Biomimetic chiral gyroids for photonic microstructures

A thesis submitted for the degree of

Doctor of Philosophy

by

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Abstract

Photonic technologies have undergone great developments over the past few decades, heavily inspired by industries such as telecommunications, solar energy, multimedia and defence to name a few. These industries have relied on the constant advancement of photonic devices, with more efficient operation, lower cost, faster speeds, and ultra-compact integration, promoting the innovation of novel materials with enhanced optical properties.

Emerging nano-photonic research fields such as photonic crystals and metamaterials have demonstrated greatly enhanced optical properties unachievable in conventional optical materials. These modern research fields have led to the development of many new photonic technologies such as supercontinuum lasers, super-resolution imaging and all-optical switches.

A photonic crystal is a periodic structure with spatial period comparable in size to the wavelength of light. Unlike unstructured materials, the dispersive properties of a photonic crystal can be engineered through the geometrical design of the structure. At these wavelengths photonic bandgaps exist, frequency bands where light is completely reflected from the photonic crystal due to interference, analogous to the electronic bandgaps formed in semiconductors. This unique control of light has inspired the development of many photonic crystal devices such as integrated optical waveguides, cavities, optical-switches and even super-prisms.
Another related photonic structure is the metamaterial, an artificially engineered material consisting of a collection of highly sub-wavelength structures, also known as meta-atoms. Unlike natural materials, the optical properties of a metamaterial is determined purely by the geometry and composition of its sub-wavelength meta-atoms. This powerful design principle provides the ability to engineer novel materials with optical properties that are not found in nature such as negative refraction and invisibility cloaking.

*Optical activity* and *circular dichroism* are two chiral-optical phenomena discovered in 1811 and 1847, respectively. These phenomena arise from the intrinsic chirality of the atomic or molecular structure of materials such as quartz crystals. Today optical activity and circular dichroism are used to form polarisation rotators, optical isolators and are even used in biological spectroscopy. However, these chiral-optical properties are relatively weak in *natural* materials, inhibiting the development of compact photonic polarisation devices.

Chiral nanostructures are excellent candidates for the development of novel materials with extremely high chiral-optical properties. When geometrical asymmetries such as chirality are introduced into a photonic crystal or a metamaterial, the photonic structure becomes highly sensitive to the polarisation of light. Through this strong chiral light-matter interaction, naturally weak phenomena such as optical activity or circular dichroism can be greatly enhanced opening up the potential for the development of microscopic polarisation devices.

The aim of this thesis is to theoretically and experimentally investigate the chiral-optical properties of three-dimensional chiral photonic microstructures. Our photonic structures are based on the biomimetic gyroid network (also known as the *srs-network*). Gyroid structures naturally occur in several biological nanostructures such as the wing scales of the *Callophrys Rubi*.
butterfly. The srs-network is a three-dimensional periodic network with both cubic symmetry and chirality and thus is an excellent platform for the development of chiral photonic crystals and chiral metamaterials with greatly enhanced chiral-optical phenomena.

In order to understand the photonic crystal properties of a dielectric srs-network, we have performed a detailed theoretical analysis of this chiral photonic crystal. We have demonstrated that the chiral srs-network possesses strong circular dichroism. To elucidate the physical mechanisms behind the observed circular dichroism, we performed a polarisation analysis of the eigenmodes of the srs-network. We have discovered that circular dichroism bands are formed within the srs-network due to the asymmetric coupling of circular polarisation to the Bloch modes of the srs-network.

Inspired by these theoretical findings, we have fabricated a series of polymer srs-networks at the micron-scale using three-dimensional laser nanolithography commonly known as the direct laser writing method. The high precision and uniformity of the direct laser writing method has allowed us to accurately replicate these complex three-dimensional chiral designs. These periodic polymer chiral networks operate as chiral photonic crystals at wavelengths comparable to their spatial period and we have experimentally characterised their optical properties demonstrating the existence of strong circular dichroism bands.

To improve the symmetry of the fabricated srs-networks we have developed the galvo-dithered direct laser writing method. We have demonstrated the symmetry correction of the fabrication voxel which eliminates unwanted birefringence, greatly enhances the mechanical stability of the microstructure and improves the axial resolution. These features have provided the ability to reduce the periodicity of the srs-network to 1.2 μm with a circular dichroism band at the important telecommunication wavelength of 1.55 μm.
These technical achievements have opened up the ability to develop a range of novel functional photonic devices with circular polarisation sensitivity. One possible application of the srs-network photonic crystal is a chiral analogue of the linearly polarising beamsplitter that was first invented in 1828 by William Nicol. By utilising the srs-network as a highly chiral material, we have fabricated and experimentally characterised a chiral beamsplitter. To the best of our knowledge this is the first experimental demonstration of a nano-engineered chiral beamsplitter. We performed numerical simulations of the beamsplitter prism, which are in good qualitative agreement with experimental results. Importantly, we have found that this phenomenon is due to the diffractive properties of the chiral PC.

The srs-network is also an attractive design for the development of three-dimensional chiral metamaterials. We have performed a detailed theoretical study of metallic gyroid networks with a variety of geometrical configurations. We have shown that a metallic srs-network performs as a metallic photonic crystal with strong circular dichroism. On the other hand, a metallic composite consisting of 4 intertwined srs-networks performs as a chiral metamaterial operating at longer wavelengths with ultra-broadband circular dichroism.

To experimentally investigate these metallic gyroid metamaterials, we have performed electroless silver deposition on gyroid networks that have been fabricated via GD-DLW within a modified polymer photoresist. We have shown the silver coating of these polymer gyroid networks and provide experimental characterisation of their optical properties at mid-infrared wavelengths. These metallic gyroid networks possess strong broadband circular dichroism and are promising candidates for the development of novel chiral metamaterials.

This thesis demonstrates for the first time that the biomimetic gyroid network is an excellent geometrical design for photonic nanostructures and microstructures. The applications of these chiral nano-photonic structures
will be of high importance to the design of microscopic polarisation devices, providing a unique functionality not possible using natural chiral materials. The operation of these gyroid structures at optical wavelengths and efficient fabrication via three-dimensional nano-lithography make them highly desirable in integrated photonic chips and nano-photonic devices.
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My first thanks goes to my supervisor, Prof. Min Gu, who has provided me with an exciting and fulfilling research project over the past 4 years. I appreciate the many detailed conversations we shared on our research and the career mentoring he has provided me. One of the most important lessons I have learnt from Min is the concept of research vision, which guides a research project along the right path. I also appreciate the confidence that he has had in me from day one and the many resources that have been provided.

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Mark Turner

Melbourne, Australia

11th February, 2013
Declaration

I, Mark Daniel Turner, declare that this thesis entitled:

“Biomimetic chiral gyroids for photonic microstructures”

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

Figs. 2.13c-f have been provided by Dr. Michael Thiel.
Figs. 2.13a,b,g and Fig. 2.14 have been provided by Dr. Gerd Schröder-Turk.
Figs. 3.10, 3.11a and 4.6c have been provided by Mr. Matthias Saba.
Fig. 6.1 has been provided by Dr. Alessandro Antonello.

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## Nomenclature

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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>bcc</td>
<td>Body-centred cubic</td>
</tr>
<tr>
<td>CBS</td>
<td>Chiral beamsplitter</td>
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<tr>
<td>CD</td>
<td>Circular dichroism</td>
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<tr>
<td>CMC</td>
<td>Constant mean curvature</td>
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<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>DLW</td>
<td>Direct laser writing</td>
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<tr>
<td>ESD</td>
<td>Electroless silver deposition</td>
</tr>
<tr>
<td>FBG</td>
<td>Fiber Bragg grating</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centred cubic</td>
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<tr>
<td>FEM</td>
<td>Finite element method</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>GD-DLW</td>
<td>Galvo-dithered direct laser writing</td>
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<tr>
<td>Acronym</td>
<td>Definition</td>
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<tr>
<td>---------</td>
<td>-----------------------------------</td>
</tr>
<tr>
<td>LHD</td>
<td>Left handed</td>
</tr>
<tr>
<td>LPBS</td>
<td>Linearly polarising beamsplitter</td>
</tr>
<tr>
<td>MIR</td>
<td>Mid-infrared</td>
</tr>
<tr>
<td>MN</td>
<td>Metallic nanostructure</td>
</tr>
<tr>
<td>MPB</td>
<td>MIT photonic bands</td>
</tr>
<tr>
<td>MPC</td>
<td>Metallic photonic crystal</td>
</tr>
<tr>
<td>MPR</td>
<td>Modified photoresist</td>
</tr>
<tr>
<td>N.A.</td>
<td>Numerical aperture</td>
</tr>
<tr>
<td>NIM</td>
<td>Negative index material</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
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<tr>
<td>NP</td>
<td>Nanoparticle</td>
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<tr>
<td>PBG</td>
<td>Photonic bandgap</td>
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<tr>
<td>PC</td>
<td>Photonic crystal</td>
</tr>
<tr>
<td>PEC</td>
<td>Perfect electric conductor</td>
</tr>
<tr>
<td>PHT</td>
<td>Plasmon hybridisation theory</td>
</tr>
<tr>
<td>RHD</td>
<td>Right handed</td>
</tr>
<tr>
<td>sc</td>
<td>Simple cubic</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>---------------------------------</td>
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<tr>
<td>SLM</td>
<td>Spatial light modulator</td>
</tr>
<tr>
<td>TE</td>
<td>Transverse-electric</td>
</tr>
<tr>
<td>TM</td>
<td>Transverse-magnetic</td>
</tr>
<tr>
<td>TPMS</td>
<td>Triply periodic minimal surface</td>
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Chapter 1

Introduction

Photonics is the study of light and its interaction with matter. Over the past few decades photonics has greatly influenced both the academic and industrial worlds. Telecommunication remains one of the largest industrial applications of photonics, with the world now connected through extremely thin glass fibres used to transmit optical signals from country to country. The development of such an advanced telecommunication industry is due to the great advancements in photonic technologies such as lasers, optical fibres, fibre amplifiers, photodetectors and many more photonic devices.

Other important applications of photonics include solar cells, light-emitting-diodes, sensing and materials processing just to name a few. With the growing size of the photonics industry, many new research fields have been developed that have led to a great impact on the photonics community. The demand for ultra-compact integrated photonic devices with enhanced physical properties has promoted the research into nano-photonics. Three of the most recent topics in the field of nano-photonics include:
Photonic Crystals (PCs): These are periodic structures used to selectively reflect, transmit and disperse specific wavelengths of light through periodic-interference within the structure. Applications of PCs today include PC fibres used commonly in super-continuum lasers (broadband laser sources with spectral bandwidths spanning from the visible up to the mid-infrared).

Metamaterials (MMs): These are artificial materials whose optical properties are not governed by the atomic response to light, but instead governed by nano-engineered meta-atoms. This allows researchers to engineer new materials with optical properties that do not exist in nature, such as a negative refractive index material. Applications of this research are still academic, but with many promising technologies including super-resolution imaging and invisibility cloaking.

Plasmonics nanostructures: These are highly sub-wavelength metallic nanostructures that are used to focus light to sizes much smaller than the wavelength and enhance the local electric or magnetic fields by several orders of magnitude. Applications of this technology include plasmonic sensing, which utilises the massive light-matter interaction between the focused fields and surrounding medium to greatly enhance the sensitivity.

Whilst these three fields of photonics are fundamentally very different, they all aim at the development of novel technologies utilising light to achieve functionality beyond that of current technologies. They also possess several common features including:

I. Materials science: These technologies often rely on the development of new materials suitable for the structuring/patterning of these materials, such as polymers, metals and quantum dots.

II. Nano-engineering: For applications at optical wavelengths all of these technologies require engineering at the nanometre-scale. A nanometre is one
billionth the size of a metre and approximately 100,000 times smaller than the width of a human hair.

**III. Geometry:** The geometry of the nano-engineered structures determine their physical properties and thus how light interacts with them. Asymmetries such as chirality induce photonic asymmetries like circular polarisation sensitivity.

In this introductory chapter we provide the basic foundations of the following photonics research fields used within this research thesis. At the end of this introductory chapter we discuss the objectives and outline of this PhD research thesis.

### 1.1 Chirality in optics

This section introduces chirality, first from a geometrical description and then how naturally occurring chiral materials possess chiral-optical phenomena such as optical activity and circular dichroism. We briefly discuss the limitations of these naturally occurring media and their most important applications used today.

Chirality is a type of asymmetry whose name derives from the Greek word *kheir* meaning *hand*. A chiral object is one whose mirror image cannot be translated or rotated back on itself. Simply put, an object that is chiral is one whose mirror image is different from itself. An object that does not possess chirality, has mirror symmetry and thus is an achiral object.

An example of a two-dimensional (2D) chiral object is the human hand, and hence the relationship to the Greek word *kheir*. Figure 1.1a contains images of a left-handed (LHD) and right-handed (RHD) human hand.
Examples of chiral objects. (a) Human hands are 2D chiral objects. (b) A LHD helix (left) and a RHD helix (right) are 3D chiral objects.

These two human hands are mirror images of each other and no translations or rotations applied within the 2D plane, can transform one object to the other. However, a 2D chiral object can be converted to its mirror image if it is rotated 180 degrees around the mirror axis. On the other hand, a three-dimensional (3D) chiral object cannot be mapped onto itself no matter what 3D translation or 3D rotation is performed to it. An example is given in Fig. 1.1b, which contains a LHD and RHD helix.

1.1.1 Optical activity

Optical activity is a physical phenomenon related to the rotation of polarisation in a chiral medium. In 1811 François Arago discovered that light could penetrate through two orthogonal linear polarisers when a piece of quartz crystal was placed in between them [1] as illustrated in Fig. 1.2. This transmission of light was due to the rotation of the polarised light through the quartz crystal, a phenomenon that occurs due to the asymmetric chiral arrangement of the crystal lattice.
Soon after, in 1815 Biot [2] discovered that tartaric acid also showed optical activity. It was later shown by Pasteur in 1848 [3] that this phenomenon was related to the chirality of the individual molecules of the liquid as opposed to the chiral structural arrangement of crystals like quartz.

![Illustration of optical activity](image)

**Figure 1.2** Illustration of optical activity. Vertically polarised light incident on the quartz crystal gets rotated by an angle $\theta$ due to the optical activity of the chiral crystal. This results in the non-zero transmission through the horizontal polariser.

Optical activity occurs when the refractive indices of LHD and RHD circularly polarised light, $n_{LCP}$ and $n_{RCP}$, respectively are not equal. This means the material is able to differentiate (discriminate) between LHD and RHD circularly polarised light. The effect of this refractive index difference is to rotate the polarisation of light when propagating through the quartz crystal or other optically active media. Note that a linearly polarised wave can be broken up as the sum of a LHD and a RHD circularly polarised wave. When this linearly polarised wave passes through an optically active media (of length $L$), one of the circular polarisation wave picks up an extra phase ($\phi$), relative to the other, where $\phi \propto (n_{LCP} - n_{RCP})L$. Assuming that the amplitudes of both waves are equal after passing through the crystal (i.e. there is no circular dichroism), the output beam is again linearly polarised but now rotated at an
angle.

Quartz has a relatively strong optical activity and today one can purchase quartz-based polarisation rotators that utilise the optical activity of the chiral media. The optical rotation from these chiral materials is analogous to the Faraday effect (also known as magneto-optical rotation), which occurs when a magnetic field is applied to a material [4]. However, unlike the Faraday effect which is non-reciprocal, optically active media do possess reciprocity.

The sign and strength of the optical activity in a material is greatly dependent on the molecular or atomic structure thus making this technique highly valuable in the characterisation of biological and chemical samples. This technique is called optical rotary dispersion and involves the measuring of the optical activity of the sample over a spectral range of interest that gives information of the structure of the sample at the molecule scale [5].

1.1.2 Circular dichroism

Similar to optical activity, circular dichroism is a physical phenomena related to the discrimination in transmission of circularly polarised light in a chiral medium. However, where optical activity is related to the refractive index of a material, circular dichroism is related to the absorption. Circular dichroism was discovered in amethyst quartz crystals by Wilhelm Haidinger in 1847 [6]. In this case the chiral crystal had different absorption coefficients depending if it was illuminated with LHD or RHD circularly polarised light.

Traditionally circular dichroism refers to the difference in absorption of chiral media, as it was used to determine information about the molecular structure of the sample. It is a popular method used commercially to characterise chemical and biological samples today. Today the term circular dichroism is also used
for differences in the reflection of LHD and RHD polarised light, which is discusses in more detail in Chapter 2.

Circular dichroism spectroscopy is preferred over optical rotary dispersion [5] as it typically has more well defined spectral features due to the sharp cut-offs of the circular dichroism absorption bands. Other applications of circular dichroism include polymer and pharmaceutical compound characterisation [7].

### 1.2 Photonic crystals

In this section we introduce the foundational theory of a PC, a structure with periodically alternating refractive index in one, two or three dimensions as shown in Fig. 1.2 [8].

Through the design of the PC symmetry, size and materials of a PC one can tailor the transmission, absorption, and reflection spectra, as well as dispersion of light [8]. Thus PCs are an excellent tool for developing novel optical devices with unique optical properties not achievable in standard materials. In this introductory section on PCs we shall discuss the fundamentals of photonic...
bandgaps, 3D PCs, metallic PCs and the broad range of applications of this emerging technology.

These PCs have the ability to manipulate light in many unnatural ways, leading to a broad range of interesting physical phenomena such as the slow light effect [9–11], the superprism phenomena [12–14], spontaneous emission enhancement[15], waveguiding [16], micro-cavity lasers [17] and many more.

1.2.1 Photonic bandgaps

A unique property of PCs is that they can be designed to have tailored dispersive features, including a photonic bandgap (PBG). This is a frequency band where due to the interference of light within the periodic structure, light cannot propagate through the PC and is instead completely reflected [8]. This phenomena can be explained by observing the form of Maxwell’s equations where no external sources or currents are present:

\[
\begin{align*}
\nabla \cdot D &= 0, \\
\nabla \cdot B &= 0, \\
\n\nabla \times E &= -\frac{\partial B}{\partial t}, \\
\n\nabla \times H &= \frac{\partial D}{\partial t} = \varepsilon(r) \frac{\partial E}{\partial t},
\end{align*}
\]

(1.1)

where \(\varepsilon(r)\) is the lossless permittivity of the material and no magnetic materials are present such that the permeability \(\mu = \mu_o\). If we now assume that the electric fields have the form of time oscillating fields \(E(r,t) = E(r)e^{-i\omega t}\) and \(H(r,t) = H(r)e^{-i\omega t}\). Then Maxwell’s equations can be combined to form the so called master equation [8]:

\[
\nabla \times \left(\frac{\nabla \times H}{\varepsilon_r(r)}\right) = \frac{\omega^2}{\varepsilon^2} H.,
\]

(1.2)
This is in the form of an eigen-equation $\Theta H = \frac{\omega^2}{c^2} H$, where $\Theta = \nabla \times \nabla \times \varepsilon(r)$, is a Hermitian operator (i.e. $\Theta^\dagger = \Theta$), the magnetic field $H$ is the eigenvector, and $\omega^2/c^2$ the eigenvalue. The operator $\Theta$ will contain certain symmetries based upon the dielectric constant $\varepsilon(r)$. As for the case in quantum mechanics, the symmetries of the operator $\Theta$ should be reflected in the solutions to the fields $H$. Note that the electric fields can be found from the solution of the magnetic field via $\nabla \times H = \frac{\partial D}{\partial t}$, so they too obey the symmetries of the operator $\Theta$. The effects of asymmetries such as chirality on the solutions to Maxwell’s equations (and hence the optical properties of a material) is a major focus of this thesis and will be discussed in later chapters.

The effects of the periodicity on the solutions of Maxwell’s equations are analogous to the effects of a periodic potential in quantum mechanics, such as that found in semiconductor crystals. Semiconductors possess 3D periodic potentials due to the crystalline atomic lattice. This leads to the formation of electronic bandgaps, an energy range where electrons cannot exist. In PCs the periodicity of the structure causes PBGs to form, a frequency range where propagating photons cannot exist [8]. Instead the solutions to Maxwell’s equations here are evanescent, i.e. they decay exponentially in strength as they propagate through the PC. Therefore, light that is incident on a PC at a frequency in the photonic bandgap, cannot transmit through, and instead is reflected back.

