position Tuning as Function of Incidence Angle**

Angular dependence transmission was employed to measure the pseudogap behaviour as a function of scanning incident angle and presented in the Figure: 6.16 (b). Transmission data was acquired at every 5° intervals for crystal oriented with normal inclined to the incident light beam in the angular range 0° to 50°. It allows investigation of psuedogap structure along specific wave vector (k) direction as determined by the incident angle. These peak positions can be defined by Bragg’s law, which is dependent
upon the incident angle, effective refractive index and the lattice parameter. The transmission spectra of BN photonic crystal at normal incidence shows a pseudogap profile \( \sim 522 \text{ nm} \) corresponding to Bragg’s peak originated form fcc (111) planes. This stop band is blue shifted and widened towards higher angle in contrast to normal incidence to the plane (111). The filling fraction was also estimated in BN infilled crystal by using effective medium approach and is \( \sim 4\% \).

![Graph](image)

Figure: 6.16(a) Optical transmission spectra taken along the (111) crystallographic axis measured on BN photonic crystal (b) Position of the pseudogap minima shift to shorter wavelengths as a function of increasing incident angle.

Angular dispersion spectroscopy allows estimation of parameters such as the interparticle distance and effective refractive index etc. using a modified Bragg’s law. Here \( n_{\text{eff}} \) and \( D \) were used as fitting parameters to adjust the theoretical expression, \( \lambda_B \) corresponds to the center of the pseudogap position in the transmission spectra. Figure: 6.17 shows the experimental pseudogap position of the stop band minima from the angular transmission spectra. Figure shows plots of peak wavelengths of the (111) plane against various \( \theta^\circ \). Equation number (6.14) has been used to fit the experimental data. Refraction in the photonic crystals has been taken into account. Figure: 6.17
shows a good fit and obeys the modified Bragg’s law. Fitted approximation gives the sphere diameter as 270 nm, and effective refractive index 1.18 respectively.

Fitted approximations suggest there is ~ 20 nm increase in the interparticle spacing of the polymer spheres in contrast to bare latex polymer measured by AFM. This expansion in the interparticle spacing is due to incorporated BN nanosheets into the system. It is attributed to thickness of BN nanosheets. As statistical AFM analysis of BN dispersion suggested that average thickness of BN nanosheets ~ 20 nm. It will modify the interparticle spacing and at the same time being a low refractive index materials, will not contribute in increasing the total effective refractive index of the system i.e. 1.18. As interparticle distance has a greater influence on the Bragg peak position than the effective refractive index. It can be understood by Bragg peak dependence on the interparticle distance and filling fraction examined in the next section.

Figure: 6.17 Bragg’s law fit to angular dispersion behaviour of BN in filtrated photonic crystals. Dash lines are theoretical fits.

6.2.4 Effect of Interparticle Distance and Filling Fraction on Pseudogap

The pseudogap determination is based on \( n_{\text{eff}} \) and \( d_{\text{hkl}} \) parameters. Reduction in interparticle distance also decreases \( d_{\text{hkl}} \) whereas filling fraction and total refraction index increases. We tried to simulate which parameters effect pseudogap position more. Results are shown in Figure: 6.18 (a) and (b) calculated by Solver tool in Microsoft excel software.
Results suggested that the lattice constant increases linearly with interparticle distance \( x \), while refractive index decreases. The pseudogap position shows a linear profile the same as \( d_{\text{hkl}} \). Our fitted results for BN photonic crystals can be explained by this hypothesis. Based on fitted parameters (\( d_{\text{part}} \sim 270 \) nm and \( n_{\text{eff}} \sim 1.18 \)), the photonic bandgap position was calculated and it was found that the Bragg peak position was \( \sim 521 \) nm, which is in agreement with our experimental value \( 522 \) nm. Interparticle distance obtained from angular dependence transmission spectroscopy calculated value \( d_{\text{part}} \sim 270 \) nm was also in agreement with our AFM image results, which also suggested \( d_{\text{part}} \sim 265 \pm 5 \) nm.

### 6.2.5 Approach to Complete Photonic Bandgap

Figure: 6.19 presented the analysed optical parameters of the photonic stop band with varying indent angle. Figure (a) displays angular dependence variation in FWHM of stop band peak of pristine and BN infilled photonic crystal. It suggests that FWHM is significantly higher for pristine photonic crystals compare to BN infilled photonic crystal and displays larger space forbidden to propagating light. As explained earlier this is due to larger index contrast in the pristine photonic crystal compared to the BN one. The refractive index of Boron nitride is \( \sim 1.18 \). Figure (b) presents the relative shift of the stop gap with change in angle of incidence (\( \lambda_{\text{shift}} / \Delta \lambda \)) that determines rate of approaching a complete photonic bandgap (\( \lambda_{\text{shift}} / \Delta \lambda < 1 \)). The pristine photonic crystal indicates a more complete photonic bandgap characteristic compared to BN infilled photonic crystal upto 25 degree scanning angle. It is worth mentioning here the iridescent colour form BN PhC are not as homogenous compared to graphene crystal, which can be attributed due to insulator nature of BN.
Figure: 6.19 Angular dependence of (a) pseudogap FWHM and (b) relative stop band shift for both pristine and BN infilled photonic crystal.

To measure the ability of BN infilled photonic crystals to approach a complete band gap, the same analysis as for graphene infilled and pristine photonic crystals was used. Figure: 6.20 plots of FWHM and photonic stop band peaks as a function of varying angle of refraction. In BN photonic crystals, superposition of pseudogap position was observed from 3.7° till 25° and disappeared later at higher angles. It suggests a lack of complete psuedogap in this photonic crystal due to low refractive index contrast.

Figure: 6.20. Stop band position (dots) and FWHM (triangles) for BN crystal as a function of the refractive angle. The black dash straight line indicates the wavelength region in which the stop band would remain for complete photonic gap case.
6.2.6 Reflectance from BN PhC

To study pseudogap and structural quality of photonic crystals, reflection spectrum is one of the efficient and conventional approaches. The Bragg reflection peak emerges from reflection of waves from parallel planes of the photonic crystal. We measured diffuse reflection spectra, using an integrating sphere and the results are shown in Figure: 6.21. Diffuse reflectance spectra were recorded for the (111) plane of the photonic crystal i.e. parallel to the normal incidence. The lattice constant of the polymer latex which is used in this will show a reflection peak in the visible region due to Bragg diffraction from the planes for BN infilled photonic crystal. The observed reflection peak is at ~522 nm. The calculated relative bandwidth of the pseudogap is ~0.059.

BN incorporation into photonic crystals does not reduce the background light scattering as significant as it is for graphene, it is attributed to insulating nature of BN, whereas graphene reduces the background scattering of the light by absorbing light outside the photonic bandgap region. The relative widths (Δλ/λ) are also smaller in BN crystal (0.059) compare to pristine crystals (0.09), whereas marginally larger than the graphene (0.057) due to larger index contrast in BN compared to graphene crystal.

Figure: 6.21 Diffuse reflection spectra of BN infiltrated photonic crystals with center position of pseudogap ~522nm.
6.3 Summary

In this chapter we have presented in depth study of the optical and morphological properties of infiltrated photonic crystals with two different nanoplatelets; graphene and boron nitride. We found that shift in the pseudogap position was ~15 nm for graphene infiltrated photonic crystals where as it was ~ 17 nm for boron nitride infiltrated. By examining the morphology of the graphene infiltrated crystals, using AFM, optical fitting and c-SAXS measurements we have determined that the interparticle spacing did not change with graphene inclusions. We therefore conclude that the modification in pseudogap position is due to changes in effective refractive index, which is a function of nanoparticles chosen for infiltration. In the case of BN infiltrated photonic crystals the change in pseudogap position is due to larger thickness of the BN flakes ~12-20 layers, which modify the interparticle spacing thus leads to modify pseudogap position and is in excellent agreement with AFM and optical fitting measurements. We determined that graphene works better to reduce scattering in the photonic crystal compared to BN infiltrated and pristine photonic crystals. A theory proposed by Söüzüer, at al that a low infill of a high index material in a low index matrix causes a large increase in the scattering strength in the periodic composite is also in excellent agreement with graphene infiltrated optical results. The infiltration of graphene also tend to modify the mechanical properties of the whole matrix and our results shows the inclusion of only 0.01 weight% of graphene substantially enhances the crystal’s hardness by over 800%, with a Young’s modulus increase of almost 240%.
As described in last chapter, inclusion of 2 dimensional layered materials in photonic crystals tends to modify the optical properties of the system. In this chapter, we replaced 2D nanoplatelets inclusion with 1-D nanotubes and studied, how crystal properties changes on incorporating 1D system. In 1-D system, SWCNTs, in particular, have been among the most studied materials for the past two decades. In the first section of the chapter, procedure to prepare SWCNTs dispersion will be presented. Thereafter, the optical properties of CNT’s dispersion and its stability over the time will be presented. In the next section, fabrication of P-PhC and carbon nanotubes incorporated photonic crystals (CNPhC) and their optical and morphological properties will be discussed.

7.1.1 SWCNTs Dispersion Preparation: Experimental Details
To disperse SWCNTs a stock solution of TritonX-100 (Fisher Scientific) containing concentration of 16mM in de-ionized water (DI) was prepared. 16mM concentration was used to disperse nanotubes as it is well above the critical micelle concentration (CMC) which is 0.3mM. 1 mg of HiPco Single Wall Carbon Nanotubes was then added to 10 ml of stock solution of water/surfactant. This dispersion was then sonicated using a probe ultra-sonicator (Branson Sonifier, model 150D) for 20 min at a power level of 20 W in an ice-cold water bath resulting in the CNT concentrations in water as high as 0.5 mg mL\(^{-1}\). To produce a dilution series this initial dispersion was then serially diluted to produce a range of dispersions with concentrations from 0.5 to 0.0001 mgmL\(^{-1}\). After each dilution the dispersions were sonicated for 5 min by tip, followed by 30 min in a low-power ultrasonic bath. To remove any large aggregates all dispersions were subsequently centrifuged at 3000 rpm for 45 min.

7.1.2 Debundling of SWCNTs: Optical Spectroscopy
The first observation to check effective dispersion of CNTs can be made with the eye, - the colour disappears and looks more transparent as concentration decreases. The inset of Figure: 7.1 shows the optical images of CNT dispersions as a function of decreasing concentration. It can be readily seen that UV-Vis spectroscopy is an effective and
sensitive technique to monitor SWCNTs dispersion in solution. There is a relationship between CNT concentration and the intensity of the absorption spectrum. In order to investigate the effect of serial dilution on dispersion of SWCNTs in water/surfactant, a series of samples with serial dilution of initial concentration was prepared. Figure: 7.1 shows the extinction coefficient over the range of the SWCNTs surfactant concentrations. The sharpness of absorbance peak is commonly used as an indication of the debundling level in dispersion.

Figure: 7.1 Absorption spectra of SWNTs dispersed in DI water/Triton-100 at a range of concentrations and inset shows the optical photograph of CNT dispersion as a function of concentration.

The absorbance at 740nm, $A_{740}$, was measured for each dispersion and then divided by cuvette path length $l$, to obtain $A_{740}/l$. The extinction coefficient values of CNT’s in higher concentrations is similar to those in lower concentrations, as indicated in Figure: 7.2 (a), where $A_{740}/l$ scales approximately linearly with the initial concentration, $C_i$. The slope of this graph determines the extinction coefficient, as per the lambert beer law at $\lambda=740$nm, is 4082 mlmg$^{-1}$m$^{-1}$. Figure: 7.2(b) shows the absorption coefficient ($\alpha$) at $\lambda=740$ nm of prepared dispersion of various CNT’s concentrations. Data has been divided by the initial nanotube concentration to plot at specific wavelength 740 nm. Graph reveals the lower absorption coefficient ($\alpha_{740}$) for larger concentration as it’s not optically transparent in this range. Absorption coefficient at 0.1 mg/mL was $\sim$ 4476.
mL mg⁻¹ m⁻¹ and approaches to 8050 mL mg⁻¹ m⁻¹ for 0.01 mg⁻¹ m⁻¹. This enhancement in absorption coefficient is an indication of debundling of CNT’s. It is due to the increased presence of small bundles as more individual number of nanotubes tends to scatter more light. Graph has been subdivided into three different segments called bundled (C stage), semi-bundled (B stage) and isolated nanotubes (A stage). The inset shows optical photographs of three different CNT dispersions corresponding to their state of debundling and displays the different optical transparency for three different optical images.