A simple example of a one-dimensional (1D) PC is the multi-layer stack, which consists of a periodic modulation of the refractive index along the direction of propagation. This PC is also known as the Bragg mirror, as the interference of light is analogous to the interference of x-rays in a crystal, where constructive and destructive interference cause certain wavelengths to be reflected. Bragg gratings are used extensively today within the fibre optics industry to selectively reflect a particular wavelength within an optical fibre by
designing a bandgap at the wavelength of operation. As with Bragg scattering in crystals, the 1D PC is dependent on the direction of propagation and geometry/symmetry of the PC. The band diagram of two different 1D PCs is shown in Fig. 1.2.1.

![Band Diagrams](image)

Figure 1.4 Theoretically calculated band diagrams for two different 1D PCs. The PBGs are highlighted in red. a) A 1D PC consisting of layers of GaAs ($\epsilon = 13$) and AgAlAs ($\epsilon = 12$). b) A 1D PC consisting of layers of GaAs ($\epsilon = 13$) and air ($\epsilon = 1$).

The band diagram for a 1D PC consisting of periodic layers of GaAs ($\epsilon = 13$) and GaAlAs ($\epsilon = 12$) is shown in Fig. 1.2.1a. In this band diagram a small frequency range exists around $\omega a / 2\pi c = 0.15$ (highlighted in red), where no modes are present (i.e. a PBG). Light in this narrowband frequency region would be completely reflected from the PC. As shown in Fig. 1.2.1b, when the dielectric contrast of the 1D PC is increased by replacing the GaAlAs layer with a layer of air ($\epsilon = 1$), the frequency range of the PBG is widened. Thus in order to develop PCs with broadband PBGs, a high refractive index contrast is required [8].

On a practical note, when considering the experimental fabrication of a PC, the PBG is formed due to the collective interference from the entire structure. Therefore, uniformity and accuracy of the fabricated structure is essential.
to forming strong PBGs. This places a high importance on the fabrication technique especially when designing PCs to operate at optical frequencies where nanoscale precision is required.

1.2.2 3D photonic crystals

We have seen that 1D PCs can possess a broadband PBG. However, due to the lack of periodic structuring in the other two dimensions, they do not possess PBGs for waves propagating perpendicular to the periodicity direction. When control of light is required in a higher dimensionality, 2D or 3D periodic structures must be considered in order to form a PCs with bandgaps in multiple directions. A 2D PC can be used to form multi-directional PBGs that prohibit light to propagate within the plane of the PC [8]. By introducing point defects to these 2D PCs one can create 2D cavities, useful for the development of micro-scale lasers [17] with enhanced emission due to the Purcell enhancement [18].

A 3D PC unlike the 2D and 1D versions, has the ability to completely prohibit the propagation of light in all directions. Such a phenomenon is called a complete PBG. One of the first experimental realisations of a 3D PC was the Yablonovite PC [19], which was fabricated from a dielectric slab, with holes drilled in it in three different directions to form a centimetre scale PC, forming PBGs in the microwave regime.

In 1994 the woodpile 3D structure was suggested in [20] and [21] as a PC with broadband complete PBG. It was later experimentally realised with an optical PBG in 1999 by stacking rods of silicon together [22] as shown in Fig. 1.5. Soon after, the woodpile PC was realised via layer-by-layer direct laser writing, in negative polymer photoresists [23, 24], chalcogenide [25] and also silicon [26].
Figure 1.5 The silicon woodpile PC, consisting of stacking of silicon rods to form a 3D periodic structure made of a high index ($\epsilon = 12$) material. a) The woodpile design. b) A scanning electron microscope (SEM) image of the silicon woodpile PC. c-d) Transmission (c) and reflection (d) spectra showing a broadband PBG around 1.6 $\mu$m. Images from [22].

1.2.3 Metallic photonic crystals

Since PCs require a periodically altering electrical permittivity, dielectrics and semiconductors are typically the materials of choice due to their low loss at optical and infrared frequencies as discussed in the previous sections. However, the range of dielectric contrasts that are available from practical combinations of materials and their corresponding fabrication methods, limits the achievable PC designs.

On the other hand, metals naturally have a large negative permittivity in the optical region. For example, silver has a permittivity of $\epsilon = -52 + 0.78i$ at
the wavelength of 1000 nm when assuming a Drude-like response [27]. This very large (and negative) value of the permittivity creates a large contrast with other dielectrics or even air. Thus metallic photonic crystals (MPCs) are candidates for the design of PCs with large complete PBGs. In Fig. 1.6 we show examples of recently fabricated MPCs reported in literature.

![SEM images and optical response](image)

**Figure 1.6** a-b) SEM images of a tungsten woodpile PC with silica background (a) and with the silica background removed (b). c-d) Optical response of the MPC showing broadband PBG at the long wavelengths and a formation of the pass-band around 5 µm (c). The reflectance spectra at different angles (d) show the existence of the long-wavelength bandgap at different angles. Images from [28].

In [28] a 4-layer tungsten woodpile PC was fabricated and shown in Figure 1.6a. This MPC was engineered by first fabricating a silicon/silica woodpile structure in a glass background. The silicon rods were then removed, followed by infiltration of the remaining holes with tungsten via vapour deposition. The silica glass was then removed to leave behind the tungsten metal PC structure. A large complete PBG from $6\mu m - 25\mu m$ was observed.
There are a few important differences between PCs based on dielectrics and MPCs. Firstly, at wavelengths much longer than the periodicity, the PC can be considered as a homogeneous material, with an average permittivity between the materials of the PC. This leads to almost 100% transmission at these long wavelengths, with the only reflection being due to that of Fresnel reflection. For a dielectric PC such as the silicon woodpile, this leads to an average permittivity somewhere between that of silicon and air. However, for metals due to the large negative permittivity the average permittivity is not that of a dielectric but instead of a diluted metal, with longer plasma wavelength. The result, is a semi-infinite bandgap as seen in that of the tungsten PC [28].

Due to the extreme contrast between metals and air, the light-matter interaction within MPCs is much stronger than that in dielectric PCs. Therefore, MPCs do not require many periods of the lattice structure to achieve a PBG with a deep transmission gap. For example the four layers of tungsten rods was enough to show a deep complete PBG in the infrared region [28]. The ability to have such strong light-matter interactions within MPCs is important for the realisation of more compact optical devices.

### 1.2.4 Applications

One of the major applications of the 1D PC is the fibre Bragg grating (FBG), a section of optical fibre that has a periodic index modulation, with periodicity close to the wavelength of operation [29]. When engineered correctly, this leads to a very high reflectivity of a specific wavelength, an excellent ability for the filtering of certain signals in a telecommunications system (i.e. the equivalent of an electronic notch filter). Today, FBGs are used extensively and for a broad range of applications in photonics [30]. For example in a fibre laser one can use these FBGs as mirrors analogous to the mirrors in a laser cavity.
Another major application of PCs is the PC fibre, used today in the generation of a super-continuum light source [31]. A PC fibre is an optical fibre that does not guide via total internal reflection but instead, confines light by a 2D PC that surrounds the core. Today super-continuum light sources are used for their ultra-broadband output (e.g. the Fianium super-continuum laser that spans from 400-2400 nm), yet laser-like high intensity. Combined with a tunable optical filter, these light sources make excellent tools for spectroscopic characterisation in the visible, near-infrared (NIR) and mid-infrared.

1.3 Metamaterials

The interaction of light with matter can be solved through Maxwell’s equations as long as the optical properties of the materials within the system are known. More specifically, the permittivity $\epsilon(\omega)$ and permeability $\mu(\omega)$, which in general are complex, frequency dependent and vary greatly between different materials. In natural materials the values of $\epsilon(\omega)$ and $\mu(\omega)$ are given by the atomic/molecular structure of the material and their values cannot be changed without changing the atomic/molecular composition. For example, a dielectric material such as glass has $\epsilon \approx 2.1$ and $\mu \approx 1$ at optical wavelengths. These optical properties of glass enables it to transmit light without any significant loss and cause light to refract. In contrast, silver has a Drude-like response giving it a very dispersive permittivity, with $\epsilon = -52 + 0.78i$ and $\mu \approx 1$ at the wavelength $\lambda = 1000\ nm$ [27], leading to its high reflectivity. The natural world provides photonics with a broad range of materials with different optical properties. However, there exist an entire realm of optical properties that cannot be found in any known natural materials.

A MM is an artificially engineered material, whose electromagnetic properties are not given purely by the atomic/molecule structure of the material, but
instead given by the engineering of meta-atoms, highly sub-wavelength metallic components designed to control light in unnatural ways. In this section we introduce the theory and concept of MMs, provide some examples and discuss their potential applications.

### 1.3.1 The concept

When light interacts with a material, such as a piece of glass, the electromagnetic fields interact with the atoms of the glass, which respond in the form of creating electric dipoles. However, since the wavelength of optical light is many orders of magnitude larger than the size of these atoms, the light does not notice the atomic structure of the glass but instead passes through the glass as though it was a completely homogeneous material, with optical properties $\epsilon(\omega)$ and $\mu(\omega)$.

The concept of MMs, invented by Pendry [32] is to design meta-atoms, artificial objects whose size ($a$) is much smaller than the wavelength of light ($\lambda$), such that a collection of these objects can be considered a homogeneous bulk material to light. More importantly, the optical properties of the MM are now given by the design of the meta-atoms. This elegant concept allows scientists to engineer the optical properties through the geometry of the meta-atoms, and lead to values of $\epsilon(\omega)$ and $\mu(\omega)$, non-existent in natural materials.

A MM is an artificial material composed of a (typically periodic) collection of highly sub-wavelength structures known as meta-atoms. The shape, size and composition of these meta-atoms define the optical properties of the MM. Thus, unlike PCs, the unit cells of MMs must be much smaller than the wavelength of light. For a lattice constant $a$, this implies $\lambda \gg a$, such that the light does not undergo refraction and diffraction upon the individual elements of the structure, and instead sees the MM as a homogeneous medium with an
effective $\epsilon(\omega)$ and $\mu(\omega)$ [32, 33].

1.3.2 Characterisation

Characterising the optical properties of MMs can be a challenge both theoretically and experimentally. Today there are many different approaches to calculating $\epsilon(\omega)$ and $\mu(\omega)$ for a MM, and in this section we shall briefly review three main methods.

Note that in a MM where the geometry does not contain any chirality and possess inversion symmetry (i.e. it has no bi-anisotropy), then the optical properties can be completely described by the permittivity and permeability:

$$D = \varepsilon_o \varepsilon(\omega) \vec{E}.$$  \hspace{1cm} \text{(1.3)}

$$B = \mu_o \mu(\omega) \vec{H}.$$  \hspace{1cm} \text{(1.4)}

Note however that these values of $\varepsilon(\omega)$ and $\mu(\omega)$ are in general tensors as MMs can be highly-anisotropic depending on the geometry of the design. Note that for all of these characterisation methods and in the field of MMs in general, the assumption that the MM can be considered as homogeneous is only strictly valid when the wavelength is much larger than the unit cell (i.e. $\lambda > 10a$). However in practice $\lambda > 4a$ or even $\lambda > 2a$ can sometimes be used, depending on the application.

1.3.2.1 Parameter retrieval

The parameter retrieval method was first introduced to calculate the optical properties of a MM [34]. This method is based on measuring the complex reflection and transmission coefficients (also known as S-parameters in the
engineering community) of an electromagnetic wave passing through a slab of the MM of interest. By making the assumption that the electromagnetic wave sees the MM as a purely homogeneous bulk material, with a defined thickness, then one can backtrack from the reflection and transmission values to calculate the associated optical properties. Note that these calculations are done at multiple wavelengths in order to calculate the MM properties over a spectral range.

For a electromagnetic wave, with incident wave-vector $k$, with complex transmission coefficient $t$, and complex reflection coefficient $r$, the wave-impedance and refractive index of a MM of thickness $d$, is given by [34]:

$$z = \sqrt{\frac{(1 + r)^2 - t^2}{(1 - r)^2 - t^2}},$$  
(1.5)

$$n = \pm \text{Re} \left( \cos^{-1} \left( \frac{1}{kd} [1 - r^2 + t^2] \right) \right) + \frac{2\pi m}{kd} \pm \text{Im} \left( \cos^{-1} \left( \frac{1}{kd} [1 - r^2 + t^2] \right) \right),$$  
(1.6)

where $m$ is an arbitrary integer that must be chosen carefully, to select the correct physical value of $n$. Due to the electromagnetic wave not being amplified by any source, the imaginary part of the refractive index must be greater than zero (lossy). The signs of the real part of the refractive index can in general be both positive or negative, which we shall discuss more in the following section. Having calculated the refractive index and impedance of the MM the associated $\epsilon(\omega)$ and $\mu(\omega)$ can be derived simply by [34]:

$$\epsilon = \frac{n}{z},$$  
(1.7)

$$\mu = nz.$$  
(1.8)
By calculating the values of $\epsilon(\omega)$ and $\mu(\omega)$ we can understand how strong the electric and magnetic response of the MM are respectively. Whilst the parameter retrieval method is a relatively simple concept and the most commonly used method to characterise MMs, it can often produce issues when trying to resolve the branching problem (i.e. when choosing the correct value of $m$), which comes from the inverse cosine function.

1.3.2.2 Field averaging (homogenisation)

Field averaging was introduced as an alternative to the parameter retrieval method [35], and is commonly used when analytical or numerical solutions of the MM are known. This method consists of taking an average of the local electric ($E(r, \omega)$) and applied magnetic fields ($H(r, \omega)$) and comparing them to the average of the local electric-displacement ($D(r, \omega)$) and magnetic fields ($B(r, \omega)$). By calculating the ratio of these fields to one another, the permittivity and permeability of the MM can be calculated, i.e. $\epsilon_{ij} = D_i/E_j$ and $\mu_{ij} = B_i/H_j$ [35].

Field averaging is also a simple concept, and unlike the parameter retrieval method, it does not have issues of branching. However, it is an analytical/numerical technique that requires measurement and integration of local fields along complex and curved paths or areas.

1.3.2.3 Bloch mode extraction

The Bloch mode extraction method was initially created for the calculation of the wave-vector within PC waveguides [36], and can be applied both theoretically and experimentally [37]. In periodic MMs this method can also be used to calculate the wave-vector and hence the refractive index of the
MM [38]. The method is based on the principle of measuring the electric (or magnetic) fields along the direction of propagation, ensuring that the field is measured multiple times per unit cell of the MM. By optimising the wave-vector of a harmonic signal to this measured field, one can derive the associated wave-vector of the MM, \( n = k/k_o \), where \( k_o \) is the free-space wave vector. The wave impedance can then be calculated as in the parameter retrieval method, as this does not suffer from any branching issues, to complete the MM characterisation.

1.3.3 Artificial magnetism and negative refractive index

Unlike at direct current and radio frequencies, naturally occurring materials have magnetic permeabilities, \( \mu(\omega) \) very close to the free space value \( \mu_o \) at optical frequencies. This is because magnetic field interactions with matter are a factor of \( \alpha^2 \) weaker than electric field interactions [39], where \( \alpha \approx 137 \) is the fine-structure constant. On the other hand, MMs can have arbitrary values of both electric permittivity and magnetic permeability, are an excellent candidate for creating magnetism at optical wavelengths.

In 1999 Pendry theoretically showed that artificial magnetism with an effective permeability, \( \mu \), could be engineered through a structure comprised of conductors with no intrinsic magnetism (i.e. \( \mu = \mu_o \)) [32]. This was achieved by arranging arrays of metallic cylinders and planar metallic rings as shown in Figures 1.7a-c [32].

When electromagnetic fields are applied to these split-ring structures the magnetic fields aligned parallel to the cylinder axis can induce a circular current around the two rings as shown in Figure 1.7b. This current loop creates a magnetic field of its own, which can enhance or counteract the incident magnetic field depending on the frequency of the incident electromagnetic
wave. The splits in the rings act as a capacitor, with current flow continuity achieved via a displacement current between the inner and outer rings [32].

![Figure 1.7](image-url) **Figure 1.7** a) Metallic split ring cylinders. b) Diagram of the current flow and charge distribution within a metallic split-ring structure. c) Effective magnetic permeability of the structure in a) and b) showing permeabilities with negative values at resonance assuming a perfect electric conductor for the metal. Image from [32].

By assuming that the metal is a perfect electric conductor, valid in the radio-frequency regime, the effective magnetic permeability of the structure of Figures 1.7a,b was calculated [32] and shown in Figure 1.7d. At the resonant frequency $\omega_o$ the permeability diverges, and for frequencies $\omega_o < \omega < \omega_{mp}$, the permeability is negative, where $\omega_{mp}$ is the frequency associated with the magnetic plasmonic resonance. Thus we see that the split-ring structure is able to create an effective “magnetic-plasma” analogous to how metals form an electronic plasma.

In theory this concept can be translated to the optical regime, and with recent improvements in nano-lithography optical magnetism has now been achieved using pairs of metallic nanorod resonators [40], as shown in Fig. 1.8. The MM here was fabricated via electron-beam lithography and showed a negative permittivity and negative permeability, creating a negative index MM, at optical wavelengths. Note that due to the high losses of metals at the optical
wavelengths, the imaginary components of the refractive index is very high. This loss can be minimised through design [41] or by introducing gain into the medium, which has recently been shown to completely remove losses all together [42].

In 1968 it was proposed [43] that a material with simultaneously negative permittivity and permeability would have a negative refractive index. That is, if $\epsilon < 0$ and $\mu < 0$ simultaneously, then the negative sign of the square root must be taken for the refractive index, i.e. $n = -\sqrt{\epsilon\mu}$. It was shown recently [44] that a negative index material (NIM) can be used to make a perfect lens i.e. one can beat the diffraction limit and in theory focus a point source down to a perfect infinitesimally small point, see Fig. 1.9.

This ability for perfect lens focusing is due to two unique features of a NIM. Firstly, light propagating in a NIM accumulates negative phase causing light to come to a focal spot after the NIM, as seen in Figure 1.9. In a conventional lens, the evanescent waves that contain high spatial frequency information of the object are lost. This is because the evanescent waves decay away from
their source and are not collected by a standard lens. However, within a NIM it was shown in [44] that the evanescent waves undergo amplification. Thus both the propagating and evanescent waves contribute to the focal spot image, implying that a perfect image can be recovered using a NIM.

![Ray diagram of a NIM focussing a point source oscillator to a point source image at the focal spot.](image)

**Figure 1.9** Ray diagram of a NIM focussing a point source oscillator to a point source image at the focal spot.

Since this initial proposal by Pendry, much effort has gone into the design and fabrication of such a NIM [33, 39–41, 45, 46]. Efforts to now scale these nanostructures towards the visible regime, and eliminating loss is required to achieve the perfect NIM lens.

### 1.3.4 Applications

Unlike PCs and plasmonics (see Sec. 1.4), the applications of MMs spread out between the optics communities working at visible or NIR wavelengths, terahertz communities working at millimetre wavelengths, and radio-wave communities operating at the centimetre-scale wavelengths. As MMs is still a very new and emerging field of research, there are very few industrial applications to date. However, there is a broad range of applications that have been proposed by the scientific community. The perfect lens based on a
NIM has been discussed in the previous section.

Invisibility cloaking is another application of MMs that has received a lot of interest in the media [47–50]. This physical phenomena is achieved via transformation optics. Pendry showed that the bending of space around an object to an electromagnetic wave [47], is equivalent to warping the electromagnetic properties of the material surrounding it. In fact this principle of transformation optics can have many more applications than just cloaking, and has even been suggested for the development of electromagnetic wormholes [51]. Recent investigations in asymmetric MMs have also been suggested as compact circular polarisation devices [52, 53], which are discussed in more detail in the following chapter.

1.4 Plasmonics

Plasmonics is an emerging field of physics that studies the interactions between light (photons) and electron oscillations in metals (plasmons). Metals are a unique class of materials that at room temperature possess plasma characteristics. Metals are often considered as a lattice of positive ions surrounded by a cloud of free electrons. This cloud of free electrons gives the metal its plasma characteristics and is the reason that plasmons exist within metallic structures. One of the most exciting features of plasmon resonances is that the electric field is tightly confined to the surface of the metallic structure, to sizes much smaller than the wavelength of light, offering a potential method to beating the diffraction limit of light and creating a huge enhancement of the electric field at the surface.