Figure: 7.2 (a) Absorbance per unit length measured at λ = 740 nm, A₇₄₀/l, as function of initial concentration of nanotubes. (b) Absorption coefficient at λ₇₄₀ nm by dividing the initial nanotube concentration, Cᵢ. Optical photograph represent three different stages from bundle to isolated nanotube dispersion.
7.1.3 SWCNT Dispersion: Stability Study

As described above, to monitor the exfoliation state UV-Vis spectroscopy was employed as a direct measure of concentration of disperse nanotubes. It is possible to use the same concept to determine the reaggregation of the nanotubes after debundling, which in turn provide stability of the nanotubes dispersions. Figure: 7.3 shows the absorbance value of the dispersion (concentration - 0.01mgml\(^{-1}\)) at \(\lambda= 740\) nm as function of time. It was observed that there is around \(~15\%\) decrease in the absorbance value within 24 hours, which corresponds to sedimentation of large bundles of SWCNTs out of dispersion. Later, the absorbance does not evolve significantly over the period of three weeks’ time, which means that the concentration of exfoliated nanotubes present in the dispersion remains virtually constant. On re-sonication the absorbance value returns to approximately to same value. This study is important in another aspect, as dispersions can be reused to infiltrate into photonic crystals and the stability of the dispersion is helpful to be sure on blending with polymer that they are in a de-bundled state.

![Graph showing absorbance over time](image)

Figure: 7.3. Absorbance of SWCNTs at 740 nm dispersion as a function of time. The dotted grey line highlights the averaged values of all the measurements.
7.2 SWCNTs Infiltrated Photonic Crystals (CNPHC): Fabrication and Morphological Results

To fabricate pristine and SWCNTs infiltrated photonic the same procedure was used as discussed previously. In a typical process, 0.04mg/ml SWCNTs (stabilized in water/surfactant) was used to infiltrate the latex polymer as this is from the concentration where nano start to become isolated. The Latex-SWCNTs dispersion was then tip sonicated in an ice-cold water bath for 10 minutes at a power level of 10 Watts using the discontinuous mode to ensure a better mixing. For comparison, pristine latex photonic crystal sample containing the same amount of TritonX-100 were also prepared.

To fabricate photonic crystals, the dispersion containing 0.01wt% (typically 2.5 mL) SWCNTs dispersion was transferred to a glass vial and kept for natural sedimentation with the open lid at room temperature (RT 22°C) to induce self-assembly of the particles combined with drying of the suspension from above. After 7-8 days a ~1 mm thick bright green colloidal crystal was obtained in the glass vial. Figure: 7.4(a) illustrates the schematic concept of fabricating the crystals under natural gravitational sedimentation process, whereas s (b) demonstrates the real dispersion in the process of making crystals via natural sedimentation process. From the figure, three different phases were observed; water, suspension and sediment. However the optical photograph was taken with the close bottle but in real sedimentation process the lid was kept open.

Figure (c) and (d) shows the optical images of the CNPhC (bright reddish - upper bottle) and pristine (whitish and opaque crystal - bottom one) at normal incidence and also tilted at angle of ~ 20° simultaneously. It is apparent that photonic crystals with SWCNTs drastically improve the reflected reddish colour while pristine reflection looks milky white and dull.
Figure 7.4 (a) shows schematic concept of natural gravitational sedimentation process (b) displays polymer dispersion representing three different phases during sedimentation process. Figure 2 (c) and (d) represent optical images of CNPhC (bright reddish - upper bottle) and pristine (whitish and opaque crystal - bottom one) at normal incidence and tilted at angle of ~ 20° respectively.

### 7.2.1 Morphological Studies

The effect of SWCNTs on the periodicity of photonic crystals is analysed by SEM and AFM. Sample preparation for SEM measurements remained the same as for pristine and discussed in previous chapters.

Figure 7.5 represents the different scanning electron micrographs and AFM micrographs on CNPhC crystal. Figure (a), (b) and (d) shows the long range ordering in the crystal, taken at a lower ~ 3000X and higher 10000X magnification respectively, taken at different positions on the crystal. Long range ordering of latex spheres was observed in the crystal growth. It contains well-ordered both (100) and (110) planes possessing square geometry, whereas image (c) reveals three different planes (111), (110), and (100) marked by red dashed lines possessing hexagonal and square geometry respectively. Inset of figure (c) shows two FFT analyses on two different (111) and (100) planes, showing orientation homogeneity over the whole sample. The crystal’s growth suffers from various imperfections or defects as can be seen in image (c), such as dislocation, vacancy, stacking faults etc. Figure (e) and (f) shows typical AFM images of the CNPhC crystal scanned on the surface and in cross-section. Both the images show well-ordered packing, the same as SEM. AFM also depicts defects in the crystal. The quality of the photonic crystals depends upon the many parameters, such as solvent evaporation, drying time, humidity, temperature, spheres size, monodispersity etc. To control all these parameters at the same time makes it challenging to fabricate defect free photonic crystals.
Figure: 7.5 SEM and AFM micrograph of a cleaved edge of a pristine photonic crystals made of a 290 nm diameter sphere. SEM images depict different crystal orientation and also imperfection. FFT Images indicate long range ordering is observed in lateral surfaces in the photonic crystal.

7.3 CNPhC: Optical Spectroscopy

7.3.1 Light Propagation Γ– L Direction

Reflectance and transmission spectroscopy has been employed to probe the pseudogap measurement in CNPhC. This section will present optical analysis of L pseudogap with respect to (111) planes for CNPHC made of 290 nm diameter particles. The spectroscopy was carried out along the Γ-L direction in reciprocal space, which is normal incidence to (111) planes. The overlay of reflection and transmission spectra along the L direction in the photonic crystals has shown in the Figure: 7.6 with peak position ~595 nm. One can observe in the region of the pseudogap the high transmittance and low reflection. As already described these crystals are not free form disorder, which hampers the optical properties of the crystals as propagating light will be scattered, and attenuated. It can be readily seen from the figure that the transmission spectra shows a more asymmetric profile and higher background compared to the reflection. The reason being; in transmission spectroscopy, one probes the whole sample thickness, which means more light will have more probability to interact with imperfect sites. In contrast to transmission, reflection probes only a few layers from the surface of the photonic crystals, which reduces the probability of light being scattered
by defect sites. Relative bandwidth ($\Delta \lambda / \lambda_b$) has been calculated by measuring the centre peak of the pseudogap and full width half maximum of the peak and is $\sim 0.03$.

![Reflectance and transmission spectra measurement of CNPhC](image)

Figure: 7.6 Diffuse reflectance and total transmission spectra measurement of CNPhC at normal incidence on the (111) planes or in reciprocal space in Γ-L direction.

### 7.3.2 Angular Dispersion Spectroscopy of CNPhC

To determine the effect of angle, herein we employed angle resolved transmission spectroscopy. Figure: 7.7 (a) shows the angle dependent spectrum for CNPhC measured from 0 to 40° at step of 5°. For the sake of clarity spectra has shown at the difference of every 10°. Initially, at normal incidence angle the peak appears at 595 nm. It was observed that the angle between the direction of propagation of light and the photonic crystal axes shifts the pseudogap position to higher energy, which is anticipated and has been described in earlier sections. The photonic bandgap also becomes less pronounced with increasing angle, which means at normal angle the diffraction is derived from (111) planes; whereas on changing the angle it will not remain the same. The CNPhC agrees with the theory that all odd or all even Miller indices generate the most efficient Bragg reflections in a fcc lattice while other planes contribute in higher order reflections at shorter wavelengths.

Figure: 7.7 (b) shows the photonic bandgap position as a function of incident angle. The modified Bragg’s law has been used to fit the experimental data.

The data clearly suggest a good fit. The fitted approximation gives the sphere diameter as 270 nm, and the effective refractive index as 1.34 for the CNPhC. These values for diameter are in agreement with those obtained from SEM and AFM measurements. The fitted results for pristine crystals estimated that the structure had shrunk ~6.8% in the
direction perpendicular to the sample surface, which corresponds to a reduction in interparticle distance \( \sim 20 \) nm. The comparison was carried out with respect to the latex polymer particle size estimated by AFM. The reason for this reduction in interparticle spacing is due to the shrinkage of latex polymer spheres during drying.

Using these parameters, gives the position of the pseudogap \( \sim 595 \) nm, this matches well with our experimentally observed value \( \sim 595 \) nm. Pristine photonic crystals made by same 290 nm diameter have been already discussed in chapter 5. Obtained optical parameters suggest incorporating nanotubes in photonic crystals increases the effective refractive index, which results in a \( \sim 10 \) nm shift to longer wavelength.

![Transmission spectra](image1)

![Angular dispersion](image2)

Figure: 7.7 (a) Transmission spectra of CNT infiltrated photonic crystals at \( 0^\circ \) to \( 40^\circ \), at the interval of \( 10^\circ \) (b) Angular dispersion of the Bragg Resonance of CNT infiltrated photonic crystals. Thick red line represents the theoretical fit.

Figure: 7.8 shows the processed optical parameters from the angular dispersion curve. The experimental data of CNPhC has been compared with pristine photonic crystals. Figure (a) displays angular dependence variation in FWHM of the stop band peak of
pristine and CNPhC, suggesting higher FWHM for pristine photonic crystals compared to CNPhC, due to larger index contrast in the pristine. In figure (b) the relative shift of the stop gap with change in angle of incidence ($\lambda_{\text{shift}} / \Delta \lambda$) was measured to check the overlap of the psuedogap as a function of angle. It can be readily seen for the figure that stop band is visible to greater angles in the CNPhC than the pristine.

Relative shift in the photonic bandgap position explain the crystal being possible to possess complete psuedogap ($\lambda_{\text{shift}} / \Delta \lambda < 1$). Though both the crystals fulfil the criteria upto 25°, however pristine photonic crystal indicates more possibility to achieve complete psuedogap characteristic compare CNPhC.

![Graph](image_url)

Figure: 7.8 Angular dependence of (a) psuedogap FWHM and (b) relative stop band shift for both pristine and CNPhC.
A different approach to measure complete photonic bandgap possibility in the crystals is analysing superposition of pseudogap peaks at scanned different refractive angles. Figure: 7.9 show the analysed and plotted graph of FWHM and stop band peak position as a function of varying angle of refraction for pristine (graph a) and for CNPhC graph (b). The square red dot represents the position of stop band wavelength, while the both triangles and circles denote the FWHM of stop band peaks. Results reveal that superposition in the stop band position was remains from 3.7° till 12° and disappeared later at higher angles, suggesting lack of complete gap in this photonic crystal due to low refractive index contrast.