This section introduces the Drude model for metals used to explain the optical properties of metals, then discuss plasmonic nanostructures and plasmon
1.4.1 The Drude model for metals

The Drude model developed by P.K. Drude in 1900 [54] is based on a simple atomic theory of electrons within metals. The Drude model accurately predicts the dielectric constant of a metal in the near to mid infrared [27] and even though it is a very simplistic model, is still used in common practice today. The Drude model assumes that the motions of electrons can be described by Newton’s 2nd law of motion taking into account the finite resistivity of the metal. The position of an electron in the metal with charge $q_e$ and mass $m_e$ in the presence of an applied electromagnetic field ($\mathbf{E} = \hat{\mathbf{x}} E_0 e^{i\omega t}$), can be described by the damped harmonic oscillator differential equation. Substitution of the solution of this differential equation into the definition of the dipole polarisation results in the definition of the Drude dielectric constant:

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\omega_c}, \quad (1.9)$$

where $\omega_p^2 = Nq_e^2/m\epsilon_0$ (in SI units) is the plasma frequency and $\omega_c = Nq_e^2/\sigma m$ is the collision frequency. A comparison of plasma and collision frequencies is given in Table 1.1 based upon the data given in [27].

<table>
<thead>
<tr>
<th>Metal</th>
<th>Plasma Frequency ($10^{16}$ s$^{-1}$)</th>
<th>Collision Frequency ($10^{13}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>1.37</td>
<td>2.73</td>
</tr>
<tr>
<td>Gold</td>
<td>1.37</td>
<td>4.05</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.743</td>
<td>6.64</td>
</tr>
<tr>
<td>Tungsten</td>
<td>0.975</td>
<td>9.18</td>
</tr>
<tr>
<td>Copper</td>
<td>1.12</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Table 1.1 Comparison of the plasma and collision (angular) frequencies for different metals [27].
It is important to note that the exact value of the collision frequency depends on the conductivity of the metal, which can vary depending on the surface roughness quality of the metallic structure [55]. A plot of the real and imaginary parts of the Drude dielectric constant for silver, nickel and copper is given in Figure 1.10.

![Figure 1.10](image)

**Figure 1.10** Drude model of the permittivity of silver, nickel and copper. a) Real part of the permittivity. b) Imaginary part of the permittivity.

As seen in Figure 1.10, at frequencies in the visible and near infrared the real part of the permittivity is negative and large. In addition, these metals are non-magnetic, thus the permeability \( \mu = \mu_0 \) and therefore the refractive index is given by \( n = \sqrt{\epsilon} \). A negative real part of the permittivity leads to a strong imaginary component of the refractive index, implying that electromagnetic fields exponentially decay very quickly within metals. Note that the Drude model is inaccurate at visible wavelengths and should thus only be used for near to mid-infrared calculations.

1.4.2 Plasmonic nanostructures

The simplest plasmonic structure is a semi-infinite metal slab that has a flat dielectric-metal interface where surface plasmons modes are formed. Surface
plasmons are plasma waves that are bound to and propagate along the surface of the semi-infinite structure [56]. For example, in the case of a metal-air interface a surface plasmon resonance occurs at \( \omega = \omega_p / \sqrt{2} \) [57]. Light of this frequency incident on a dielectric-metal interface can couple to these surface plasmons, which then propagate along the surface until they couple out to free space, or attenuate due to the losses within the metal. The trapping of light at the surface of the metal makes surface plasmons very useful for enhanced light-matter interactions such as surface-enhanced Raman scattering [58].

![Figure 1.11](image_url)  
**Figure 1.11** The resonant absorption properties of colloidal solution of gold nanoparticles (black) versus the flat absorption profile of a thin film of gold (blue) and a comparison with Mie theory of spherical gold nanoparticles (red). Image from [59].

Recently, there has been a growing interest in nanoscale particle-like structures that are engineered to have unique plasmonic properties [59–64]. These particle plasmons can have tailored plasmonic resonances depending on their size, shape and dielectric constant of their embedding medium. A distinct feature of these particle plasmonic structures is that plasmon oscillations are localised to around the nanoscale particle acting as an highly sub-wavelength optical
cavity, with an extremely small modal volume. This feature is one of the most exciting of plasmonics and leads to the ability to create 3D hot spots of light (localised modes of high intensity) much smaller than the wavelength of light.

The most fundamental plasmonic particle is the metallic nanosphere, which has a fundamental dipole plasmon resonance at $\omega = \omega_p / \sqrt{3}$ [61]. An example is given in Figure 1.11, which compares the absorption spectra of bulk thin film gold with a colloidal solution of gold nanoparticles (NPs) [59]. The gold NPs show a strong absorption resonance at 2.25 eV and the absorption at frequencies below this resonance has now been quenched.

Geometry is an important feature of plasmonics just as it is in PCs and MMs and the introduction of chiral geometries has been recently investigated (see Sec. 2.5).

### 1.4.3 Plasmon hybridisation

In this section we discuss the plasmon hybridisation model used to predict the modes of metallic nanostructures containing thin metal coatings, a geometrical feature that will become important in Chapter 5 and 6 of this thesis (gyroid structures with thin metal coatings).

The plasmon hybridisation model describes the plasmon interactions in thin metallic shells or multiple plasmonic particle systems [60, 61], analogous to the hybridisation model used in molecular orbital theory. This model has been used extensively for its ability to elucidate the geometrical dependence of these plasmonic properties. In this theoretical model a metallic plasmonic structure is assumed to be made of just two components [60, 61], a fluid of free electrons and a rigid, stationary, background of positive ions (atomic nuclei and their bound electrons). Solving the natural modes for this fluid motion
results in the plasmon resonances of the metallic nanostructure.

The plasmon hybridisation model is an excellent model for predicting the plasmon resonances in metallic nanostructures with thin metal shells, such as the spherical nanoshell. The plasma modes of the nanoshell can be described by the hybridisation of the plasma oscillations of a metallic nanosphere and metallic nanocavity, as seen below in Figure 1.12.

![Figure 1.12](image_url)  
**Figure 1.12** Plasmonic hybridisation of a metallic nanoshell. a) Weak coupling. b) Strong coupling. Image from [61].

On the left in Fig. 1.12 the plasmon oscillations located at the inner and outer surfaces of the nanoshell are far apart and thus interact weakly. This creates a weak splitting of the plasmonic resonant frequencies. On the right in Fig. 1.12 the inner and outer surfaces are brought closer such that these plasma oscillations strongly interact and cause large splitting in the plasmonic frequencies.

Note that the plasmonic hybridisation model relies on the quasi-electrostatic assumption, which limits the structure to be much smaller than the corresponding plasmonic wavelength given by $\lambda_p = \frac{c}{f_p}$, where $f_p$ is the plasma oscillation
frequency of the system. In the dipole limit (a limit for \( \lambda_p \gg d \), where \( d \) is the structure size) the plasmonic hybridisation model works accurately. As the structure size increases, the plasmonic frequency is red shifted due to retardation of the Coulomb potential [65]. Retardation is also responsible for electromagnetic chirality (magneto-electric coupling) and magnetism [66].

During the period of this thesis we developed an extension of the plasmonic hybridisation model, which includes the effects of retardation [67]. The derivation and results of this model applied to several metallic nanoparticles is given in Appendix A.

1.4.4 Applications

The exciting ability to confine and interact with light at a highly-sub-wavelength scale, well beyond the diffraction limit has led to the development of many applications. Nanoparticles, and their geometrical sensitivity to polarisation and wavelength has made an excellent candidate for a novel media to be used in five-dimensional optical data storage [64], where gold nanorods were used as recordable media. Sensing also greatly benefits from the strong light-matter interactions, where due to the tight confinement of light to a plasmonic surface the intensity of light interacting with the environment can be enhanced orders of magnitude [68]. Plasmonic nanoparticles have been shown to have very strong and tunable scattering/absorption properties, a useful property that has attracted scientists working towards the improvement of the efficiency of solar cells [69–71]. The interaction between multiple plasmonic nanoparticles is very sensitive when the distance is comparable to the size. This phenomena has been suggested as a possible means of monitoring the folding of long protein chains by using tiny metallic nanoparticles as 3D plasmon-rulers [72].
1.5 Thesis objective

The objective of this thesis was to investigate 3D microstructures that are inspired by nature (biomimetic) with exotic geometrical properties such as chirality and cubic symmetry. We show that these 3D chiral microstructures lead to a novel platform for the development of chiral PCs, MMs and plasmonics. More specifically, these 3D chiral microstructures possess strong polarisation sensitivity useful for the manipulation of optical polarisation and as shown here are realisable via state-of-the-art direct laser writing techniques.

![Diagram](image)

**Figure 1.13** Flow of this PhD thesis methodology.

In this thesis we have chosen the following research methodology illustrated in Fig. 1.13. In order to design and innovate novel 3D chiral designs for photonics, we have taken inspiration from the biological photonic nanostructures found in the *Callophrys Rubi* butterfly and fabricated these 3D chiral microstructures
using a state-of-the-art direct laser writing (DLW) system, which we designed and built during this PhD thesis. These 3D chiral biomimetic photonic microstructures are then used at platforms for investigating their PC, MM and plasmonic properties.

This PhD thesis aims to achieve its objective by completing the following tasks, which are grouped into three major components:

**A: Theoretical and experimental investigation of the optical properties of a dielectric srs-network** (Chapter 3)

1. Develop 3D cubic chiral designs that are practically realisable using the biomimetic gyroid networks as a design basis.

2. Numerically simulate the transmission of circularly polarised light through dielectric srs-networks and investigate their circular dichroism properties.

3. Perform band structure calculations on the dielectric srs-network to develop a deeper understanding of the physical mechanisms behind the circular dichroism properties.

4. Use the DLW method to experimentally fabricate polymer srs-networks and determine the structural integrity of these microstructures via electron microscopy.

5. Experimentally characterise the transmission of circularly polarised light through the fabricated polymer srs-networks and compare these measurements with the numerical predictions.

6. Investigate the optical properties of chiral composites consisting of multiple intertwined dielectric srs-networks.

**B: Fabricate srs-networks with true cubic symmetry and develop an optical chiral beamsplitter** (Chapter 4)
1. Understand the effects of the intrinsic fabrication voxel elongation of the DLW method on the optical properties of srs-network.

2. Develop a new galvo-dithered DLW method (GD-DLW) to compensate for the fabrication voxel elongation and preserve the cubic symmetry of the srs-network.

3. Using the GD-DLW method reduce the unit cell size of the fabricated srs-network such that the circular dichroism band is centred at the wavelength of 1.55 $\mu$m.

4. Design and fabricate an optical chiral beamsplitter based on the optimised circular dichroism properties of the srs-network.

5. Build a characterisation experiment for the broadband characterisation of the chiral beamsplitting phenomenon and compare results with theoretical calculations.

C: Theoretical and experimental investigation of the optical properties of a metallic srs-network (Chapters 5 & 6)

1. Numerically simulate the transmission of circularly polarised light through a range of metallic gyroid-based nanostructures/microstructures at a range of different frequency regimes (visible, near-infrared and mid-infrared).

2. Identify which metallic gyroid designs operate as chiral PCs or chiral MMs and determine if the circular dichroism of the srs-networks can be improved using metals instead of dielectrics.

3. Investigate the difference in the optical properties of solid metallic srs-networks compared to dielectric srs-networks coated with an optically thin layer of silver.
4. Perform the selective metallisation of dielectric srs-networks maintaining the complex 3D chiral geometry and not reducing the transparency of the sample substrate.

5. Experimentally characterise transmission properties of these 3D metallic gyroid structures and compare results with theoretically predicted calculations.

1.6 Outline of the thesis

This thesis has the following structure:

Chapter 2, Review: This chapter begins with a review of the state-of-the-art results of 3D nanofabrication of dielectric and metallic microstructures via DLW and post-process metallisation. We then review recent research developments in the investigation of the effects of chiral asymmetries within PCs, MMs and plasmonics. The use of biomimetics for photonic microstructure design is then reviewed, including a detailed discussion on the gyroid structure, its origin in nature, and how gyroid-based designs are excellent blueprints for developing 3D chiral nanostructures.

Chapter 3, Biomimetic chiral gyroid photonic crystals: In this chapter we discuss the geometrical features of the srs-network in detail and how we have designed our 3D microstructures for DLW. We provide a detailed theoretical analysis of this dielectric chiral PC and explain the origin of circular dichroism bands. The fabrication results of the srs-network for a 3 µm unit cell size are then presented and the formation of a circular dichroism band at 3.4 µm is demonstrated. Then finally we show that multiple intertwined srs-networks can be fabricated and demonstrate more broadband circular dichroism.
Chapter 4, Cubic symmetry and chiral beamsplitters: This chapter focusses on the importance of cubic symmetry in the development of functional chiral devices. We demonstrate how to overcome the intrinsic asymmetry of the DLW method through galvo-dithering and show that the srs-network can be scaled down to a unit cell size of 1.2 μm. This much smaller srs-network is then shown to possess a strong circular dichroism band at the telecommunications wavelength of 1.55 μm. These important achievements have facilitated the development of a chiral beamsplitter at optical wavelengths based on the srs-network PC. To be the best of our knowledge we experimentally demonstrate for the first time a nano-engineered chiral analogue of the linearly polarising beamsplitter. We finally elucidate the physical mechanism behind the chiral beamsplitting phenomenon through numerical simulations and observe good qualitative agreement with experimental observations.

Chapter 5, Numerical investigation of metallic gyroids: In this chapter we provide a thorough theoretical analysis of a variety of metallic gyroid structures. We first show that the metallic srs-network acts as a chiral PC with stronger circular dichroism compared to the dielectric srs-network. Then we discover that the intertwining of 4 metallic srs-networks can lead to the transmission of light at much longer wavelengths, allowing this metallic composite to perform as a chiral metamaterial with superior circular dichroism properties. Finally we investigate the optical properties of metal coated gyroid networks and metallic gyroids based on the electro-deposition method.

Chapter 6, Fabrication of metallic gyroid photonic microstructures: This chapter serves as an outlook towards the development of a range of metallic gyroid metamaterials. We demonstrate the silver coating of polymer srs-networks via well-established electroless silver deposition methods. We show that a conductive layer of silver can be formed on these chiral gyroid networks and provide experimental characterisation of these chiral PCs and
Chapter 7, Conclusions: In this chapter we provide a summary and discussion of the results of this thesis. We then discuss the outlook of this research and propose future research based on the findings of this thesis.
Chapter 2

Review

2.1 Introduction

Whilst optical phenomena associated with chirality such as optical activity and circular dichroism are well understood, recent developments in nanotechnology have inspired the development of new chiral photonic nanostructures. A broad range of geometrical designs, both two-dimensional (2D) and three-dimensional (3D) have been proposed most of which are based on simple geometrical objects such as spirals, helices and crosses. Experimentally, a range of nanofabrication methods have been used, each with their own advantages and disadvantages that limit the scope of their suitable geometrical designs.

This chapter begins with a brief review of the recent advances in 3D fabrication techniques, specifically direct laser writing and post processing techniques for metallisation. This is then followed by brief reviews of the recent use of chirality within photonic crystals (PCs), metamaterials (MMs) and plasmonics nanostructures. Finally we review the photonic properties of biological nanostructures such as iridescence, with a specific focus on the biomimetic
gyroid structures, which have greatly inspired the photonic designs in this thesis.

2.2 Fabrication of 3D microstructures

2.2.1 Direct laser writing

Direct laser writing (DLW) is a 3D nano-fabrication technique developed over the past two decades [73] to what is now a well-established technology, with several commercially available systems on the market. With the ability to create arbitrary-shaped 3D nanostructures and microstructures, with resolutions as small as 68 nm [74], DLW is a powerful technology for many fields of research.

The DLW method typically uses an ultrafast laser (femtosecond or picoseconds lasers). However a recent report has shown sub-micron resolution from DLW with continuous wave lasers in certain materials [75]. The laser source is tightly focused to a diffraction limited focal spot, using a high numerical aperture objective lens, forming an ultrahigh intensity of light (see Fig. 2.1a). The sample, which contains a photoresist that is transparent at the wavelength of operation, is placed at the focal spot. The transparency is critical for the ability to write 3D structures, as it allows the laser to pass through the entire photo-resist without attenuation. However, due to the very high intensity supplied by the tight focussing condition, nonlinear processes such as two-photon absorption occur [73], which triggers reactions such as photo-polymerisation [73], micro-explosion [76] or even photo-reduction of metals [77, 78]. Due to the nonlinearity of these photo-reactions, the reaction can only take place at the centre of the focal spot where the intensity is highest, leaving the surrounding material relatively unmodified. The sample is then
moved using a 3D nano-translation stage and the focal spot drawn through the sample tracing out the desired 3D design.

Figure 2.1  a) The principle of the DLW method. An ultrafast laser is focused into a transparent photoresist, where at the diffraction limited focal spot, nonlinear photo-reactions occur such as polymerisation. This focal spot is then traced out in an arbitrary 3D pattern as designed by the user. b) A 3D spiral (helix), fabricated via DLW to demonstrate the arbitrary 3D patterns that can be drawn. Image from[73]. c) Scanning electron microscope (SEM) image of the 3D voxel from DLW, and a comparison of the lateral and longitudinal resolutions for different exposure times. Image from [79].

In the case of a negative polymer photoresist, after the DLW has completed, the sample is then rinsed with a solvent, to remove the unwritten material, leaving behind only regions where the focal spot has traced through and caused photo-polymerisation to occur. One of the first microstructures drawn to demonstrate the arbitrary 3D designs that can be made with DLW was the spiral in [73].
and is shown in Fig. 2.1b.

Much effort has gone into the development of DLW in a range of different photo-resists including photo-polymers [73, 80, 81], photo-reduction of silver [77, 78], chalcogenide glass [25, 74], bio-compatible materials [82] and even quantum dot nano-composites [15, 83, 84]. Post processing techniques can also be applied to modify the material properties of the 3D structure, including inversion techniques with silicon [26], infiltration of quantum dots [15, 83], electroless metal coating [85–88] and electro-deposition with conducting metals such as gold [52, 89].

Whilst in theory arbitrarily shaped microstructures can be written using DLW, there are two practical limitations of this method. Firstly, the 3D voxel (or pixel) that is traced out to form the microstructure has a limitation on its size. The exact maximal resolution that is achievable is dependent on the photoresist and wavelength of operation. For example, when using commercially available polymer photoresists such as IP-L [26], Ormocer [13] and SU-8 [90], the smallest voxel size that can be produced is typically around 100 nm in the lateral direction and 300 nm in the vertical direction. The reason for the unequal sizes in the lateral and vertical axes of the voxel is due to the unavoidable elongation of the diffraction limited focal spot [79] and an example of the elongated 3D voxel is shown in Fig. 2.1c. In higher index materials such as chalcogenide glass, the diffraction limited focal spot is even more elongated, and can even become worse when spherical or birefringent aberrations are introduced [91].

The second practical limitation as with any 3D structure is structural integrity. An important feature of any photoresist is the mechanical strength and lack of distortions such as shrinkage [81, 92]. As well as the material dependence, the design of the 3D structure, must take into account these mechanical requirements and it is quite common for microstructures to be fabricated with
square [23, 93] or circular [94] frames to support the structure.

### 2.2.2 Super-resolution fabrication

Due to the ever increasing demand for higher resolution recent efforts have been made to further improve the resolution well beyond the diffraction limit [50, 95–97]. These methods achieve their high resolution features by using two laser beams to illuminate the sample, inspired by the recent developments in stimulated emission depletion microscopy [98].

![Figure 2.2](image)

**Figure 2.2** Super-resolution focussing of excitation (red) and depletion (green) beams. Calculated (a) and experimentally measured (b) intensity profiles. All scale bars are 200 nm. Image from [50].

The first laser beam is focused as in standard DLW to excite the laser writing photo-reaction (e.g. photo-polymerisation). The second beam is then applied to stop this photo-reaction, either via stimulated emission depletion (STED-DLW) [50, 97] or photo-inhibition [95, 96] (the photo-excitation of a chemical reaction that inhibits the writing process). By aligning the position and controlling the shape of these two focal spots, the resulting fabrication voxel volume can be significantly decreased as shown in Fig. 2.2 and in theory has no
limit. In practice however, finite contrast between the excitation and depletion cross-sections lead to a saturation of the depletion phenomena [50].