Figure: 7.9 (a) and (b) Stop band position (dots) and FWHM (triangles) for Pristine and CNPhC respectively as a function of the refractive angle. The black dash straight line indicates the wavelength region in which the stop band would remain for complete photonic gap case.
7.3.3 **Application: Compact Strain-Sensitive Flexible Photonic Sensors**

Although pristine photonic crystals cannot possess a complete bandgap, infiltration can tune their properties. However, there are ranges of other applications that don’t need a complete gap such as sensors. Tuning the psuedogap position dynamically has been a key area of research in photonic crystals. Literature suggests that in response to external stimulus periodic structures can be altered, resulting in a change in psuedogap position. Generally it has been achieved by temperature, light, electric and magnetic field, index contrast, solvent, lattice constant etc. This tuning of the psuedogap is generally achieved by changing the lattice parameters and altering the refractive index in the material. Mechano responsive (MR) photonic crystals are also very popular approach of dynamic tuning, where they can be stretched or compressed to alter the lattice constant. However, this approach is generally, focused on hydrogel/elastomer photonic films. There are a few theoretical predictions that an ellipsoidal structure also offers the possibility to lift the degeneracy of the photonic band gap.[309] Xia at al. have reported shape transition and colour change by applying strain.[310] Choi et al. reported significant bandgap tuning by applying compressive stress in composite crystals.[311] In spite attracting tremendous attention for sensing and many other applications, the low mechanical strength is still a challenge to achieve complete reversible behaviour.

This section will describe optical properties of pristine and CNPhC. Optical measurements were performed using a miniature fibre optic spectrometer (Arcspectro-HT Arcoptix) and Linkam a stretching stage. For such measurements, ~ 2 x 1 cm strip was cut from the original photonic crystals. The measurements were carried out slightly above the glass transition temperature as photonic crystals are stiff and brittle below this, which makes them difficult to stretch.

Figure: 7.10 (a) and (b) shows the change in stop band position as a function of different rate of strains for pristine and CNPHC. In both the spectra, it is clearly visible that the stop band position of the (111) plane is shifting to higher energy as function of strain. It is attributed to decreasing the spacing of (111) planes, which will result in a blue shift for the stop band positions. It can be explained by schematic shows in figure (d), elongation in horizontal direction due to stain causes the (111) planes approaches to each other, which results in a decrease in (111) planes spacing. The overlay shift in the pseudogap position with increasing strain showed in figure (c) exhibit linear behaviour.
Pristine photonic crystals show a total shift of ~30 nm in the stop band position, whereas it was 40 nm for CNPhC, suggesting possible tunability of bandgap across Figure 7.10 (a) and (b) UV/vis transmission spectra different strains showing strain-dependent shift of the Bragg wavelength for pristine and CNPhC. (c) Transmission spectra of the both PhC at different strains (d) schematic presentation of strain-dependent change in lattice constant of PhC and shows the shift of PhC color from red to green with increase in strain.

from red to green wavelength in the visible spectrum. The noisy spectrum in the higher energy region is due to limitation of light sources at those wavelengths. Figure (d) shows optical images of the color tuning of CNPhC on elongation, shows the change in color from red to green as a function of strain.
7.4 Summary

This chapter contains two sections. In the first section debundling of single-walled nanotubes has been demonstrated by dilution of nanotube dispersions in the DI Water/Triton X-100 surfactant. Our nanotube dispersions were stable against sedimentation and further aggregation for a period of more than a month. We demonstrated population of isolated nanotubes increases with decreasing concentration and this isolation range appears ~0.04 mg/mL. We estimated absorption coefficient at $\lambda= 740$nm that is 4082 mlmg$^{-1}$m$^{-1}$ and is in agreement with other reported literature values. In the second section, pristine photonic crystals infiltrated with nanotube have been fabricated. The morphological studies on this crystal show well-ordered growth of the crystal. Later, pseudogap position measured by transmission spectroscopy was observed ~ 595 nm, which shows a ~ 10 nm shifted to longer wavelength compared to pristine photonic crystal due to increase in effective refractive index. The pseudogap position for nanotube infiltrated crystals was in agreement with the Bragg law. The calculation of optical parameter by optical fitting suggests interparticle spacing ~ 270 nm and is in agreement with AFM studies. In the end, the potential application of these photonic crystals as stress strain sensor is presented. We showed that the pseudogap position can be tuned across the visible region as a function of different strain rate which is attributed to reduction in the interlayer spacing of (111) planes, thus results in blue shift for the pseudogap position. Although strain sensitive PhCs have been presented before, this is the first time upto to our best knowledge that such measurement has been carried out on nanotube infiltrated photonic crystal for sensor application.
Chapter 8 Conclusion and Perspective

8.1 General Conclusion

Three dimensional photonic crystals are considered very promising for their peculiar periodic properties in the confinement and propagation of light. This thesis is related to the fabrication and investigation of three dimensional photonic crystals that respond to light over a desired range of frequencies, by perfectly reflecting them, or allowing them to propagate only in certain directions. In particular, the focus is on the optical properties of 3D PhC produced with a self-assembly based approach.

This thesis has built up detailed and comprehensive studies on undoped (pristine) and the Infiltrated three-dimensional photonic crystals operate in visible wavelength range fabricated by using the natural gravitational sedimentation method. To obtain such structures, a versatile and innovative method of latex based templated self-assembly has been tested, based, in a suspension containing the infiltrating material, through a mechanism of evaporation. It was the first time to the best of our knowledge we demonstrated direct fabrication of 2D layered nanoplatelets and one dimensional nanotube incorporated photonic crystals working in visible wavelength range. The introduction of nanoplatelets and nanotube in this ordered lattice has the purpose of studying a possible influence on the optical and mechanical properties of the resultant photonic crystals.

In particular, it emphasizes the infiltration effect of two dimensional nanoplatelets (Graphene and Boron nitride) and one dimensional single walled carbon nanotubes into latex based templated assemblies of photonic crystal’s morphological and optical properties. We demonstrated the ability of tuning the photonic bandgap properties by altering the optical parameters such as refractive index and interparticle spacing.

Fabricated photonic crystals are robust, thick and freestanding with thickness around ~ 1mm. Free-standing photonic crystals also offer the characterization flexibility to carry out and design various measurements.

Chapter 5 describes the general fabrication procedure of pristine photonic crystals made of two different sphere diameters. In this chapter, estimation of pseudogap position and
other important parameters (FWHM, interparticle distance, total refractive index) of photonic crystals, which govern the main properties of the crystals has been investigated. The photonic crystal made of 255 nm gives Bragg stop band ~ 505 nm whereas; it was 586 nm for 290 nm which is in excellent agreement with simulated stop band position with TMM and FDTD method. The morphological studies presented in this chapter for both the crystal made of 255 and 290 nm diameter shows long range ordering with some minor defects visible. Theoretical bandstructure and simulated reflection spectra were calculated and compared with experimental spectra were found in excellent agreement along Γ-L direction. This chapter also describes the optical parameter calculation by using Bragg’s law fitting and calculated interparticle spacing matches well with atomic force microscopy results. Tuning the pseudogap position across the whole visible range has also been presented by using four different sphere diameters 255, 262, 290 and 325 nm which, gives stop band position at 505, 545, 586, and 726 nm respectively. Finally this chapter closes with the brief insight about the effect of disorder on the optical properties of the photonic crystals by measuring the total incident light at normal incidence.

In chapter six we introduce the infiltration of photonic crystals with two dimensional nanoplatelets. Two different materials, graphene and boron nitride, were used to infiltrate the base photonic crystals while photonic crystal fabrication procedure remains same as described in chapter 5. These photonic crystals were thoroughly investigated by spectroscopy to determine the effect of incorporation of two-dimensional materials on optical properties of photonic crystals. We then demonstrated that these nanofillers can tune the pseudogap position by altering the effective refractive index or by interparticle spacing significantly. In this chapter, we demonstrated that incorporating a very low weight fraction (0.01 %) significantly changes its color as compared with that of the pristine PhC. This is so because the infiltration of graphene significant reduces the background diffuse scattering by light absorption outside the photonic bandgap region thus enhances contrast between the peak reflectivity of pristine and infiltrated crystal. It clearly shows the spectral control capability of the infiltrated PhC with graphene. Furthermore, it was found that the infiltration of graphene with only 0.01 wt. % substantially enhanced the PhC’s hardness by over 800% and the Young’s modulus by approximately 240%. Small angle x-ray scattering measurements have also been carried out to measure the interparticle spacing in the pristine and graphene incorporated photonic crystals and results were found in
excellent agreement with our microscopic and spectroscopic results, indicating that the observed shift in the stop band positions are due to overall change in total effective refractive index in contrast to any changes in the interparticle spacing. Angular dependent spectroscopy was performed for all graphene and born nitride infiltrated crystals and a value of interparticle spacings were found ~ 238 nm and ~270 nm respectively and found to be in excellent agreement with Bragg’s theory.

Chapter seven introduces natural gravitational sedimentation assisted latex based templated assembly of bare photonic crystals and infiltrated with single walled carbon nanotubes and optical investigation. In the first section of chapter seven, we investigated the debundling procedure of single walled carbon nanotubes by means of non-ionic based surfactant approach to address the issue of aggregation and achieve stable carbon nanotube dispersion. In the next section we fabricated the single walled carbon nanotube incorporated photonic crystals. The photonic crystals made with 290 nm particle diameter polymer. We demonstrated that using a debundled CNTs dispersion of SWCNTs shows homogenous iridescent colours. The stop band position was measured to be ~ 595 nm, which is ~ 10 nm larger than the pristine crystals and is attributed to change in total effective refractive index. We have also demonstrated the tunability in the optical properties of fabricated photonic crystals by applying external mechanical force. The mechanical stress induces alters the periodicity of the photonic crystal and consequently modifies photonic stop band position. To demonstrate the concept, we investigated the effect of mechanical stress on the transmission behaviour and observed a very wide tunability (~30 nm) in the beam propagation direction. This concept provides a means to achieve real-time, dynamic control of photonic bandgap position and will thus expand the applications of photonic crystal structures in advanced photonic sensors.

8.2 Recommendations and Further Work

There are numerous conceivable opportunities and directions for future work related to this thesis results. A better theoretical understanding of these photonic crystals with two-dimensional sheets in the void would be of major benefit.

- This study has focused the optical response study of the photonic crystals in the low energy region where the stop band arises form diffraction of (111) planes. It will be interesting to determine the effect of high energy bands on the optical response on the photonic crystal, as in this high energy region interesting
phenomena occurs such as Super Prism effect where many energy bands overlap and exhibits different behaviour than of the (111) pseudogap.

- A systemic study of polarization and angle dependent optical proprieties will be an asset. As incident light with different polarization will couple, with certain bands depending upon their symmetry character.

- More rigorous analysis needs be done on an experimental and theoretical basis, into how the optical behaviour is changing due to incorporation of one dimensional and two dimensional materials and immediate work is the simulation studies on the infiltrated photonic crystals to determine the effect of infiltration of two dimensional nanoplatelets on the bandstructure diagrams of the photonic crystals.

- On to the simulation side, we have performed the reflection/transmission measurement onto the normal angle of incidence, it will be interesting to do simulation studies for higher incident angles and compare with experimental data.

- Thicker samples generally possess large number of defects, so some investigation should be carried out to determine effect of defects on the optical properties of the crystals.

- Tunable photonic crystals to change photonic bandgap are based on the changing lattice constant or refractive index, which shift the photonic bandgap position upto few 100 nanometres. It will be very exciting to study full tuneable range across all visible range.

- Photonic crystals can modify the emission properties of luminescent materials. This has already been achieved for inorganic materials. There are no reports of incorporating luminescent nanosheets as recently few new reports regarding making of luminescent nanosheets such MoS$_2$ layered materials. It will be interesting to incorporate such luminescent sheets into the crystals and study the optical behaviour. I did some preliminary measurements on MoS$_2$ incorporated photonic crystals and results have been shown in appendix.
References


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Appendices

A1. Transfer Matrix Formalism

Standard matrix formalism has been used for a medium made of successive parallel layers to calculate reflection and transmission coefficients. It was consider that an incident light irradiation is defined by its electric field:

$$\tilde{E} = E_0 \cdot \exp \left(\omega t - \vec{k} \cdot \vec{r}\right) \vec{u} \ldots \ldots \ldots \ldots (1)$$

Where $\omega$ is circular frequency in the $z \leq 0$ region of index $n_0$, $\theta_0$ on a medium consists of $N$ finite parallel layers (perpendicular to $z$, in the $z \geq 0$ region) and ended by a region of index $n_{N+1}$. In eq. (1), $\vec{k}$ and $\vec{u}$ are wave and unit vector respectively, exhibiting the direction of polarization. This formalism allows going from one layer to another layer with certain boundary conditions, mainly continuity of the tangential components of electric and magnetic fields $E$ and $H$ at an interface. It takes into account the transmission and reflection components while propagation in each layer, and propagation at an angle satisfying the Snell's law at the successive interfaces. The both polarization TE and TM, dealt separately, and an arbitrary input polarization has to be processed as a linear combination of principal polarizations.