![Figure 2.3](image_url)  
**Figure 2.3** SEM images of a series of lines fabricated on a surface using the standard DLW method ((a) and (c)) and STED-DLW ((b) and (d)). Lines are separated by \( a = 200\text{nm} \) ((a) and (b)) and \( a = 175\text{nm} \) ((c) and (d)). Image from [50].

Whilst in its early stages of development this technology is promising for the ability for 3D laser writing to achieve resolutions comparable to that of nature’s nanostructure self assembling methods, allowing scientists to truly replicate 3D biological nanostructures, produce PCs with bandgaps down to the ultraviolet and MMs operating in the visible [50].

### 2.2.3 Post DLW metallisation

In the previous two sections we discussed 3D nano-fabrication via DLW, primarily in dielectric materials such as polymers. Whilst dielectrics materials such as glass and polymers are excellent low-loss materials for the development of PCs, introducing metals to these architectures are required to investigate MM and plasmonic properties. It has been shown that DLW directly of metallic structures can be achieved via photo-reduction [77, 78]. However, these methods typically have poor surface roughness and the high resolution fabrication in 3D is yet to be demonstrated. Therefore significant improvements of photo-reduction resists are required before this method can be used to develop high
quality optical metamaterials.

Instead, introducing metals to these 3D microstructures after their development is a more practical solution. In this case the 3D dielectric microstructure acts as a template, which gets infiltrated by metals via a number of methods we shall now discuss. It is important that a high quality metallic coating can be developed on the dielectric structures. Smooth metallic coatings will help to minimize resistance and thus minimize losses of the metal [55].

The three main processes used to fabricate 3D metallic (or metallodielectric) PCs and MMs have been chemical vapour deposition (CVD) [28, 99], electrodeposition [89] and electroless deposition [85–88].

CVD has been used to create all-metallic tungsten PCs with complete photonic bandgap (PBG) [28] as shown in Fig. 2.4a. A 3D silicon woodpile template was first fabricated, followed by infiltration with tungsten via CVD. The silicon was then removed to leave behind a pure 3D microstructure made entirely out of tungsten, 4 rod layers thick. It should be noted that one side-effect of the CVD method is that small keyholes are formed during the infiltration. In [99], CVD was used to coat silver on 3D SU-8 template that was written using the DLW method. Silver has a much lower loss than tungsten at optical wavelengths and thus is a better metal of choice for PCs and MMs. However, CVD coats all surfaces within the sample, including the 3D dielectric template and the glass substrate will be coated with metal. However, to allow the transmission of light through the substrate during experimental characterisation, the metallisation method must be able to selectively coat only the polymer template and not the substrate it is standing on.

In [89], an electro-deposition technique was used to coat a polymer PC with nickel to form a 3D metallic woodpile using a commercially available electrodeposition system and is shown in Fig. 2.4b. Up to 11 layers of the woodpile
Figure 2.4  SEM images three different metallic 3D microstructures, where metallisation of dielectric templates was achieved via chemical vapour deposition of tungsten (a) [28], electro-deposition of silver (b) [89] and electroless plating of silver (c) [85].

structure was entirely coated. However this fabrication technique requires complete wetting of the template before electro-deposition, slow deposition rate to prevent hydrogen generation at the cathode, and the template to have both good chemical and mechanical stability [89]. It also requires a geometrical connectivity, which exists in simple woodpile [89] and spiral microstructures [52], but not in more complex 3D structures such as the bi-chiral PC [88]. This is due to part of the 3D structure being filled with metal blocking other sites of the structure from the metallisation process, leading to voids where no metal can infiltrate [88].

The other method used commonly in metallisation of 3D microstructures is electroless silver plating [85–88]. In [85] the photoresist was chemically modified to adhere more strongly to silver and the results are shown in Fig. 2.4c. These 3D polymer templates were fabricated on top of a glass substrate that has been treated with a hydrophobic coating, which inhibits the deposition of silver particles to the substrate during the electroless silver plating. The polymer template is then activated with $\text{SnCl}_2$ to form a layer of tin ions on the surface, which will attract the attachment of silver during the electroless plating. Silver is then deposited onto the surface by dipping the structure into a solution including silver nitrate for about 15 minutes and the process
is stopped by washing with acetone. This technique was shown to be able to form a conductive silver coating with silver particle sizes as small as 10 nm [85], whilst keeping the substrate relatively uncoated with silver particles (i.e. keeping it transparent).

In [100] an acrylate based microstructure was fabricated using 2PP and subsequently coated with silver using electroless deposition. This was achieved by first functionalising the acrylate polymer structure using alkylamines \((NH_2(CH_2)_3NHLi)\), then coating the surface with gold nanoparticles (Au NPs), which bind to the aminated polymer surfaces only and not the glass substrate. The Au-particle functionalised structure is then put in a silver bath for 20-130 minutes. During this time silver particles are then deposited at the gold nanoparticle sites and over time a silver coating is formed whose thickness ranged between 20 nm to 40 nm for bath times of 20 to 60 minutes, respectively [100]. This technique was then applied later to forming silver coatings on SU-8 structures in [86], which is a more preferable polymer for 2PP due to the small amount of shrinkage in SU-8 compared to the acrylate based polymers [86] and the results are shown in Fig. 2.5 (left). Note when a gum arabic solution was introduced to the electroless plating solution to slow down the reaction, the substrate was not coated with silver. However, to achieve a homogeneous coating with good (direct current) DC conductivity the authors in [86] showed that the faster reaction without gum arabic is required. Thus this method introduces a trade-off between conductivity and selectivity.

An alternate method to having a high quality silver coating with a transparent substrate is to perform the electroless silver coating without selectivity, i.e. coating the substrate as well as the 3D template. Then, after this post-processing step the 3D structure, which is suspended above the substrate by four pillars on the corners of the structure can be mechanically transferred from the silvered substrate and to a new glass substrate [88] and shown in Fig.
Figure 2.5 Left) SEM images (a-d and f) and an x-ray spectrum (g) of a silver coated SU-8 microstructure via selective electroless silver coating, using a solution of gum arabic to slow the plating process, and tin activation of the polymer template to achieve selective coating. [86] Right) SEM images of a silver coated SU-8 microstructure without selectivity, which is suspended above the substrate by found pillars on the corners of the structure. The microstructure is then mechanically transferred to a new substrate before optical characterisation. Image from [88].

2.5 (right). This method is limited to photoresists that are solid such that the 3D microstructures can be written above the substrate without mechanical attachment to a substrate, which cannot be done in liquid photoresists such as IP-L or Ormocer. In addition, during the mechanical transfer distortions to the microstructure may occur, due to the harsh forces applied whilst removing the microstructure from its original substrate.

The most recent developments of electroless silver plating of 3D DLW templates [101] uses a modified photoresist inspired by the work in [102], which introduces metal binding materials to the photoresist. In this method
no surface activation is required such as the tin activation used in [86, 88]. This has shown to lead to a high quality silver coating, with reasonable DC conductivity of up to $5.71 \pm 3 \times 10^6 \Omega^{-1} m^{-1}$ (compared to the bulk DC conductivity of silver which is $6.3 \times 10^7 \Omega^{-1} m^{-1}$) and the results of the coating of a woodpile polymer template are shown in Fig. 2.6. Optical characterisation performed on the metal coated woodpile, shows high transparency at short wavelengths demonstrating the transparency of the substrate and low transparency at long wavelengths demonstrating high conductivity of the metal coating.

This method demonstrated in [101] will be our method of choice for metallisation of 3D microstructures, due to the simplicity of the silver coating method (no surface activation, or hydrophobic substrate preparation required), high resolution (and low shrinkage) of the photoresist for DLW and high conductivity of the final silver coating comparable to that of bulk silver.

Figure 2.6  a) SEM image of a silver coated woodpile structure fabricated using DLW in a chemically modified photoresist, which contains metal binding sites, allowing for the selective deposition of silver. b) Optical characterisation of the metal coated woodpile, showing high transparency at short wavelengths (demonstrating the transparency of the substrate) and low transparency at long wavelengths (demonstrating high conductivity of the metal coating). Images from [101].
2.3 Chiral photonic crystals

PCs are periodic structures that are built from a periodic repetition of a unit cell that is made up of smaller elements. For example the woodpile PC discussed in Section 1.2 is a 3D PC made from an array of dielectric rods [23, 24, 26, 83, 103–106]. When these dielectric rods are stacked in a woodpile geometry, structures such as fcc and fct can be realised and 3D photonic bandgaps (PBGs) can be formed.

Other types of PC structures can be realised by using different geometrical elements. For example, in [107] a spiral elemental (i.e. a helix) was used to form PCs with arbitrary crystal symmetry by altering the rod width, spiral radius, orientation and lattice constant. In this theoretical study spiral PCs [107] were shown to be able to create simple cubic (sc) symmetry with a PBG gap width $g_w = 16.8\%$, face-centred cubic (fcc) symmetry with $g_w = 27.8\%$, and body-centred cubic (bcc) symmetry with $g_w = 20.0\%$. The fcc and bcc structures required each adjacent spiral element to be translated half its unit cell height. These large gap widths make spiral PCs a potential candidate for developing a broader bandwidth PC than the woodpile variants. The chiral properties of these spiral PCs was not investigated here, as at the time the motivation was to search for PC geometries that possess complete PBGs, wavelength regions where light of all polarisations in all directions are forbidden.

Fabrication of such complicated 3D PCs is not an easy task, particularly when compared to the 3D woodpile structure. Thus an approximation of the circular spiral structure using a square spiral structure was used in [108]. This structure was made using straight rods rather than circular to suit fabrication techniques such as glancing angle deposition (GLAD), see Fig. 2.7a. PBG widths were shown to be only slightly smaller than the circular technique with $g_w = 24\%$ theoretically predicted. In [109] silicon square spiral PCs with PBGs covering
2.5 \( \mu m \) – 2.75 \( \mu m \) were fabricated using the GLAD technique. In [110] a square spiral PC was fabricated using DLW in SU-8. This PC had PBGs at wavelengths as low as 2 \( \mu m \). Following this, in [111] produced a circular spiral PC, as shown in Fig. 2.7b demonstrating PBGs at wavelengths as low as 880 nm.

![Square spiral PC fabricated using the GLAD technique. Image from [109]. b) Circular spiral PC fabricated using DLW in the polymer photoresist SU-8. Image from [110].](image)

Soon afterwards, the chiral properties of these spiral PCs were investigated [94, 112, 113]. Due to the chiral asymmetry (handedness) of these spirals (helices), strong circular dichroism can be observed at certain wavelengths, manifesting in the existence of polarization stop bands [114]. These polarisation stop bands are formed due to the chirality of the spirals forming partially left-handed (LHD) or right-handed (RHD) circularly polarised Bloch modes. The strength of this circular polarisation is given by the C value defined in [114] and redefined in [115] in Fourier representation to improve numerical efficiency. The formation of these strong circular dichroism bands could possibly be used as a broadband circular polariser, the limitations of this 3D microstructure are that this square array of spiral has only uniaxial chirality (i.e. it is not chiral when looked at from the side) and the PC is highly anisotropic (does
not possess cubic symmetry). In order to produce chiral effects in multiple directions, extending the functionality of this chiral PCs, it is required to design more complex 3D chiral PCs.

This was the motivation behind the development of the bi-chiral PC [90], which was also developed via the DLW method. The bi-chiral PC consisted of helices orientated along all three Cartesian axes forming an interconnected network with both chirality and cubic symmetry (i.e. it was chiral and appeared the same when looking from the top and sides). The bi-chiral PC in [90] was inspired by blue phase cholesteric liquid crystals [116–118] and consisted of a fully interconnected network of circular helices. By choosing the handedness of the helices as well as the corners of these helical arrangements, the authors in [90] were able to control the strength of the circular dichroism as shown in Figs. 2.8a-d. Specifically, when the handedness of the helices were opposite to that of the handedness of the corners as in the naturally occurring blue phase cholesteric liquid crystals the circular dichroism was weak. See Figs. 2.8e,f for SEM images of the bi-chiral PC. On the other hand, when the handed helices and corners were equal, the PC showed stronger circular dichroism.

The application of cubic chiral designs such as the bi-chiral network may have applications in MMs, where the chiral geometry can be utilised to create phenomena such as negative refraction. Recently, a metallic version of the bi-chiral structure was demonstrated [88] possessing broadband strong circular dichroism with reduced angular dependence, compared to uniaxial or planar chiral nanostructures. However, due to the connectivity of the 3D networks, there was a relatively high frequency cut-off of propagating modes, prohibiting the formation of any interesting MM phenomena. This is a critical disadvantage to 3D MMs made of connected networks.
Figure 2.8  a-d) Experimental measured (left) and theoretically calculated (right) transmission spectra of LHD (black) and RHD (red) polarised light through the bi-chiral PC. e) SEM images of the 4 different bi-chiral PCs. f) SEM image of one of the bi-chiral PCs, showing excellent uniformity, mechanical strength and low shrinkage. Images from [90].

2.4 Chiral metamaterials

As discussed in Sec. 1.3, MMs are artificial materials whose optical properties are governed by the geometry of the highly sub-wavelength structure (sometimes known as meta-atoms). Metamaterials with chiral geometries have recently received interest demonstrating huge optical activity [119–122] and strong circular dichroism [52, 119, 123, 124], much larger than the effects found in naturally occurring materials or biological nanostructures. These huge chiral-optical phenomena arise from the chirality of the meta-atoms, causing
strong discrimination in the optical properties of the MMs for LHD and RHD polarised light.

In fact these chiral effects have been shown to lead to unnatural phenomena such as a negative refractive index [125, 126], inspired after predictions that when the chirality of a material is stronger than the electric/magnetic dipole response a negative refractive index can be formed for one circular polarisation [127, 128]. In [128] it was shown that the refractive index of RHD (+) and LHD (-) light in a chiral MM is given by:

\[ n_{\pm} = \sqrt{\varepsilon_{\text{eff}} \mu_{\text{eff}}} \pm \xi_{\text{eff}} \]  

(2.1)

where \( \varepsilon_{\text{eff}}, \mu_{\text{eff}} \) and \( \xi_{\text{eff}} \) are the effective permittivity, permeability and chirality (which in general is known as the bi-anisotropy tensor) of the MM, related to the constituent fields by:

\[ D = \varepsilon_0 \varepsilon_{\text{eff}} E + \frac{i}{c_0} \xi_{\text{eff}} H, \]

(2.2)

\[ B = \mu_0 \mu_{\text{eff}} H - \frac{i}{c_0} \xi_{\text{eff}} E, \]

(2.3)

where \( E \) and \( H \) are the applied electric and magnetic fields of the electromagnetic wave and \( D \) and \( B \) are the displacement and magnetic field vectors within the MM. As the absolute value of the effective chirality \( \xi_{\text{eff}} \) increases to become larger than \( \sqrt{\varepsilon_{\text{eff}} \mu_{\text{eff}}} \), the refractive index given in Eq. 2.1 becomes negative for one of the circular polarisations and remains positive for the other polarisation. This is a mechanism for achieving a negative refractive index MM through the chiral geometry of the sub-wavelength structure and does not require the double negative permittivity and permeability originally proposed by Veselago in 1968 [43].

Figure 2.9 shows the experimental results of a chiral MM operating at radio
frequencies demonstrating a negative refractive index due to its chirality [126]. It consists of two layers of metallic crosses, stack on top of each other, with the top layer rotated relative to the bottom (see Figs. 2.9a,b). This non-parallel alignment of the layers induces chirality, a sense of twist to the system, and the net result is a strong circular discrimination in the optical properties. Specifically, the refractive index of RHD and LHD circularly polarised light is different, owning to the presence of the chirality parameter, labelled as $\kappa$ in [126] and at a frequency of 6.5 GHz it can be seen that the strong value of $\kappa$ leads to a negative index for RHD light.

![Figure 2.9](image)

**Figure 2.9** Negative refractive index due to geometrical chirality in a MM, from. a) Schematic of the bi-layer of metallic crosses rotated relative to each other to form a chiral MM. b) Photograph of the fabricated metallic MM, with unit cell size 15 mm, which is highly sub-wavelength at the operating radio frequencies between 5-8 GHz. c) The refractive index spectra for RCP (red) LCP (blue) and unpolarised (black) light. The chirality of the metamaterial is shown in green. Images from [126].

Fabrication technologies such as electron beam lithography used in [119, 121, 123, 129, 130] can be utilised to make planar nanostructures with 2D chirality.
By applying a multi-step process of lithography involving multiple layers of planar nanostructures carefully aligned on top of each other [119, 121, 123], this technique can be used to extend these planar geometries to 3D chiral nanostructures with a few layers (typically several hundred nanometres thick). The development of thicker MMs using electron beam lithography is impractical due to the long processing times and limitations of alignment between subsequent layers.

On the other hand DLW is a cheap, efficient and flexible method for making 3D MMs, with resolutions down to 68 nm [74]. Whilst this resolution is still an order of magnitude behind electron beam lithography, DLW is still suitable for the development of MMs operating in the near and far infrared, and with the development of super-resolution DLW technologies as discussed in Sec. 2.2.2, the resolution of this 3D nanofabrication technique may approach that of electron beam lithography, and pave the pathway towards the exciting realm of 3D visible MMs.

In Fig. 2.10 are the results of a 3D MM consisting of gold helices. The fabrication was performed using DLW in a positive photoresist to create a 3D template of helical cavities. These cavities were then infiltrated with gold using electro-deposition, forming an array of gold helices [52]. Due to the chirality of the helices strong circular dichroism was observed and for helices with 2-3 turns (vertical periods) a broadband response was observed. This phenomena in [52] was explained to be a micro-scale analogue to the helical antennae used commonly in radio-frequency communications. It was also discussed in [52] that the wavelengths where these strong chiral resonances were observed, remained at relatively short wavelengths compared to the unit cell size, i.e. $a/2 < \lambda < a/3$, which is in the regime between PCs and the effective medium regime. Thus the application of the MM retrieval methods would not result in physically meaningful results. Modifying the structural design to either
reduce the unit cell size or red-shift these modes to long wavelengths would be required to properly consider this a true MM.

![Image of gold helix MMs]

**Figure 2.10** a-b) SEM images of the gold helix MMs. (a) The MM after electrodeposition of gold into the polymer template. (b) After the gold has been removed leaving behind a square array of gold helices. c) Experimentally measured and theoretically calculated transmission spectra for RCP (blue) and LCP (red) incidence. Images from [52].

## 2.5 Chiral plasmonics

Recently, chiral structures have been the focus of many nano plasmonic designs due to the strong chiral optical phenomena [129, 130]. Chirality can be engineered into plasmonics by a plasmonic nanoparticle with a chiral shape. An example of a 2D chiral object is the gammadion, which was initially used as a planar chiral structure for MMs [123, 125, 131], showing broken time reversal [131].

Interestingly, the plasmonic modes of a nano-scale metallic gammadion was shown to have highly chiral fields [129, 130]. Interestingly, the effect of this chirality on the plasmonic gammadion nanostructures was shown to lead to two very different physical phenomena, nanoscale plasmonic motors [130] and enhancement in the circular dichroism spectroscopy method [129] shown in
Fig. 2.11 and Fig. 2.12, respectively.

**Figure 2.11**  
a) SEM image of the plasmonic nano-motors made from gold gammadions.  
b) Electric field intensity and the Poynting vector distributions of the resonant mode at 810 nm.  
c) Numerically calculated torque on the gammadion due to the chiral distribution of the fields around the plasmonic nanostructure. Images from [130].

In the demonstration of light driven nano-motors [129] a gold gammadion sandwiched between dielectric plates was able to be rotated by the application of light, by utilising the torque generated by the rotational direction of the Poynting distribution. This net non-zero value of the rotational force is due to the chirality of the nanoparticle, and was shown to have both a positive and negative sign depending if the fundamental or second order plasmonic mode is excited, which have opposite rotational flows.

It was recently shown in [132] that the helicity of light (i.e. its chirality) is related to the circular dichroism of chiral biomolecules. The enhancement of the helicity observed in photonic nanostructures could therefore lead to the enhanced sensitivity of circular dichroism spectroscopy. This phenomenon has been recently demonstrated using gold chiral nanoparticles with strong chiral fields [129]. This led to orders of magnitude improvement in the sensitivity
of the measurement of the circular dichroism of complex biomolecules such as haemoglobin [129].