![Diagram of Transfer Matrix Formalism](image)

From figure A1 notations, one can outline the tangential component of the amplitude component of the E and H field at the generic boundary between the $(i-1)^{th}$ and $i^{th}$ layers as $E_{i-1,i}$ (respectively $H_{i-1,i}$). For the $i^{th}$ layer, the refractive index is defined as $n_i$, the thickness as $d_i$ and the propagation angle as $\theta_i$ with

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\[ n_0 \sin \theta_0 = n_i \sin (\theta_i) \ldots \ldots \ldots \ldots \ldots (2) \]

The transfer matrix \( M_i \) then appears when comparing the \((i-1)\)th and \(i\)th layers boundary, with the \(i\)th and \((i+1)\)th layers boundary.

\[
\begin{bmatrix}
E_{i-1,i} \\
H_{i-1,i}
\end{bmatrix} = \begin{bmatrix}
\cos(\delta_i) & j \sin(\delta_i) / Y_i \\
Y_i \sin(\delta_i) / \cos(\delta_i)
\end{bmatrix} \begin{bmatrix}
E_{i+1,i} \\
H_{i+1,i}
\end{bmatrix} \ldots \ldots (3)
\]

so that

\[
M_i = \begin{bmatrix}
\cos(\delta_i) & j \sin(\delta_i) / Y_i \\
Y_i \sin(\delta_i) / \cos(\delta_i)
\end{bmatrix} \ldots \ldots \ldots (4)
\]

in equation (3) and (4)

\[
\delta_i = \frac{2\pi}{\lambda} n_i d_i \cos \theta_i \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5)
\]

and \( Y_i \) depends on the polarization:

for TE polarization: \( Y_i = n_i \cos(\theta_i) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6) \)

for TM polarization: \( Y_i = n_i / \cos(\theta_i) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7) \)

For \( N \) number of layers, the total matrix is the product of individual transfer matrices, which will also led to calculate the input and output tangential fields by multiplying the different transfer matrices:

\[
\begin{bmatrix}
E_{0,1} \\
H_{0,1}
\end{bmatrix} = M \begin{bmatrix}
E_{N,N+1} \\
H_{N,N+1}
\end{bmatrix} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (8)
\]

With

\[
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix} = M_1 M_2 \ldots M_N \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (9)
\]

The tangential components at the input and output boundaries:

\[ E_{0,1} = E_0 (1 + r) \ldots \ldots \ldots \ldots \ldots (10) \]
\[ E_{N,N+1} = t \cdot E_0 \] ....... ....... ....... (11)

\[ H_{0,1} = E_0(1 - r)Y_0 \] ....... ....... (12)

\[ H_{N,N+1} = E_0tY_{N+1} \] ....... ....... ....... (13)

with \( r \) and \( t \) the standard reflection and transmitted amplitude coefficients

\[
    r = \frac{E_r}{E_0} \quad \text{and} \quad t = \frac{E_t}{E_0} \] ....... ....... (14)

Hence one can deduce:

\[
    r = \frac{Y_0A + Y_0Y_{N+1}B - C - Y_{N+1}D}{Y_0A + Y_0Y_{N+1}B + C + Y_{N+1}D} \] ....... ....... (15a)

\[
    t = \frac{2Y_0}{Y_0A + Y_0Y_{N+1}B + C + Y_{N+1}D} \] ....... ....... (15b)

From these two equations reflection and transmission intensity coefficients can be calculated:

\[
    R = r \cdot r^* \] ....... ....... ....... ....... ....... ....... ....... ....... ....... ....... (16)

and

\[
    T = \frac{n_{N+1} \cos(\theta_{N+1})}{n_0 \cos\theta_0} \cdot tt^* \] ....... ....... ....... ....... ....... ....... ....... ....... ....... ....... (17)

A2. Multi peak fit of Bragg Peak of Photonic Crystal made of 290 nm

In terms of reciprocal space the Bragg diffraction process is associated with Brillouin zone where photonic band gaps open up are essential and when the Laue conditions are satisfied the Bragg diffraction occurs \( k_s = k_i + \mathbf{g}_{hkl} \), where \( k_i \) and \( k_s \) are the wave vectors of the incident and scattered lights, respectively, and \( \mathbf{g}_{hkl} \) is the reciprocal lattice vector.

If the Laue condition holds simultaneously for two planes with different Miller indices \((h_1k_1l_1)\) and \((h_2k_2l_2)\), the spectra show special effects caused by multiple Bragg diffraction of light.

Photonic crystals made with sphere diameter shows doublet at higher incident angles.
from 25 to 30 degree and move to longer wavelength with increasing angles, which can be explained as a results of simultaneous diffraction from the (111) and (200) planes. Figure A1 shows the multi peak fitting of the transmission data for two different incident angles.

A2. Gaussian fit of the double Bragg resonance for photonic crystal at 25 and 30 degree. Red dots shows the Gaussian fit.