Figure 2.12 Ultra-sensitive plasmonic chiral biological sensors via chiral nano-plasmonic gammadions a) Experimentally measured circular dichroism (CD) spectra of the gold gammadions before (red) and after (black) adsorption with Haemoglobin. b) Illustration of the chiral Haemoglobin biomolecule. c-d) Electric field (c) and chirality (d) distributions for the fundamental resonance of the chiral nanoparticle when excited by LCP light. Fields are normalised to that of incident light. Image from [129].

2.6 Biomimetic gyroid structures

Biomimetic designs are naturally mechanically robust, as evolution of self-assembly rarely leads to the development of mechanically unstable/impractical structures. Along with their superb mechanical properties, many biological specimens also contain interesting geometrical features such as cubic symmetry and chirality, thus are great inspirations for the designs of 3D nano-photonic devices. In this section we shall review the biologically inspired gyroid structures and its exotic geometrical properties useful for photonic devices.
2.6.1 Biological inspiration

Biomimetics is the adaptation of structure that has been found to exhibit certain properties in living systems for the design of synthetic systems in fields such as nano-photonics. The biomimetic design of photonic nanostructures that exploit the ingenious photonic geometries employed by living organisms – in particular in insects, beetles and crustaceans – is a further current field of research [133–135].

While modern 3D electron microscopy methods allow one to understand the complex spatial nanostructures formed by nature, advances in nanofabrication methods such as electron beam lithography with resolutions below 10 nm [136] allow for the accurate replication of these structures for custom-designed photonic applications. The generation of colour by biological PCs that reflect light with frequencies corresponding to photonic band gap is well-understood for various organisms including butterfly wing scales [137, 138], insect cuticles [139], weevils [140], bird feathers [141] and marine lifeforms [142]. Iridescence, the dependence of the reflection rate on the incident angle of light, is a common biological feature [142–144]. Natural anti-reflection coatings based on gratings have been identified in the visual systems of moths and have indeed been mimicked for industrial application [145]. Similarly, photonic designs found in the eyes of various organisms have allowed polarisation sensitive vision, in particular linear-polarisation [146] and also, less well studied, in circular polarisation [147].

Many of these biophotonic structures are 2D (such as the hexagonal cylinder pattern in the sea mouse [142]) or variations of a 2D pattern (such as the tree-like lamellae grating responsible for the strong iridescence in the Morpho butterfly [144]). However, intricate 3D nanostructures based on ordered or disordered spatial networks are also observed in several organisms. Amongst
these are the chiral ordered porous structure known as the gyroid or srs-networks found in several green butterfly species [137, 148, 149], and is shown in Fig. 2.13.

Figure 2.13  Photograph (a) and optical (b) and SEM microscopy images (c-f) of the wing and wing-scales of Callophrys Rubi butterfly, courtesy of Michael Thiel. (g) Spatial structure of the chitin phase of Callophrys Rubi. The right fraction of the 3D body represents a subset of the tomographic data; the left side represents a solid body bounded by a parallel surface to Schoen’s triply-periodic gyroid minimal surface [150]. Also shown is a single srs-network tracing the centres of the void phase (orange). Courtesy of Gerd Schröder-Turk.

A structure, biological or synthetic, which discriminates between LHD and RHD circularly polarised light must have a 3D chiral spatial structure. It is by now well established that some organisms have visual sensitivity to circular polarisation, such as mantis shrimps [147]. In green butterflies, the 3D chiral srs-network structure, realised in the porous chitin phase of the wing scales [137, 148, 149], has recently been shown to lead to a difference in the reflection of LHD and RHD circularly polarised light [115] by analysing the polarisation states of the Bloch modes of these biological PCs.
2.6.2 Gyroid surface and srs-networks

The gyroid is a three-dimensional triply periodic minimal surface (net curvature of zero) with a group symmetry of $I\bar{3}d$ discovered by Schoen in 1970 [150]. An example of an infinitesimally thin gyroid surface is shown in Fig. 2.14, which partitions space into two interweaving labyrinths domains that are depicted by the orange and green sides of the surface.

![Figure 2.14](image)

**Figure 2.14** a) The gyroid surface coloured orange on one side and green on the other, and the RHD (red) and LHD (green) srs-networks contained within the surface. b) Close up view of the gyroid surface along [100] showing the LHD 4-fold helical axis of the srs-network. c) Close up view of the gyroid surface along [111] showing the RHD 3-fold helical axis of the srs-network.

The gyroid has channels that go through the structure in the [100] and [111]
crystallographic directions. These channels resemble a spiral-like shape and are indeed chiral, with green and orange channels having opposing handedness. Thus the infinitely periodic gyroid surface has zero net geometrical chirality due to equal amounts of LHD and RHD curvature. Realized as an achiral sheet of finite thickness, the gyroid surface is ubiquitous in self-assembled materials, including lipid systems [151–153], copolymer systems [154–157], mesoporous silicas [158, 159], germanium oxides [160] and also in cubic intra-cellular membranes [161, 162].

Gyroid structures self-assembled within diblock copolymers (consisting of polystyrene (37% wt) and polyisoprene [157]) are formed when a transformation occurs from the lamellae morphology to the gyroid morphology during the annealing of the copolymer system at $120^\circ C$. This gyroid structure can be conceptually formed by thickening the infinitesimally thin surface of the gyroid shown in Fig. 2.14 symmetrically into both labyrinths (and thus maintaining the achiral symmetry). This thickened surface is made up of the minority phase, which in [157] was styrene. The majority phase, isoprene makes up the green and orange chiral channels.

The srs-network [163] named after the Si network in the poly-cationic $SrSi_2$ crystal [164] is a cubic chiral network with space group $I4_132$. The srs-network has a 4-fold screw helix along $[100]$ and a 3-fold screw helix of opposite handedness along $[111]^4$. In this thesis we define a RHD srs-network as one whose 4-fold axis is RHD. Materials structured according to just a single chiral srs-network are less common in nature than that of the achiral gyroid surface, but have been reported in zeolites [165], terblock-copolymers [154],

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1We have used crystallographic notation here. An object with a screw axis rotates about this axis simultaneously translating along the axis. An object with n-fold screw axis corresponds to an object that possess n-fold rotational symmetry about the axis. For example, a triangle has 3-fold rotational symmetry. When this triangle is stretched into the third dimension a 3-fold screw axis is formed. Similarly, a square stretched into the third dimension forms a 4-fold screw axis.
butterfly wing scales [137, 148, 149], chiral structures derived from the MCM-48 mesoporous silica [166] and from mesoporous germanium oxides [160].

Alternatively, materials structured according to the srs-network can be obtained by chemical removal of two of the three components of the \( I_4_1_3_2 \) phase in linear tri-block copolymers, e.g. in gold [167], at a length scale around 50 nm and will be discussed in more detail in the next section. A self-assembly for a larger length scale is currently not available, but using the butterfly structure as template for inorganic replica has been demonstrated e.g. in silica [168], with a lattice parameter of approximately 300 nm.

2.6.3 Copolymer gyroid photonic crystals

As the gyroid and srs-networks are 3D periodic structures, the electromagnetic eigenmodes within these periodic structures are periodic Bloch modes. If the gyroid structure is made of materials with significant dielectric contrast, photonic bandgaps can arise. Through tailoring of the size and dielectric filling fraction of these gyroid nanostructures (which can be done within a small working regime in copolymer chemistry) one can engineer optical properties such as photonic bandgaps at spectral regimes of interest [169–171].

In 1999 the fabrication of 3D gyroid PCs was achieved via the synthesis of diblock copolymers in the gyroid morphology [169]. In this work the copolymer had a small dielectric contrast between the two phases isoprene and styrene. By selectively modifying one of the phases of the copolymer gyroid shown in Fig. 2.15a, one can induce a larger dielectric contrast into the structure. This was achieved in [169] by selectively etching the poly-isoprene phase, they were able to produce a gyroid structure with air channels as shown in Fig. 2.15b. This thickened gyroid surface possesses much larger dielectric contrast, than the original styrene-isoprene copolymer. The lattice constant (3D unit cell size)
of the gyroid nanostructures fabricated using this technique is typically in the range of 10-50 nm. Thus the PC with air channels would possess bandgaps in the UV where the polymer has high absorption and thus impractical for photonic devices.

![Figure 2.15](image1)

**Figure 2.15** a) Copolymer gyroid structure consisting of polystyrene-polyisoprene. The polyisoprene has been preferentially stained and appears bright here. b) Selectively etching of the poly-isoprene phase creates a gyroid structure with a thickened surface and air double network. Image from [169].

In 2002, the same group were able to increase the size of the gyroid structure to periods of about 250 nm by modifying the molecular weight of the polymers thus altering the self-assembly process in which the gyroid structure is formed [172]. Again, by selectively etching the block copolymer a gyroid structure with significant dielectric contrast was fabricated as shown in Fig. 2.16a where a SEM image is taken of a fragment of the gyroid structure. Fig. 2.16b contains the reflection spectra of the gyroid structure before and after the selective etching. Due to the increased lattice constant of the structure a photonic bandgap in the visible regime is now observed.

A similar technique was used in a different type of triply-periodic minimal surface (TPMS), called the Schwarz P structure [173]. In this work, sea urchin
skeletal plates that possessed the Schwarz P structure were used as templates to fabricate copper structures with unit cell sizes of approximate 30 µm. These copper microstructures were then shown to have greatly improved mechanical stability over non-periodic porous copper samples. The extra mechanical strength was attributed to the TPMS geometry, which allows strain to be distributed uniformly throughout the structure. This feature of mechanical stability should also apply to other TPMS structures such as the gyroid, and is a strong advantage to biomimetic designs for the realisation of practical designs for 3D DLW.

![Figure 2.16](image.png)

**Figure 2.16** a) SEM image of a copolymer gyroid structure with one phase etched to form a dielectric-air PC with unit cell size of around 250 nm. b) Experimentally measured reflection spectra showing strong reflection peak around 350 nm corresponding to the bandgap of the gyroid PC. Image from [172].

2.6.4 Metallic gyroid crystals

During the candidature of this PhD thesis, interest from the MMs community in 3D cubic chiral designs motivated the attention of the self-assembly chemists to develop metallic gyroid crystals [167]. Chemical self-assembly is a great candidate for the fabrication of 3D MMs as they naturally have extremely
small unit cell sizes, typically around 10-50 nm. These small sizes are perfect for optical MMs and they can be made with large crystal sizes compared to DLW. The downside however is the lack of control of the uniformity, unit cell size and filling fraction as the gyroid morphology is only self-assembled under certain conditions. In addition, the boundary surfaces and crystal orientation cannot be controlled as in engineering methods such as DLW.

![Image of fabrication method for realizing the chiral gold MM](image)

**Figure 2.17** a-d) Illustration of the fabrication method for realizing the chiral gold MM. (a) Three polymer materials are used to make the gyroid structure, consisting of isoprene, styrene and ethylene in blue, grey and red, respectively. (b) The blue isoprene phase is etched away and filling with gold in (c). Finally the remaining polymers are removed leaving behind just the gold chiral srs-network. (e) Simulation image of the srs-network along [111]. (f) SEM image along the [111] crystal axis of the gold srs-network. (g) Perpendicular (grey) and parallel (red) polarised reflection spectra from the gold chiral srs-networks showing strong linear birefringence. (h) Experimentally measured (full circles) and numerically calculated (open circles) circular dichroism (gyrotropic transmission) values of the chiral nanostructure. Images from [167].
By using a self-assembled gyroid structure as a nano-template with 50 nm unit cell size, followed by the selective etching of one of the chiral domains of the 3D nanostructure and infiltration with gold (via electro-deposition) the authors in [167] were able to successfully fabricate an optical MM based on this chiral srs-network as shown in Fig. 2.17. Experimental reflection data using polarised light showed that the effects of the boundary clipping points induced strong linear birefringence in the reflection spectra. This effect is greatly enhanced in the metallic structures than that observed in dielectric PCs. Circular dichroism was also observed, at wavelengths in the visible regime.

Whilst the work in [167] was a great step forward towards the development of 3D visible MMs, there still lacks a theoretical understanding of the MM properties [174]. Particularly, the effective parameters were not measured or calculated, and thus how such a chiral nanostructure would perform as a true MM is uncertain from these experimental results.

Soon after these experimental results were published, it was then theoretically demonstrated that 3D MMs based on the gyroid networks could lead to very exciting MM properties [174]. In this theoretical work, it was shown that gold gyroid MMs similar to those experimentally demonstrated in [167] could lead to negative refraction in multiple directions at the same frequency as shown in Fig. 2.18. Whilst the authors claimed an isotropic behaviour, the band structure showed that the optical properties varied in different directions, thus the MMs were not strictly isotropic. However, the single gold gyroid did not possess a negative index and transmission modes cut off at longer wavelengths due to the connectivity of the 3D MM, confirming the experimental results in [167].

Interestingly, when one considers a gyroid consisting of both a LHD and RHD gold srs-network, a capacitive coupling between the networks is formed removing this long wavelength cut-off and forming bands that show negative
refraction [174]. It was also mentioned that the loss of gold destroyed the negative index effect, and silver had to be used instead. This structural design is an experimentally realisable configuration and has now motivated those working in the self-assembly community to consider the fabrication of silver MMs using polymer templates from copolymer self-assembly.

Figure 2.18  a-c) Illustration of the proposed fabrication procedures required to realise the gyroid MMs. (a) The achiral double gyroid, consisting of two LHD and RHD intertwining chiral networks. (b) The same as in (a) but with a hollow centre in the rods, to reduce the filling fraction of metal. (c) A single chiral gyroid network as experimentally realised in [167]. d-e) Band structure analysis of the double gyroid (d) and single gyroid (e) gold MMs. Images from [174].
2.7 Discussion

As we have seen in this review chapter, the combination of state-of-the-art DLW and post-process metallisation provides the ability to experimentally investigate the optical properties of a broad range of innovative PCs and MMs. Unlike other lithographic methods such as electron-beam lithography, DLW possesses unmatched flexibility in the fabrication of 3D microstructures with resolutions below 100 nm [74]. Therefore, DLW is the ideal fabrication method for the investigation of 3D chiral photonic microstructures in this thesis.

The introduction of chiral asymmetries to the design of PCs, MMs and plasmonics has emerged recently due to the discovery of huge enhancements of naturally weak phenomena such as optical activity [119–122] and circular dichroism [90, 113, 115, 123, 125, 175] in these chiral nanostructures. Most of these chiral designs are based on simple elements such as helices or twisted nanoparticles. Besides the bi-chiral PC [90], there remains a lack of investigation on cubic chiral PCs and MMs. Cubic symmetry is an important geometrical feature for the development of isotropic photonic devices with control of the chiral-optical properties in all three dimensions.

We then introduced the biomimetic gyroid structure that is found in several biological species such as the Callophrys Rubi butterfly [149]. The gyroid surface possesses a pair of cubic chiral networks of opposite handedness called srs-networks. In the follow chapters of this thesis we shall investigate the chiral-optical properties of a variety of dielectric and metallic microstructures based on the srs-networks. We shall show that the srs-networks are excellent photonic structures for the development of unique 3D cubic chiral photonic microstructures for PC and MM applications.
Chapter 3

Biomimetic chiral gyroid photonic crystals

3.1 Introduction

The major aim of this thesis is to design, build and characterise new photonic microstructures with chirality and cubic symmetry. In this chapter we propose the use of the biomimetic gyroid networks as a design basis for investigating cubic chiral photonic crystals (PCs). We will demonstrate the high quality fabrication of these three-dimensional (3D) networks via direct laser writing (DLW) [175] and show chiral-optical phenomena such as circular dichroism, through both numerical simulations and experimental measurements. Here we aim to address the following questions:

1. What is the simplest cubic chiral network that is practically realisable via DLW?

2. What are the optical properties of dielectric gyroid PCs and how do they vary with geometry?
3. Do strong circular dichroism bands exist and if so, what is the physical mechanism that creates them?

4. Can the srs-networks be fabricated via DLW with sufficient accuracy and uniformity?

5. Are we able to experimentally measure significant circular dichroism and photonic bandgaps (PBGs)?

6. Does the intertwining of multiple networks improve the chiral-optical properties of the gyroid PC?

This chapter has the following structure. Section 3.2 introduces the geometrical features of the srs-network and explains why the srs-network is an excellent platform for the development of 3D chiral photonic microstructures. Then in Sec. 3.3 we discuss the design of gyroid structures that are practical to fabricate via DLW. Having established these design principles, in Sec. 3.4 we numerically investigate the optical properties of dielectric srs-networks and discover the formation of strong circular dichroism bands. In addition we provide a comparison between the transmission spectra with the band structure of the PC to get a deeper understanding of the physical mechanisms behind the observed circular dichroism. In Sec. 3.5 we present the fabrication of these 3D srs-networks, which shows excellent uniformity and with minimal distortions. These srs-networks are then characterised through experimentally measured transmission spectra and the results are discussed in Sec. 3.6. In order to determine if these chiral-optical properties can be further improved, we investigate the optical properties of chiral composites based on multiple srs-networks intertwined with each other in Sec. 3.7. We show that these even more complex 3D microstructures are still experimentally realisable and compare the experimental transmission spectra with numerical simulations. We then discuss the chiral 4-srs composite in Sec. 3.8 whose chiral geometry
leads to an even stronger circular dichroism than the single gyroid network. Finally we conclude the chapter with a discussion of these results in Sec. 3.9.

3.2 Chiral srs-network features

In this section we discuss the geometrical features of the srs-network and explain why it is an excellent platform for the development of chiral photonic microstructures. It is important to first discuss the geometry of the gyroid surface and the srs-network to fully understand the optical properties of the

Figure 3.1  a) The achiral gyroid surface coloured orange on one side and green on the other and the RHD (red) and LHD (green) srs-networks. b) Close up view along [001] illustrating the LHD 4-fold screw axis (green) and the RHD 4-fold screw axis (red). c) Single unit cell of the srs-network viewed along [001]. d) Close up view of the gyroid surface along [001] showing the RHD 3-fold helical axis of the srs-network. e) Close up view of the gyroid surface along [111] showing the RHD 3-fold helical axis of the srs-network. c) Single unit cell of the srs-network viewed at an oblique angle.
gyroid structures investigated in this thesis (a review of the gyroid was given in Sec. 2.6.2). Important features of this geometry include:

1. The gyroid is an achiral 3D surface (with space group $Ia3d$) that forms a boundary between two srs-networks of opposite handedness as shown in Figs. 3.1a,b.

2. The srs-network is a cubic chiral network (with space group $I4_132$) and is named after the $SrSi_2$ crystal [163].

3. The srs-network is fully interconnected.

4. The srs-network has a 4-fold screw axis along $[100]$ and a 3-fold screw axis of opposite handedness along $[111]$ as shown in Figs. 3.1c,d.

5. The srs-network is the simplest cubic chiral network from a topological point of view (i.e. it has the highest degree of symmetry).

Note that whilst the name “gyroid” refers to the achiral minimal surface [150], other structures that are related to this surface are often called “gyroid structures”. For example in [148] the srs-network is called the “single network gyroid”. In this thesis we have used the following conventions:

1. A right-handed (RHD) srs-network is one whose 4-fold screw axis along $[100]$ is RHD and whose 3-fold screw axis along $[111]$ is left-handed (LHD). Vice versa for a LHD srs-network.

2. We choose a co-ordinate system where the crystallographic directions $[100]$, $[010]$ and $[001]$ are along the X, Y and Z axes, respectively.

3. Note that all of the simulations in this thesis will be performed for light propagating along $[001]$ unless otherwise stated.
Due to the cubic symmetry of the srs-network, the 4-fold screw axis can be observed whilst looking at the srs-network along all three Cartesian axes (i.e. X, Y and Z). Therefore, unlike a structure consisting of a square array of helices (spirals), the srs-network has the possibility to exhibit chiral-optical effects such as circular polarisation sensitivity in multiple directions, with possible isotropic properties as well. As well as the advantages of cubic symmetry for multi-directional physical phenomena, cubic symmetry provides the complex 3D structure with mechanical integrity. This is an important issue to consider when it comes to the experimental realisation of these microstructures as we shall see within this chapter.

![Figure 3.2](image.png)

**Figure 3.2** a) A single unit cell of the srs-network based on a LHD CMC surface filled to 50% filling fraction viewed at an oblique angle. b) An CMC srs-network structure containing 3x3x2 unit cells.

Note that gyroid surface and srs-network are mathematical objects that are infinitesimally thin (i.e. they take up no physical space). When designing photonic microstructures based on these mathematical geometries, one must consider in what way we can transform these infinitesimally thin objects into solid structures with finite thickness. A simple way to make a solid structure from the srs-network is inflate the lines to form rods with a user-defined radius $r$. This happens to be a practical solution for nano-engineering via DLW as we shall see in Sec. 3.3.
However, in nature the srs-network is formed naturally via the formation of constant-mean-curvature (CMC) surfaces such as that found in the *Callophrys Rubi* butterfly [137, 149]. The CMC surface of the srs-network can be thought of inflating the lines of the network such that the surface is formed with constant pressure (according to the Young-Laplace formula) [115, 176]. The result is a chiral structure with a finite filling fraction (porosity) with the same symmetry properties of the srs-network. An example is given in Figs. 3.2a,b, which contains computer simulation images of a LHD CMC srs-network surface with an inflation such that the filling fraction is 50\%\textsuperscript{1}. Note that the mirror image of this CMC surface transforms the chirality to the opposite handedness, e.g. from RHD to LHD.

Note that the periodic srs-network is fully interconnected, an important feature for realising 3D microstructures via DLW that do not require any other support, such as free standing spirals fabricated in [94], which required a surrounding frame with a mesh grid to hold the spirals in place. Of course when the periodicity is broken by forming a terminating boundary, this creates a point where the interconnectivity of the periodic structure is broken, thus one must carefully design the clipping conditions of the boundaries, which we shall discuss in the following section.

### 3.3 Designing a practical microstructure

In order to theoretically and experimentally investigate the optical properties of the srs-network, one must first consider the specific design of the 3D microstructure. In this section we discuss the design of srs-network microstructures to be fabricated via DLW. We have considered two different designs based

\textsuperscript{1}Another way to think of the CMC srs-network surface is by filling half of the space defined by the infinitesimally thin gyroid surface. Depending on which side of the gyroid surface is filling the CMC srs-network surface can be either RHD or LHD.
on two fabrication methods, the raster scan method and the network-write method. We shall compare these methods and discuss why the network-write method is most suitable for DLW. The experimental setup of the DLW method used here and in the rest of this chapter consists of a custom built DLW system that has been developed in [13, 23, 24, 83] and is shown in Fig. 3.3.

The DLW setup consisted of a Ti:Sapphire femtosecond laser operating at the wavelength of 800 nm with a pulse width of 150 fs and a repetition rate of 75 MHz. This infrared laser was converted to the wavelength of 580 nm using an optical parametric oscillator. The wavelength of 580 nm was chosen instead of the more commonly used 800 nm, to reduce the size of the diffraction limited focal spot while maintaining a high power output from the parametric conversion. The laser exposure was controlled by a mechanical shutter. The laser beam then passed through a combination of a beam expansion and
spatial filter (15 μm pinhole) to overfill the objective lens with a uniform beam intensity. This expanded beam was then focused by an oil immersion objective (Olympus, N.A. 1.4, 100X). We used the commercially available negative photoresist IP-L (Nanoscribe Gmbh), which has a refractive index of n = 1.52. The photoresist was sandwiched between two microscope coverslips and then mounted on a piezo nano-translation stage (P-562, Physik Instrumente). The motion of the nano-translation stage was controlled by sending computer commands via a controller (E710, Physik Instrumente). An infrared light source was placed below the sample and the sample was confocally imaged using a short pass dichroic mirror and charge-coupled device (CCD) camera.

3.3.1 Raster scanning

The raster-scan method was based on discretely sampling the structure to form a voxelisation of any arbitrary 3D structure. Analogous to the 3D raster scanning in a commercial 3D printer, this method consists of writing individual 2D cross-sections of the 3D model, layer-by-layer. In Fig. 3.4 we show the cross sectional layers of the voxelised CMC srs-network surface (see Fig. 3.2 for the design) consisting of a 3x3 periodic array of the CMC unit cells. The filling fraction\(^2\) is ff = 50% for this structure and the 3D array is made up of an array of 50 x 50 x 50 voxels.

This raster scanning method is easily adapted to the DLW method. However, in order to have an accurate replication of this complex 3D structure, a dense voxelisation array will be required, making fabrication times very slow. In order to test the feasibility of this method for the replication of these gyroid srs-networks, we fabricated a small gyroid network with a cubic unit cell size

\(^2\)The filling fraction (ff) is defined as the volume of the polymer srs-network within a single unit cell divided by the volume of the total unit cell (i.e. \(a^3\)).
Figure 3.4  Cross sections of a 3D voxelisation of the LHD CMC srs-network surface, with filling fraction $ff = 50\%$ at different $Z$-axis positions in the unit cell. The units of the $X$ and $Y$ are measured in unit cells. a) $Z = 0$, b) $Z = 0.2$, c) $Z = 0.4$, d) $Z = 0.6$, e) $Z = 0.8$ and f) $Z = 1.0$, where $Z$ is measured in unit cells. Note that $Z = 0$ and $Z = 1$ are identical as the unit cell repeats itself every spacing of 1 unit cell.
of 4 $\mu m$ and with an overall small size of just 3x3x1.5 unit cells. The voxelised data set shown in Fig. 3.4 was used for the raster scan trace.

Figure 3.5 contains scanning electron microscope (SEM) images of a gyroid structure fabricated using the raster scan method. For the fabrication shown in Fig. 3.5 an average laser power (measured immediately before the objective) of 1.3 mW was used. The translation stage that performed the raster scan moved at a relatively slow speed of 10 $\mu m/s$. This slow speed was used to ensure that the fine spatial details contained in the short lines were accurately written. After the DLW process had been completed the sample was rinsed with 2-propanol for 20 minutes in a Petri dish. This rinsing procedure washes away the unpolymerised photoresist, leaving behind the written 3D microstructure. Nevertheless, the structure shown in Fig. 3.5 shows good replication of the chiral gyroid design shown in Fig. 3.2. However, from the tilted SEM image we see that the line-by-line approach leads to layer discretisation, due to the finite size of the voxelisation. There seems to be little distortion and shrinkage of the structure, illustrating the mechanical stability of this structure for fabrication.

![Figure 3.5 SEM images of a LHD CMC srs-network surface fabricated by the raster scanning method. a) View from the top, b) View from an oblique angle. The scale bars are 2 $\mu m$.](image)

However, due to both the slow speed of the translation stage movements and
the high density of voxel points to be written, this relatively small structure took over 3 hours to fabricate. In order to fabricate structures large enough for optical characterisation, we would require a volume increase of at least two orders magnitude. These lengthy time scales are completely impractical and due to drifts in the laser power or other mechanical drifts, the uniformity of the structure may be comprised over these long time scales.

Note that the speed of fabrication could possibly be improved by using a spatial light modulator (SLM) to form an image in the shape of the 2D cross section shown in Fig. 3.4. This is achieved by applying a complex phase distribution that can be calculated using vectorial Debye theory [177], which forms an image in the diffraction limited focal plane of the laser. By printing the 2D cross section of the srs-network, rather than raster scanning, fabrication speeds could be greatly enhanced.

3.3.2 Network-writing

A different method to fabricating the chiral srs-network without trying to replicate the curved CMC chiral gyroid domain, is the tracing of the points of the srs-network. Whilst this would result in a different microstructure to the CMC network, it would belong to the same symmetry group (i.e. the $I4_132$) and thus have the geometrical advantages we seek (cubic symmetry, chirality and interconnectivity).

We have found through numerical simulations that apart from a very small shift in the spectrum (typically 1-2%), there are no qualitative differences in the PC properties. By fabricating just the srs-network, these 3D microstructures should be realisable with smaller unit cell sizes compared to the voxelisation of the raster scan. This approach would also be much faster than the raster scanning as it requires only one pass of the laser writing per segment of the
In Fig. 3.6 we plot the RHD srs-network\(^3\). The unit cell of the srs-network shown in Fig. 3.6a appears to have a disconnected component from the rest of the unit cell structure. However, by rearranging this unit cell configuration by translating certain rods to the neighbouring unit cell one can make a fully connected unit cell as shown in Fig. 3.6b. Due to the symmetry of the srs-network the unit cell can be broken down into 4 sub-unit cells, which consists of 3 rods that form a twisted (chiral) U-shape and is illustrated in Fig. 3.6b by the colours red, blue green and cyan. The bottom layer shown in red would first

\(^3\)Note that the choice in the handedness of the srs-network is arbitrary.
be written by using DLW. The next layer shown in blue would then be written, which connects neighbouring red layers. And then the green and cyan layers would follow similarly. This method can be used to construct large gyroid network structures as shown in Fig. 3.6c, which consists of a 5x5x5 array of the unit cell shown in Fig. 3.6b. Fabrication of such a structure would consist of writing the first layer of red sub-unit cells at the bottom of the structure (i.e. an array of quarter unit cells). This is then followed by the fabrication of the blue layer, which connect the layer of red sub-unit cells together. Finally the green and cyan layers are written to complete the unit cell.

Note that whilst the interior of the gyroid structure is mechanically stable due to its interconnectivity, at the boundaries of the structure the network rods are no longer fully-connected and are more susceptible to distortions.

### 3.3.3 Boundary design

In order to maintain a structure with good overall mechanical stability one needs to pay attention to the cleaving of the boundary. Here in this thesis we primarily use two conditions for cleaving the boundary, one based on a pyramid-like shape and the other with flat cubic boundaries. In Fig. 3.7 we compare the srs-network (each is 4 unit cells wide, and 2 unit cells tall) with basic, pyramid and cubic boundary conditions.

The basic boundary condition does not apply any specific clipping of the 3D structure and results in free standing, unsupported rods at the boundaries of the structure. This is impractical as these unsupported components are easily distorted during the washing of the sample.

The pyramid boundary condition has the most structurally stable boundaries as there are no free standing rods. Here the width of the top layer is narrower
than that of the bottom layer. If the number of unit cells is increased in the lateral direction (i.e. in the directions of X and Y) then the top layer of the pyramid would also increase in width. When designing a structure for transmission characterisation, it is important to ensure that the width of this top layer is wide enough for the measurement aperture, which is typically around 10 unit cells wide.

![Figure 3.7](image_url) Designing the boundaries of the RHD srs-network for DLW. a-c) View from the top ([1001]). d-f) View from the front ([100]). g-i) View from an oblique angle ([1 0.2 0.3]). In (a) (d) and (g) no clipping of the boundary has been applied leading to unsupported rods at the ends. In (b) (e) and (h) a pyramid like shape has been used for mechanical stability. In (c) (f) and (i) cubic boundary conditions have been used, which have connected rods at the face of the boundary.

The cubic boundary condition has flat boundaries that are normal to the Cartesian axes, with the rods at the boundary being clipped such that they are not free standing. Whilst this leads to connected rods at the faces of the
cubic structure, at the edges there is an unavoidable row of free standing rods that could possibly distort during the fabrication process. However, the effect of this edge distortions should be minimal to the rest of the structure as we shall see later in the chapter.

3.4 Numerical simulations

In order to gain a physical understanding of the optical properties of the srs-network PC we shall first discuss the theoretical analysis of this chiral PC. In this section we present the numerical simulation of the transmission and reflection of incident circularly polarised plane waves on the srs-network PC. We have used the commercially available CST Microwave Studio, using the frequency domain finite element method (FEM). The meshing of the srs-network is done by first breaking the surface into small triangulated segments and then the internal volume of the structure is meshed by forming tetrahedrons from these triangulated surfaces. In order to improve the replication of curved surfaces, rather than having a finer triangulated mesh, CST Microwave Studio applies a curve to the surface mesh, which greatly improves the mesh quality at low mesh densities. This improves both the accuracy and efficiency of the simulation.

In these simulations, a unit cell boundary condition is used, which assumes a periodicity in the X and Y directions. The boundary conditions in the Z-direction are assumed to be open boundaries for incident plane waves to enter and exit the system. By exciting the structure with circularly polarised plane waves at different frequencies one can measure the reflection and transmission spectra, analogous to an experimental spectroscopy measurement. Here we only simulate frequencies for \( \omega a/2\pi c < 1 \) (where \( \omega \) is the frequency of light, \( a \) is the unit cell size and \( c \) is the speed of light in vacuum), where we only
need to consider the propagation of the fundamental Floquet modes, i.e. no higher order modes such as $TE_{01}$ or $TM_{01}$ need to be considered at the open boundaries.

There are four main measurements that we shall use to characterise the optical properties of these srs-network PCs:

**Transmission:** This is the amount of RCP/LCP polarised light that is able to transmit through the PC maintaining its excitation polarisation state. We label the transmission of LCP and RCP light in the figures as “LCP” and “RCP,” respectively.

**Transmission conversion:** This is the amount of RCP/LCP polarised light that is able to transmit through the PC but undergoes a switch in its polarisation state. We label the polarisation conversion of LCP to RCP and RCP to LCP light as “L2R” and “R2L,” respectively.

**Reflection conversion:** This is the amount of RCP/LCP polarised light that is reflected from the PC but undergoes a switch in its polarisation state. The same labels L2R and R2L for transmission conversion are used for reflection conversion.

**Reflection:** This is the amount of RCP/LCP polarised light that is reflected from the PC maintaining its excitation polarisation state. We label the reflection of LCP and RCP light in the figures as “LCP” and “RCP,” respectively.

Note that circularly polarised waves incident on an air-dielectric interface have a change in their polarisation state under external reflections and maintain their polarisation state under internal reflections.

Images of the srs-network are given in Fig. 3.8. Here the srs-network has been built by connecting short circular rods together in the shape of the srs-
network. The rods have a radius $r = 0.05$ (relative to the unit cell size), which gives a 3.2% filling fraction of the dielectric srs-network (i.e. 96.8% of the volume is the air background). Note that the starting and finishing points of the structure along the $Z$-axis has been chosen to replicate the fabrication design that builds the PC in layers of the sub-unit cell layers. It is important to note that the arbitrary control of the geometry, size, orientation and boundary cleaving conditions of the microstructure designed for DLW, discussed here is a major advantage over self-assembly methods, which have very little control over these parameters, which are critical for developing photonic devices.

Figure 3.8 Images of the 3D network consisting of rods joined together in the shape of the 3D cubic chiral srs-network. The total structure here is made of a 3x3x4 array of unit cells with the radius of the rods (relative to the unit cell size), $r = 0.05$, giving a filling fraction of 3.2%. a) Side view. b) Top view. c) Zoom in view nearly along [100] to illustrate the LHD chirality of the 4-screw axes.

3.4.1 Results for the srs-network

Here we discuss the numerical simulations of srs-networks using the frequency domain FEM (CST Microwave studio). Unless otherwise stated, the geometrical parameters of the srs-network used in this chapter are:

- The cubic unit cell size is $a = 3 \, \mu m$ (chosen for realisation via DLW).
• The filling fraction of the polymer srs-network is $f = 30\%$.

• The refractive index of the polymer is $n = 1.52$.

• The number of unit cells along the direction of propagation is $N_z = 4$.

• The direction of the light propagation is along [001] (the Z-axis).

In Fig. 3.9 we plot the transmission, transmission conversion, reflection conversion and reflection spectra at the wavelength regime of interest that shows the fundamental bandgap of the PC, which for the 3 $\mu$m unit cell srs-network corresponds to 3.3 - 4.8 $\mu$m. The density tetrahedral mesh of the numerical simulation was chosen such that the spectra does not shift more than 0.5% of the original wavelength by further increasing the mesh density.

![Figure 3.9](image) Numerically calculated transmission and reflection spectra along [001] for a RHD srs-network. The RHD srs-network PC has $a = 3 \mu$m, $f = 30\%$, $n = 1.52$ and $N_z = 4$. The red and blue curves are for RCP and LCP incidence, respectively. a) Transmission. b) Transmission conversion. c) Reflection conversion. d) Reflection (note both LCP and RCP curves perfectly overlap).
As can be seen by these spectra, the PC is seen as a transparent homogeneous material for the longest wavelengths, with nearly 100% of both LCP and RCP light being transmitted. Note that the small oscillations in the transmission at these long wavelengths are due to the finite size of the PC, which creates Fabry-Perot-like effects. At 4.0 μm, the transmission starts to decrease with an increase in the reflection conversion for both polarisations, reaching a minimal transmission at 3.8 μm. This region will later on be shown to be due to the formation of a photonic bandgap (PBG). There is a small difference in the transmission between LCP and RCP light at the band edge here, suggesting that the attenuation due to the bandgap is greater for RCP light than LCP light.

At wavelengths between 3.3 μm to 3.8 μm we see the formation of transmission and reflection bands, where the response of LCP and RCP is completely different. For RCP light we see a very large reflection band from 3.43 μm to 3.8 μm. Most importantly, in this frequency band there are wavelengths bands where LCP has significantly high transmission. This region is known as a circular dichroism band and has also been previously demonstrated in circular spiral PCs [94, 112, 114]. Within this circular dichroism band, the transmission of the LCP light contains sharp resonances where large reflection occurs. These very sharp resonances are due to the interference between forward and backward propagating modes and have been observed previously in spiral PCs, where it was theoretically investigated using coupled mode theory[178]. Due to the very narrow line-width of these resonances of around 5-20 nm, these would be nearly impossible to detect using experimental methods such as Fourier transform infrared (FTIR) microscopy. This is because the positions of these sharp-resonances are highly dependent on the angle of incidence. Experimental characterisation methods such as FTIR microscopy, have a finite angle of incidence onto the sample due to the focusing of the illumination source (i.e. it is not a plane wave incident on the PC as in simulation). This leads to
an effective smoothing of the measured spectra and will be discussed in more
detail in Sec. 3.6.

The transmission conversion is very small at all wavelengths, except when
these sharp resonances occur. Transmission conversion is related to the linear
birefringence of the structure. Whilst the srs-network has cubic symmetry,
the termination of the periodic structure leads to a small amount of linear
birefringence. However, the transmission conversion is very small and in
experiments where these sharp resonances are smoothed out, transmission
conversion would be negligible. Similarly, the reflection that does not convert
the polarisation of light is also very small except at the shorter wavelengths,
where high bands are excited and sharp resonances occur.

3.4.2 Comparison with band diagrams

In this section we investigate the physical mechanisms behind the circular
dichroism observed from the numerically simulated transmission and reflection
spectra of the srs-network. By comparing the theoretically calculated band
structure with an analysis of the polarisation state of the Bloch modes [115],
the circular dichroism can be explained. For the band structure calculations,
the srs-network is based on the LHD CMC srs-network surface\(^4\) as found in
the wing scales of the *Callophrys Rubi*. These nanostructured wing scales are
made of chitin, a biological material with refractive index \(n \sim 1.55\) [115] very
close to that of the polymer networks we are investigating in this thesis (\(n =
1.52\)). In order to predict the reflection/transmission spectra from a finite sized
PC, the Bloch modes of these 3D dielectric PCs are calculated along [001],

\(^4\)It is important to note that the handedness of the CMC srs-network is arbitrary and
that a change of the handedness of the structure (i.e. from LHD to RHD) results in the
simple change of the circular polarisation state (i.e. from LCP to RCP). Note that there is
currently no evidence that srs-networks found within the *Callophrys Rubi* butterfly has a
particular handedness throughout its entire wing.
followed by the analysis of their polarisation states and coupling to free space plane waves.

The Bloch modes have been calculated using the MIT photonic bands (MPB) software package (and the CMC srs-network surface with filling fraction of 20.5\% was approximated by using $512^3$ voxels). The time-averaged magnetic fields are expressed in Bloch modes, $\mathbf{H}_{k,n}(r) = \sum_G h_G e^{i(k+G) \cdot r}$ where $\mathbf{k}$ is the wave-vector of the Bloch mode of mode $n$ and $\mathbf{G}$ is the Fourier series frequency of the magnetic field $h_G$. The frequency of the Bloch modes are related to the wave-vector by the dispersion relation $\omega_n(k)$. These magnetic fields are then clipped at a certain plane within the PC, and the 2D fields at that plane are analysed. The circular polarisation state of the Bloch modes was then analysed for a wave incident on the PC with wave-vector $\mathbf{q}$, by calculating the circular dichroism index, $C$, which is given by [115]:

$$C = \text{sgn}(\mathbf{q} \cdot \nabla_k \omega(k)) (C^+_{k,n} - C^-_{k,n})/(C^+_{k,n} + C^-_{k,n}), \quad (3.1)$$

where

$$C^\pm_{k,n} = \left| \sum_G (\mathbf{e}_x + i\mathbf{e}_y) \cdot h_G \int_P e^{i(k+G) \cdot r} dxdy \right|, \quad (3.2)$$

where $\mathbf{e}_x$ and $\mathbf{e}_y$ are the identity vectors along the X and Y directions, respectively, $P$ is the clipping plane of the 3D PC and $\text{sgn}$ is the sign function.