A3  Pristine and Graphene Photonic crystals: Repeatability Studies

Ordering quality of the latex spheres remains the most critical parameter and strongly affects the optical properties of fabricated photonic crystals. Photonic crystals grown on substrate with few layer thicknesses generally provide better ordering compared to thick photonic crystals grown by the sedimentation technique. During growth these thick crystals generate various types of disorders in the crystals, including stacking faults, dislocations, point defects and different size of domains. Stacking faults are one of the most common, with densities ~ 10% in sedimented thick photonic crystals, while in thin film photonic crystals it is ~1%. Different sized domains, having various orientations also contribute internal disorder during the self-assembly process. On a pragmatic level ordering is also influenced by polydispersity, concentration of the suspension, substrate flatness, the height of the sediment, temperature, and humidity etc. All these factors affect the optical properties of the photonic crystals and results varied among different samples prepared in the same batch. We prepared various pristine and graphene infilled photonic crystals from one batch and observed significant
effects on the pseudogap peak positions. Figure A1 depicts plot between various pristine and graphene infilled photonic crystal in the same batch.

Figure (a) shows the variation in the stop band position for different photonic crystals. It is attributed to possible changes in the growth condition, which can create structural disorders and which affect the optical properties of the system. Samples with ~505 nm pseudogap were the most repeatable one and have been chosen for our studies. Figure (b) shows the variation in stop band for graphene infilled photonic crystals, where with ~520 nm stop band position crystals were the most repeatable and has been selected for studies. Inset of the graph show two different graphene infilled photonic crystals prepared at the same time. Photonic crystals in the left appears as it has been phase separated during growth and create structural disorder and also possess large disoriented domains, which will alter its optical properties. On the other hand, crystal in the right is well ordered and provides homogenous green diffraction. Optical photograph for pristine crystals has not been included as the crystals are translucent, which make it difficult to observe difference by bare eyes.

A3. Variation in Photonic stop band peak position of Infilled Graphene and Pristine photonic crystals with different specimens.
A4  MoS$_2$ Nanosheets

MoS$_2$ dispersion prepared by the use of non-ionic surfactant in DI water with ad of ultra-sonication to exfoliate Nanoflakes and prepared with starting concentration 0.74 mg/ml. Figure a in A3 show optical image of the MoS$_2$ dispersion in water kept in the glass vial after sonication. As observed from the figure (b) and (c) in general, the MoS$_2$ flakes are irregularly shaped and are multi-layered. Specially figure (b) it is very clear variation in the contrast with increasing number of layers. We measure the lateral dimensions of a large number of flakes ~ 200. We chose to measure the dimension along the long axis and assign it as the length, L, and the dimension perpendicular to the long axis as the width, w. The measured mean MoS$_2$ flake length is $\langle L \rangle = 0.49 \mu m$. The figure (c) shows the photoluminescence spectrum observed from few-layer MoS$_2$ samples. The PL intensity measured at room temperature under excitation at 2.85 eV. The photoluminescence (PL) spectra show a dominant peak at 1.85eV.

![Image](image)

Figure A4 (a) Optical image of MoS$_2$ dispersion in water using TritonX-100 as stabilizer (b) and (c) TEM images of grid coated a MoS$_2$ flakes at different resolution (d) Histogram analysis of the flake length via statistical analysis of TEM showing average length of the flakes ~ 500 nm (e) shows the PL spectrum of MoS$_2$ samples under excitation at 2.85 eV.

A5  MoS$_2$ Infiltrated Photonic crystals: Preliminary Results

Procedure similar to graphene or boron nitride infilled PhC was adopted to make photonic crystal with MoS$_2$. Figure A3 shows three different optical photograph of the photonic crystal taken at different viewing angles. The photonic crystal reflects bright green colour and on careful observation number of tiny domain reflecting bright green spots are also visible. The bottom pictures has been taken at larger angle, it reflects bluish colour due to Bragg’s law of reflection.
A5. Three different optical micrographs of MoS\textsubscript{2} infilled photonic crystals took at different viewing angles.

Figure (A5) shows the normal to the plane and angular dependent transmission spectra of the MoS\textsubscript{2} embedded photonic crystals. As is evident in this figure, prominent stop bands (shaded grey region) appear at the wavelengths of around 440 and 520 nm with center of the peak positioned at ~ 474 nm, which arise due to diffraction of waves on a three-dimensional crystal made of polymer (dielectric) spheres. The dip or stop band peak depends on the lattice period of the crystal. Angular dependent spectroscopy is shown in figure (b) from 0 to 30° at step of 5° and exhibit shift of the first-order Bragg’s peak to a shorter wavelength as the incident angle increases. In addition to the angular resolved spectra of MoS\textsubscript{2} embedded photonic crystals the optical absorbance spectra of MoS\textsubscript{2} dispersion is also plotted in the same spectrum. For the sake of clarity optical absorbance spectra of MoS\textsubscript{2} dispersion was also plotted and presented in the inset of the figure. MoS\textsubscript{2} is an emerging layered material that experiences a distinct transition from an indirect bandgap to a direct bandgap material, when reduce from multilayers to monolayer. Literatures of MoS\textsubscript{2} have reported distinct photoluminescence (PL) at around 1.9 eV which were attributed to bandgap transition in the K-point of the Brillouin zone. It has also been reported that in monolayer MoS\textsubscript{2} valance band splits at the K-point due to spin–orbit coupling two separate exciton bands, the A (674 nm) and B (616 nm) excitons.

It can be readily seen from the inset figure that the absorbance spectra shows strong natural absorption or exciton bands (a and b) in our dispersion with peak positioned at 674 and 616 nm, which matches well with previous published literature. Another
interesting feature observed with angular transmission spectra of MoS$_2$ embedded photonic crystal, were presence of exciton bands in the transmission spectra along with photonic bandgap of the photonic crystal. As expected, it is also seen that exciton features doesn’t shift with any change in the incident angle. A zoomed image of the exciton bands is shown for clear picture.

Fig A5 Optical transmission spectra taken along the (111) crystallographic axis measured on MoS$_2$ photonic crystal at normal incidence (b) Angular dependence transmission spectra of MoS$_2$ infiltrated photonic crystals ranging from 0 to 30$^\circ$ at 5$^\circ$ interval. Position of the transmission minima shifts to shorter wavelengths as a function of various angles. Inset of figure (b) represents the optical absorbance of MoS$_2$ dispersion showing exciton bands and zoomed picture exciton bands show no shift in exciton positions.