When $C = +1$ the Bloch mode at that plane in the PC is 100\% RHD circularly polarised and when $C = -1$ it is 100\% LHD circularly polarised. A value of $C = 0$ means the Bloch mode has no preference to either LHD or RHD circular polarisation. To determine how strongly light couples to these Bloch modes, we have defined the coupling coefficient $\beta$, which by the average of the coupling to both the RCP and LCP modes:

$$\beta_{k,n} = (C^+_{k,n} + C^-_{k,n})/2. \quad (3.3)$$
The value of C allows one to approximate the circular polarisation of the Bloch modes and the results for the LHD CMC srs-network surface is shown in Fig. 3.10a. The dispersion curve $|\mathbf{k}|$ is shown in Fig. 3.10b. For the fundamental band of the PC there are two degenerate modes that differ only by their value of $C = 1$ and $C = -1$. These two fundamental modes start to lose their circular polarisation (i.e. $C$ approaches zero) as they approach the band edge at the frequency $\omega_1$. A PBG region exists between frequencies $\omega_1$ and $\omega_2$. This results in the total reflection for both LCP and RCP polarisations as seen in Fig. 3.10d.

![Figure 3.10](image)

**Figure 3.10** Polarization analysis of the band structure for a LHD srs-network with a filling fraction of the chitin network being $f = 20.8\%$. a) Circular dichroism index, $C$. b) Band diagram dispersion relation along $[001]$ ($\Gamma - H$). c) Coupling index, $\beta$. (d) Reflectance coefficient, $R$, calculated using the scattering-matrix method, for RCP (red) and LCP (blue) incidence respectively. The colours of the points in (a-c) are proportional to the value of $C$, where $C = +1$ is red and $C = -1$ is blue. The point radius is proportional to the value of $\beta$. Black dots represent Bloch modes, which have neither RCP or LCP polarisation (i.e. $C = 0$). Image courtesy of Matthias Saba [115].

At frequencies between $\omega_2$ and $\omega_3$ we have a circular dichroism band, coloured in red. In this region there is one mode that folds back on itself. Thus at any
particular frequency within this regime, there are two modes light can couple to. As can be seen by the circular dichroism index one of these modes is RCP and the other LCP. One would expect then that this region would not be a circular dichroism band, as both RCP and LCP modes co-exist. However, the existence of a mode is not enough to determine the transmission/reflection. One must also consider how light external to the PC couples into these modes, i.e. the value of $\beta$, which is shown in Fig. 3.10c.

The value of $\beta$ is also represented by the size of the points in Figs. 3.10a-c. The coupling coefficient is compared with the reflection spectra, for RCP (red) and LCP (blue) incident light, calculated with the scattering-matrix method for a comparison and plotted in Fig. 3.10d. The increase of the reflection before $\omega_1$ is due to the decrease of the coupling of the incident planes waves to the PC Bloch modes and then from $\omega_1$ to $\omega_2$, within the bandgap, both LCP and RCP are fully reflected. Within the circular dichroism band the RCP mode has a relatively large coupling coefficient, however, the LCP mode has a very weak coupling. Thus in this regime we expect the LCP incident light to be reflected, as it cannot couple efficiently into the PC Bloch modes. Note that the handedness of the polarisation with the broadband reflection (LCP) matched the handedness of the LHD srs-network in this case. This is in agreement with the sign of the circular dichroism observed for dielectric circular spiral PCs [90, 94].

For frequencies between $\omega_2$ and $\omega_3$ the single Bloch mode that is LCP has very weak coupling, thus neither RCP and LCP light is able to couple into the PC in this regime, leading to a low-coupling region [115] for both polarisations. In this frequency region external planes waves are not able to couple to any Bloch mode and is thus reflected off the PC as shown in Fig. 3.10d. Note that regions where $\beta$ does not vary greatly with frequency are regions where the reflection spectra are relatively constant.
To summarise, it is not just the formation of bandgaps that determines the transmission of polarised light through a PC (and hence circular dichroism), but also the coupling coefficient as well. Further, the circular polarisation state of these Bloch modes should be considered when determining effects such as circular dichroism.

In Fig. 3.11, we compare these theoretical results with our numerical simulations of the LHD srs-network based on straight rods with a circular cross section, with identical refractive index and filling fraction conditions as the band structure calculations for the LHD CMC srs-network surface. The band structure from Fig. 3.10b is compared with the numerical simulated transmission spectra in Fig. 3.11. The two plots have been scaled and positioned such that the two Y-axes of the plots co-align.

**Figure 3.11** Comparison of the band structure of the LHD CMC srs-network surface with the numerically calculated transmission spectra for a LHD srs-network, with refractive index $n = 1.52$ and a filling fraction $f = 20.8\%$ for both calculations. a) Band diagram of the LHD CMC srs-network surface [115]. b) Numerically calculated transmission spectra of RCP (red) and LCP (blue) incident light on a rod-based srs-network.
The comparison in Fig. 3.11 between the band structure analysis and the numerically simulated transmission spectra show an excellent qualitative agreement. There are minor differences in the frequencies of the bands, which is most likely due to the minor difference between the voxelised CMC srs-network used for the band structure and the rod-based srs-network we have used in the numerical simulations.

### 3.4.3 Dependence on the filling fraction

Here we investigate the effect of the polymer filling fraction on the transmission spectra of the srs-network based on straight rods with circular cross section. Note that the handedness of the srs-network here and for the rest of this chapter has been arbitrarily chosen to be RHD without any loss in generality.

![Numerically calculated transmission spectra of a RHD srs-network for varying filling fraction of the srs-network.](image)

**Figure 3.12** Numerically calculated transmission spectra of a RHD srs-network for varying filling fraction of the srs-network. a) Fill = 19%. b) Fill = 26.9%. c) Fill = 35.9%. d) Fill = 46%. 
In Fig. 3.12 we plot the transmission spectra for the srs-network with $N_z = 4$ and varying the filling fraction from $f = 19\%$ to $f = 46\%$. It is well known for PCs that an increase in the filling fraction causes a red-shift in the spectra [8]. The results here show that as the filling fraction of the srs-network is tuned from $f = 19\%$ to $f = 46\%$ the PBG central wavelength shifts from 3.6 $\mu$m to 4.1 $\mu$m. Note that the position of the first sharp resonances is always near the peak of the transmission band for LCP in the circular dichroism band.

### 3.4.4 Dependence on the number of unit cells

In this section we numerically investigate the dependence of the number of unit cells along the direction of propagation ($N_z$) on the optical properties of the srs-network. Figure 3.13 contains the transmission spectra for four different values of $N_z$. For $N_z = 2$ we see that the band edge is not as sharp, due to the tunnelling of the evanescent Bloch modes for small PC thickness. However, the circular dichroism band is still very prominent perhaps due to the fact that the circular dichroism is the result of circularly polarised low-coupling (as discussed in Sec. 3.4.2). Interestingly, there is only 1 sharp resonance in the circular dichroism band, suggesting that the number and position of these sharp resonances is related to the number of unit cells, $N_z$.

As the number of unit cells is increased from $N_z = 2$ to $N_z = 8$ the band edge at 3.9 $\mu$m becomes sharper and is nearly vertical at $N_z = 8$, where the bandgap region from 3.75 $\mu$m to 3.9 $\mu$m is well defined. However, the existence of many more sharp resonances in the circular dichroism region makes the transmission band for the LCP (i.e. between 3.5 - 3.75 $\mu$m) harder to distinguish.
Figure 3.13  Numerically calculated transmission spectra of a RHD srs-network for varying number of unit cells along the direction of propagation $N_z$. The cubic unit cell size is 3 $\mu$m and the filling fraction is 30%. Red and blue curves are for RCP and LCP transmitted light respectively. a) $N_z = 2$. b) $N_z = 4$. c) $N_z = 6$. d) $N_z = 8$.

The effect of the value of $N_z$ on the polarisation conversion is investigated in Fig. 3.14.

Figure 3.14  Numerically calculated transmission conversion spectra of a RHD srs-network for varying number of unit cells along the direction of propagation $N_z$. The cubic unit cell size is 3 $\mu$m and the filling fraction is 30%. Red and blue curves are for R2L and L2R respectively. a) $N_z = 2$. b) $N_z = 8$. 
For both $N_z = 2$ and $N_z = 8$ the polarisation conversion is negligible except at the location of the sharp resonances. Note if the srs-network was to be used as a circular polariser, the lack of polarisation conversion at nearly all frequencies is a very important feature.

### 3.4.5 Dependence on the boundary clipping position

As we expect the coupling of the incident plane wave to be different at differing clipping planes of the 3D PC, here we investigate the dependence of the transmission spectra on the position of the clipping plane of the 3D PC. This is an important geometrical parameter to understand experimental results, where the clipping plane of the srs-network at the input structure-substrate interface may vary over the entire area of the PC due to finite surface-flatness of the glass substrate. An illustration of the clipping plane is shown in Fig. 3.15.

![Illustration of the clipping of the srs-network](image)

**Figure 3.15** Illustration of the clipping of the srs-network. a) The original srs-network with the clipping region highlighted with dashed lines with thickness $N_z$ unit cells. b) The clipped srs-network with a reduced thickness $N_z - d$ unit cells.

Figure 3.16 contains a plot with 5 simulation curves for various clipping planes of the 3D PC. Here we have clipped the input face of the PC with a clipping
thickness of $d$ (measured in number of unit cells), i.e. the total thickness of the PC becomes, $N_z - d$. As we vary $d$ from 0.1 to 0.5, it can be clearly seen that the effect of the clipping plane has a negligible effect on the transmission spectra and should not cause any noticeable effects for the dielectric PCs in the following experiments.

![Figure 3.16](image)

**Figure 3.16** Numerically calculated transmission conversion spectra of a RHD srs-network for varying clipping depth, $d$. a) Transmission of LCP. b) Transmission of RCP.

### 3.5 DLW results of 3 μm srs-network

In the previous sections we have established both a design principle for fabricating the srs-network (see Sec. 3.3) and a detailed theoretical understanding of the chiral-optical properties of this chiral PC (see Sec. 3.4). In this section we demonstrate the DLW of the srs-network with unit cell size 3 μm and with pyramid boundary conditions, followed by the experimental characterisation results in Sec. 3.6.

The experimental setup used for the DLW method here was the same as in Sec. 3.3.1. A fabrication speed of 10 μm/s was used such that the velocity of the scanning of the rods is relatively uniform. The DLW of the 3D microstructures starts by writing first the bottom quarter unit cell layer (the red layer in Fig. 3.7), which is intentionally written at 0.5 μm to 1 μm below the glass-
polymer interface. This ensures that microstructure will be attached to the glass coverslip over the entire area of the microstructure. Failing to do this procedure may result in the microstructure being written above the surface, leading to the washing away of the microstructure during the wash out process. After the DLW procedure, the sample is rinsed in 2-propanol for 20 minutes and then dried at room temperature.

Figure 3.17 SEM images of the srs-network fabricated via the DLW method. The overall srs-network has a pyramid shape to avoid distortions at the boundaries due to termination of the interconnected srs-network. a-c) Views of the srs-network along [001]. d-f) Views of the srs-network approximately along [111]. (a,b,d,e) are SEM images with scale bars 10 μm in (a,d) and 2 μm in (b,e). (c,f) are computer simulations of an srs-network to compare with the SEM images.

As can be seen in Fig. 3.17 the fabricated polymer srs-network replicates the network topology excellently with high uniformity, minimal distortion and no noticeable shrinkage. This structure consists of 10 unit cells wide at the bottom, 4 unit cells wide at the top and 3 unit cells in height. The zoomed in SEM image in Fig. 3.17b, clearly shows the RHD 4-screw axis of the srs-network along [001] (top view). It should be noted that the computer
simulated structures are smaller than the ones in the SEM image (they are 6 unit cells wide at the bottom), such that the details in the topology (screw axes) can be clearly seen.

Whilst the topology of the srs-network is well replicated, when looking at the structure from an oblique angle as shown in Figs. 3.17d,e, the elongation of the voxel along [001] (i.e. the Z-direction) leads to a breaking of the cubic symmetry of the fabricated 3D microstructure. We expect the elongation of the voxel to be approximately 3 (the voxel height along the Z-axis relative to the voxel width along the X-axis and Y-axis) based on the SEM images, which is similar to that discussed in similar DLW experiments [26, 93]. The effects of this voxel elongation and how to overcome this issue is the topic of the next chapter.

Having demonstrated the feasibility of the fabrication of these chiral srs-networks via DLW we have subsequently designed and fabricated much larger srs-networks as shown in Fig. 3.18, for the purpose of optical characterisation with an FTIR microscope. These much larger microstructures also have a 3 μm unit cell size and have adopted the pyramid-like shape for mechanically stable boundaries. The entire microstructure is 22 unit cells wide at the bottom (66 μm), 14 unit cells wide at the top (52 μm) and 4 unit cells (12 μm) in height. Based on the numerical simulation results discussed in Sec. 3.4, we expect a large circular dichroism with just 4 unit cells in height.

The microstructures shown in Fig. 3.18 have excellent uniformity, demonstrating the high quality of the DLW method and more importantly the mechanical stability of the srs-network design. The pyramid-like shape in Fig. 3.18b is clearly seen, with a large flat top ideal for transmission spectroscopy. In the higher magnification SEM images shown in Figs. 3.18c,d, one can clearly see the RHD chirality of the 4-screw axes along [001]. These fabrication results have been published together with the characterisation results in the following
section in [175].

Figure 3.18  SEM images of a much larger RHD srs-networks with 3 μm unit cell size, pyramid-like shape. The entire microstructure is 22 unit cells wide and 4 unit cells in height. a) Four srs-networks fabricated with different fabrication powers. b) One of the srs-networks fabricated with optimal DLW conditions. c-d) Close up views of (b). The scale bars are 20 μm in (a), 10 μm in (b) and 1 μm in (c,d).
3.6 Experimental characterisation of the srs-network

In this section we shall discuss the experimental characterisation of the 3 µm srs-network via FTIR microscopy (Thermo Nicolet)[175], which allows us to measure the transmission of light over a broad range of wavelengths between 1 µm to 10 µm and has been used to characterise the PBG properties of many PCs previously [15, 23–25, 105]. The FTIR microscope operates by focussing a broadband light source (which emits from the visible to far-infrared) onto a selected micron-scale sample area. All transmission spectra measured here have been normalised relative to the transmission through the sample substrate (130 µm thick borosilicate coverslip). The FTIR microscope uses a Cassegrain reflector with numerical aperture $N.A. = 0.4$, corresponding to an illumination angle of 18 – 41° relative to the normal of the sample. In order to illuminate the sample along [001], the sample was mounted at a 30° custom built mount on the microscope stage and a custom built pinhole [83] was added in between the Cassegrain and sample to reduce the illumination angle. The result is the illumination of the structure with a focused aperture, normal to the substrate allowing for the characterisation along [001] with a 10° illumination angle (i.e. ±5° relative to the normal). Ideally, a very small pinhole is used such that the illumination angle is less than 1° and thus the incident light can be considered as a true plane wave. However, there are two limitations to this:

1. The amount of excitation signal passing through the pinhole, which is significantly reduced for smaller pinhole sizes, lowering the signal to noise ratio.

2. Diffraction of the aperture window due to the finite numerical aperture, which is significantly increased for smaller pinhole sizes.
The pinhole with a 10° illumination angle was found to have the best compromise of accuracy, signal to noise ratio and diffraction. Circular polarisation excitation is achieved by using a combination of an infrared linear polariser (ColorPol MIR), which operates from 1 μm to 5 μm and an achromatic MgF₂ quarter-wave plate (Bernhard Halle), which operates between 2.5 μm to 7 μm.

![Figure 3.19](image.png)

**Figure 3.19** Experimentally measured transmission spectra of a RHD srs-network with unit cell size 3 μm and \( N_z = 6 \) fabricated using DLW in IP-L polymer photoresist shown in Fig. 3.18. Red and blue curves are for RCP and LCP transmitted light respectively.

In Fig. 3.19 we show experimentally measured transmission spectra of circularly polarized light through the RHD srs-network shown in Fig. 3.18. The transmission spectra along [001] have approximately 100% transmission at long wavelengths with the formation of band gaps and circular dichroism bands at wavelengths shorter than 3.5 μm. At wavelengths between 3.25 μm to 3.45 μm there is a circular dichroism band where LCP has high transmission and RCP has low transmission. The bandwidth of this circular dichroism stop band is approximately 6% and is comparable with that of the bi-chiral PC [90].
At shorter wavelengths where higher order Bloch modes are excited there are also regions with significant circular dichroism, but these are not as broadband and strong as the fundamental circular dichroism.

These experimental results are in qualitative agreement with the numerical simulation results discussed in the previous section, however, experimentally measured transmission spectra do not contain any sharp resonances. To understand this, we must consider the experimental measurement conditions carefully. In our numerical simulations of the srs-network transmission spectra we find that the spectra is red-shifted by 6% when light is incident at an angle of $\pm 5^\circ$ relative to the normal (not shown here). Thus our experimental excitation illuminates the sample with a cone of light between $\pm 5^\circ$ and will cause a smoothing of the spectra with a bandwidth of around 6% of the central wavelength.

![Figure 3.20 Images of the 3D srs-network design in CST consisting of elongated rods with an aspect ratio of 3:1 (i.e., 3 times longer along Z-direction), based on the experimentally fabricated srs-networks. a) Side view. b) Top view. c) Oblique view.](image)

In order to compare these FTIR results with numerical simulations we have recalculated transmission spectra for the RHD srs-network using the geometrical properties measured in the SEM images in Fig. 3.18. This srs-network contains rods that are 400 nm wide in the X and Y directions...
that are elongated by a factor of 3 in the Z-direction to account for the intrinsic elongation of the focal spot and is shown in Fig. 3.20. To account for the experimental angle of illumination, the transmission spectra has been smoothed using a top hat smoothing filter of bandwidth 100 nm (chosen based on numerically observed shifting of spectra due to small angular deviations of incident plane wave) and the resulting transmission spectra is shown in Fig. 3.21. For this spectra, we see excellent qualitative agreement with the experimental measurement. We expect the minor differences between the spectra (such as the lack of the sharper features) to be due to minor distortions of the DLW microstructure over the large area of the PC. Nevertheless, the replication of the circular dichroism band in the experimental data shows that the DLW method is able to replicate these srs-networks with a high degree of accuracy, demonstrating the formation of circular polarisation stop bands.

Figure 3.21  Numerically simulated transmission spectra of a RHD srs-network with unit cell size 3 \( \mu m \), \( N_z = 6 \) and with a smoothing filter of bandwidth 100 nm applied to account for the finite opening angle of the focusing condition in experiments. Red and blue curves are for RCP and LCP transmitted light, respectively.
3.7 Chiral composites

In this section, we discuss the chiral-optical properties of multiple srs-networks intertwined to form a chiral composite. Geometrically, it is possible to arrange two, three, four or eight like-handed srs-networks into a structure of cubic symmetry [179–181]. These networks intertwine with each other (i.e. they do not intersect at any point in space) and form chiral composites, new materials based on a combination of chiral constituents with differing chiral-optical properties as discussed here.

![Image](image.png)

**Figure 3.22** a) The LHD srs-network coloured in blue. b) The RHD srs-network coloured in red. c) The chiral 2-srs composite containing two intertwining LHD srs-networks. d) The achiral 2-srs composite containing two intertwining LHD and RHD srs-networks.

The two composites considered in this section are the *chiral 2-srs* and the *achiral 2-srs* composites. The chiral 2-srs consists of two same-handed srs-networks that are displaced by half a unit-cell along one of the Cartesian axes...
and is shown in Fig. 3.22c. On the other hand, the achiral 2-srs consists of one LHD and one RHD srs-network, thus cancelling out the net chirality of the overall structure as shown in Fig. 3.22d.

We have fabricated two different chiral 2-srs and achiral 2-srs composites, each consisting of two srs-networks with same and opposite handedness respectively. In Fig. 3.23 we show SEM images of the fabricated chiral (Figs. 3.23a,b) and achiral (Figs. 3.23c,d) 2-srs composites.

![SEM images of composites](image)

**Figure 3.23** SEM images of a chiral composites consisting of two intertwining srs-networks. a-b) The chiral 2-srs consisting of two RHD srs-networks. c-d) the achiral 2-srs consisting of a RHD and LHD srs-network. The scale bars are 10 μm in (a) and (c) and 1 μm in (b) and (d) respectively.
The individual srs-networks have a unit cell size of 3 μm and a pyramid-like shape as in the previous section. One can clearly see that the networks intertwine with each other, and the RHD and LHD screw axes can be observed in the zoomed in views of the SEM images. This demonstrates the unique ability of DLW to not only fabricate single srs-networks, but also multiple intertwined networks as well. The number of networks that can be intertwined is limited by the size of the structure relative to the resolution of the DLW method. In Chapter 6 we shall show that with correct compensation of the voxel elongation, we can even fabricate the chiral 4-srs structure proposed by [115].

In order to understand the photonic properties of these chiral composites, in Fig. 3.24 we have experimentally measured the transmission spectra (Figs. 3.24a,c), as for the single srs-networks, and compared the results with numerical simulations (Figs. 3.24b,d). The transmission spectra in Figs. 3.24a,b clearly demonstrate that the chiral 2-srs provides circular dichroism due to the existence of two RHD srs-networks that intertwine, however the strength of the circular dichroism is not as strong as that of the single srs-network.

On the other hand, the transmission spectra in Figs. 3.24c,d for the achiral 2srs does not show any circular dichroism. The small differences between the RCP and LCP for experimental measures in Fig. 3.24c is most likely due to asymmetries caused by minor imperfections of the fabricated achiral 2-srs microstructure. The numerical simulation in Fig. 3.24d has identical spectra for LCP and RCP that perfectly overlap.
Figure 3.24 Transmission spectra for the chiral composites consisting of two intertwining srs-networks. a-b) Experimentally (a) and numerically (b) obtained transmission spectra of the chiral 2-srs consisting of two RHD srs-networks. c-d) Experimentally (c) and numerically (d) obtained transmission spectra of the achiral 2-srs consisting of RHD + LHD srs-networks. Note that the RCP and LCP curves in (d) perfectly overlap due to the achiral symmetry of this composite.

On a side note, it is possible to induce chirality with the RHD and LHD double srs-network by changing the filling fraction of one of the srs-networks and breaking the achiral symmetry. This allows for a continuous variation of the chirality of the network and may be of interest for structures where a gradual, continuous variation in chirality is required.

The ability to fabricate chiral composites provides an extra degree of freedom for the construction of novel photonic devices. To demonstrate the possibilities
of these chiral composites, we have fabricated a 3D photonic microstructure shown in Fig. 3.25.

![Figure 3.25 SEM images of a 3D microstructure that consists of three different domains, demonstrating the flexibility of DLW of these chiral srs-networks. The left domain is a RHD srs-network, the right domain is a LHD srs-network, and the middle domain is the achiral composite where the two srs-networks overlap. The unit cell size of the srs-networks is 3 \( \mu \text{m} \). a) The entire microstructure, the scale bar is 10 \( \mu \text{m} \). b) Zoom in view of the RHD srs-network. c) Zoom in view of the achiral composite (RHD + LHD). d) Zoom in view of the LHD srs-network. The scale bars in (b-d) are 2 \( \mu \text{m} \).]

This microstructure contains two individual srs-networks of opposite handedness that only partially overlap leading to three distinct spatial regions, a RHD region (left), an achiral region (middle) and a LHD region (right). Each of these distinct regions will have different amounts of circular dichroism and more importantly at the interfaces of these materials unique chiral-optical functionalities can be constructed. This will be the topic of Sec. 4.6 where
we show that these chiral srs-networks can be used to build devices such as chiral beamsplitters, which could be of great interest for the development of polarisation devices in applications such as integrated quantum optics with circularly polarised qubits.

### 3.8 Chiral 4-srs composite

The 4-srs is a cubic chiral geometry that was recently shown to be an excellent design for a chiral PC with broadband circular dichroism [115]. These theoretical predictions were based on the 4-srs made from a high index material such as silicon, but other high index materials such as chalcogenide are also suitable.

The 4-srs is a unique geometry and has certain geometrical differences to the srs-network. In Fig. 3.26 we illustrate how the 4-srs has been geometrically constructed. This illustration contains 4 structures, consisting of 1, 2, 3 and 4 intertwined networks respectively viewed along the Z-axis (i.e. along [001]). The first structure in Fig. 3.26a has just a single srs-network that is coloured blue. By performing a translation of half a unit cell along the X-axis (i.e. along [100]) we create the red srs-network shown in Fig. 3.26b. This is the chiral 2-srs we have introduced in the previous section. Next the green srs-network is added by the translation of the red srs-network by half a unit cell along the Y-axis (i.e. along [010]) as shown in Fig. 3.26c. Finally in Fig. 3.26d the yellow srs-network is added by the translation of the green srs-network by half a unit cell anti-parallel to the X-axis (i.e. along [-100]). These four srs-networks intertwine without touching and all have the same handedness (LHD 4-screws in Fig. 3.26). Thus the 4-srs is a chiral structure with LHD chirality along [001].
We have already demonstrated the fabrication and characterisation of the achiral and chiral 2-srs composites that consisted of two intertwining polymer networks. However, the fabrication of four intertwining complex 3D networks is even more challenging. Nevertheless, with the right fabrication conditions we shall demonstrate the fabrication a polymer 4-srs template in Sec. 3.5.
As well as having cubic symmetry and chirality, the 4-srs has another important geometrical feature. The unit cell for this structure is half as wide as the single srs-network and is shown in Fig. 3.27a,b. For example, consider the single LHD srs-network with 3 μm unit cell size. If we intertwine four of these identical LHD srs-networks, the result is a 4-srs with unit cell size 1.5 μm. This reduction in the unit cell size reduces the volume by 1/8 of that of the single srs-network. When looking at the unit cell of the 4-srs at an oblique angle as in Fig. 3.27b, we see that the 4-srs is made up of disconnected corners. These corners when periodically repeated, join up to other corners of different colours (e.g. green to yellow, or blue to red).

![Figure 3.27](image)

**Figure 3.27** The unit cell of the 4-srs. a) View along [001]. b) View at an oblique angle. c) A 3x3 array of 4-srs unit cells viewed along [001].

We shall now investigate the optical properties of the LHD 4-srs network. Before we analyse metallic structures we shall briefly discuss the PC properties of dielectric 4-srs networks as proposed in Ref. [115]. In Fig. 3.28 we plot the transmission of light through a 4srs network with unit cell size a = 1.5 μm (i.e. each single srs-network has 3 μm periodicity), total filling fraction, ff = 26.5% and number of unit cells thick $N_z = 6$ (i.e. it is 9 μm thick). We have varied the refractive index of the dielectric from $n = 1.5$ to $n = 2.3$.

For RCP incident light there is almost 100% transmission for all wavelengths between 1.5 μm to 6 μm. On the other hand, for LCP incident light there is a
bandgap that forms between 2 μm to 3 μm. The bandgap position, bandwidth and depth is dependent on the refractive index. For \( n = 1.5 \) (similar index to IP-L polymer resist), the bandgap is very weak. Whereas for \( n = 2.3 \) (close to the index for soft glasses like chalcogenide) the bandgap is much stronger and more broadband. This suggests that unlike the single srs-network, the 4-srs only supports circular dichroism bands for high index dielectrics.

**Figure 3.28** Numerically simulated transmission spectra for a LHD 4-srs, \( a = 1.5 \) μm, \( \text{ff} = 26.5\% \) and \( N_z = 6 \). a) Transmission of LCP light. b) Transmission of RCP light.
The high transmission at all wavelengths for one polarisation and strong bandgap for the other polarisation is an excellent feature of the 4-srs. In addition, unlike the single srs-network, the 4-srs does not contain any sharp resonances within the transmission bands due to the existence of just a single mode for each polarisation at these wavelengths [115]. Thus the 4-srs is a superior PC design for use as a circular polariser compared to the single srs-network.

In Chapter 6 we shall demonstrate the fabrication of a polymer 4-srs, which is used as a template for the fabrication of cubic chiral metamaterials (MMs). The fabrication and characterisation of the 4-srs in chalcogenide, which has a refractive index of $n = 2.45$ [182] has recently been performed by the PhD student Ben Cumming and will be presented in his thesis.

### 3.9 Discussion

Here we have proposed a novel platform for 3D chiral PCs based on the srs-networks found in the butterfly *Calliphrys Rubi*. We have discussed our methodology to designing practical structures for DLW, particularly in the design of the boundary of the periodic structure. We have used commercially available FEM software to numerically investigate their PBG properties and have shown that these chiral srs-networks lead to the formation of circular dichroism bands.

These formation of these strong circular dichroism bands have been explained using a polarisation analysis of the band structure [115]. Using the DLW method we have been able to successfully replicate these srs-networks with unit cell sizes of 3 µm and showed the excellent fabrication quality achievable using DLW through characterisation via SEM imaging. We have experimentally
characterised the circularly polarised transmission of these chiral PCs, which show strong circular dichroism around 3.4 \( \mu \text{m} \). These experimental results are in excellent agreement with the numerical simulations and theoretical band structure calculations.

We have also shown that chiral composites based on two srs-networks of opposite (achiral 2-srs) or equal (chiral 2-srs) handedness can be fabricated to further engineer novel photonic devices. We have numerically and experimentally characterised these chiral composites showing that the achiral 2-srs does not possess circular dichroism whilst the chiral 2-srs does [175]. In order to form chiral PCs with even stronger circular dichroism we have investigated the 4-srs composite that was proposed in [115]. We showed that this highly complex composite possesses strong circular dichroism when constructed with higher refractive index materials such as chalcogenide glass. This has motivated further research efforts into the development of chalcogenide gyroid photonic microstructures.

![SEM images](image)

**Figure 3.29** SEM images of a butterfly-shaped gyroid microstructure based on the biomimetic chiral srs-networks. The entire butterfly is made up of a unit cell thick RHD srs-network and the word **CUDOS** is made up of the achiral 2-srs (RHD + LHD composite). a) SEM image with scale bar 10 \( \mu \text{m} \). b) Close up SEM image of the letters **CU** showing the two different domains, the 1-srs background, and achiral 2srs letters. The scale bar is 2 \( \mu \text{m} \).

To conclude this chapter we have fabricated a RHD srs-network with a unit
cell size of $a = 1.5 \, \mu m$ and with an overall shape of a butterfly (our inspiration from which the srs-networks came from) in Fig. 3.29. The name CUDOS (an acronym for our research centre, the Centre for Ultrahigh-bandwidth Devices for Optical Systems) is embedded in the butterfly by the interweaving of a second LHD srs-network.

In the next chapter we shall address the issue of the focal spot elongation, which breaks the cubic symmetry of the original srs-network design and apply this to the development of a chiral beamsplitter.
Chapter 4

Cubic symmetry and chiral beamsplitters

4.1 Introduction

In this chapter we present the first experimental demonstration of the chiral analogue of the linearly polarised beamsplitter invented in 1828 by William Nicol. In order to achieve this milestone we have addressed the following questions in this chapter:

1. How does the elongation of the fabrication voxel affect the optical properties of the cubic chiral gyroid networks?

2. Can we improve the standard direct laser writing (DLW) method to overcome this fabrication issue?

3. Can we scale the size of the srs-networks to smaller length scales for operation at optical wavelengths?

4. What functional devices can be built from these srs-networks?
This chapter has the following structure; in Sec. 4.2 we investigate the effect of the focal spot elongation inherent in the DLW method and its effects on the optical and mechanical properties of 3D microstructures. In Sec. 4.3 a novel fabrication method is developed to overcome this issue, which leads to greatly improved mechanical and optical properties as discussed in Sec. 4.4. In Sec. 4.5 we show that these technological advances provide the ability to scale the size of the srs-networks, facilitating the development of circular dichroism bands at optical telecommunications wavelengths. The cubic chiral srs-networks are then used to develop a chiral beamsplitter (CBS), which in Sec. 4.6 we show leads to the first experimental demonstration of a circular polarisation analogue of the commonly used linearly polarising beamsplitter (LPBS).

4.2 Elongation of the fabrication voxel

In our fabrication results of the srs-network via DLW (see Sec. 3.5), we noticed an elongation of the fabricated rod cross sections. The cross sectional elongation is approximated to have an aspect ratio of 3:1 (axial resolution relative to the lateral resolution) and leads to a breaking of the cubic symmetry of the srs-network. This elongation of the fabrication voxel in DLW is well known [79] and a few methods have been created to partly recover this asymmetry. For example, apodisation filters known as shaded-ring-filters have been shown to improve the axial resolution of the focal spot by around 20% but with the disadvantage of losing significant laser power and forming side-bands [183, 184].

Alternatively one can use the multi-line write method [26, 182] where the rods of the 3D microstructure are written multiple times, each displaced laterally by a small amount. The net effect is a widening of the rods in the lateral
direction, reducing the cross sectional aspect ratio. For example, in [182] the aspect ratio of the rods written in a chalcogenide woodpile microstructure was reduced from 4.46 to 1.53. However, this method is inefficient and increases the fabrication time by a factor of 3-5 depending on the multiple number of lines written. In addition, specific materials that do not have significant proximity effect must be carefully chosen [26] to avoid over-polymerisation during this process. The multi-line write method becomes even more inefficient when fabricating complex microstructures such as helices or srs-networks where the line displacement must be made in both the X and Y directions to ensure that the widening in the rod is the same in all directions in the XY plane.

To the best of our knowledge achieving a perfectly symmetric voxel in DLW has not yet been achieved. However, it remains a necessary feature to remove unwanted linear birefringence and to preserve the symmetry of cubic designs.

The effect of the voxel elongation on the srs-network is demonstrate in Fig. 4.1 where we have numerically simulated the transmission of circularly polarised light along [100] (i.e. along the X-axis), where the elongation of the rods along [001] induces linear birefringence in the XZ and YZ planes. The same simulation conditions were used as in the previous chapter. The rods of the srs-network have aspect ratio of 3:1 (i.e. 3 times longer in the Z direction), a unit cell size of 3 \( \mu \text{m} \), and contains 4 unit cells in the direction of propagation.

The transmission spectra given in Fig. 4.1a shows that the elongation of the rods of the srs-network does not affect the formation of a circular dichroism band, i.e. the structural remains geometrically chiral (as expected). However, the transmission spectra in Fig. 4.1b shows that significant polarisation conversion (LCP to RCP and vice versa) is induced due to the linear birefringence of the PC in the XZ plane. Note that polarisation conversion (LCP to RCP and vice versa) poses a problem for the development of circularly polarised optical devices such as polarisation filters and CBSs (see Sec. 4.6).
We shall now discuss how this structural linear birefringence has an effect on the transmission of linearly polarised light. In Figs. 4.1c,d we have shown the numerically simulated transmission spectra of the elongated srs-network using transverse-electric (TE) and transverse-magnetic (TM) excitation along [100] and [001] respectively. For propagation along [100] where the linear birefringence is observed, a significant difference between the TE and TM spectra is seen.

On the other hand, when light propagates along [001], the elongation of the fabrication voxel along [001] does not induce linear birefringence in the XY plane. Therefore for these transmission results shown in Fig. 4.1d we observe no significant differences in the spectra for TE and TM polarised light. Whilst there are minor differences in the TE and TM spectra, these are practically negligible and their origin have have been discussed in Sec. 3.4.

![Figure 4.1](image_url) **Figure 4.1** Numerically simulated transmission spectra demonstrating the effects of the elongation on the optical properties of the RHD srs-network. a,b) Transmission (a) and polarisation conversion (b) for propagation along [100] for circularly polarised illumination. Note that the L2R and R2L curves in (b) perfectly overlap. c-d) Transmission of linearly polarised light propagating along [100] (c) and [001] (d).
4.3 Galvo-dithering direct laser writing (GD-DLW)

For the 3D nano-fabrication of gyroid structures herein, we have used a completely new laser fabrication system. This experimental setup has a much smaller footprint due to the use of a compact fibre laser. The turn-key operation and stable output of the fibre laser, makes it an excellent laser source for DLW. A schematic of the experimental setup for the GD-DLW is shown in Fig. 4.2.

![Schematic of the GD-DLW setup.](image)

The GD-DLW method consists of illumination with a Fianium femtosecond fibre laser operating at the wavelength of 533 nm, with a pulse width of 270 fs and repetition rate of 50 MHz. Directly after the laser is a spatial filter. The power of the laser beam is controlled electronically using a power controller.
system (LPC, Brockton Electro-Optics Corp) that operates using a fast liquid crystal and linear polariser to attenuate light. The power controller system also acts as a noise filter, reducing power fluctuations from the laser source up to 1 kHz. A mechanical shutter is used to control the light exposure during fabrication.

The most important addition to the GD-DLW setup is the introduction of a 2D galvo-mirror (Thorlabs), which is controlled via the computer. Using the galvo-mirror, the laser beam is steered using a 4-f imaging system into a oil immersion objective (100X, 1.4 N.A., Olympus). A piezoelectric nano-translation stage (P563.3CD with an E712 controller, Physik Instrumente) was used to trace out the microstructures in the commercial photoresist IP-L (Nanoscribe GmbH).

![Figure 4.3](image)

**Figure 4.3** The GD-DLW method and its effect on the fabrication voxel. a) Schematic of the GD-DLW setup consisting of a 2D galvo mirror and 4f imaging system used to dither the laser focus. b) Illustration of the circular dithering applied by the galvo mirrors. c) Effect of the galvo-dithering on the fabrication voxel greatly reducing the aspect ratio.
To address the issue of the elongation of the fabrication voxel discussed in the previous section we have developed the galvo-dithered direct laser writing (GD-DLW) method. This novel fabrication method uses a galvo-mirror and 4f imaging system to trace the focal spot in a circular motion within the focal plane. This leads to a correction of the voxel asymmetry as shown in Fig. 4.3a,b.

The dithering of the focal spot is achieved by using the galvo-mirrors to trace out a very small circular path in the focal plane. The radius of the dithering is comparable to the voxel resolution and is performed at very high speeds compared to the fabrication speed. A frequency of 500 Hz was used, which is fast enough for the translation speeds of 10 $\mu$m/s used to fabricate the srs-networks.

To approximate the effect of the galvo dithering on the fabrication voxel, in Fig. 4.3c we plot the fabrication voxel of the original and dithered DLW methods in blue and red respectively. We have considered a focal spot with a 3D Gaussian distribution of full-width half maximum of 300 nm in the XY plane and 900 nm in the Z direction. The blue and red cross sections of the fabrication voxel are calculated based on a threshold value of 0.1 relative to the maximum intensity of the voxel with and without dithering respectively. The dithered voxel (red) has been calculated by taking the average of 50 Gaussian focal spots that have been translated in a circular distribution. The width and height of the DLW (GD-DLW) fabrication voxel is labelled as $\Delta X_{DLW}$ ($\Delta X_{GD}$) and $\Delta Z_{DLW}$ ($\Delta Z_{GD}$), respectively. By comparing the two fabrication voxels, we see that the fabrication voxel is widened in the focal plane (i.e. $\Delta X_{GD} > \Delta X_{DLW}$). Most importantly, the galvo-dithering causes the fabrication voxel to become shorter in the Z direction (i.e. $\Delta Z_{GD} < \Delta Z_{DLW}$), improving the overall resolution of the 3D fabrication method.

Note this is a very simplistic model that does not take into account the highly
complex nonlinear photo-polymerisation process that includes thermal effects and diffusion. However, it provides us with a simple understanding of how galvo-dithering can be used to improve the fabrication voxel symmetry.

4.4 GD-DLW fabrication results

In this section we discuss the fabrication of srs-networks using the GD-DLW method. In Fig. 4.4 we show a SEM image of an array of srs-networks of unit cell size \(1.2 \mu m\), which is 10 unit cells wide and 3 unit cells tall. We have varied two parameters of the GD-DLW method. Vertically, we have varied the laser power (P) and horizontally we have varied the galvo-dithering amplitude (A) that is proportional to the voltage applied to the galvo mirrors (one unit of A corresponds to a \(0.013^\circ\) rotation of the mirror).

Figure 4.4  SEM image of srs-networks fabricated using GD-DLW demonstrating the beneficial effects of the galvo-dithering on the mechanical strength. The power of the laser (P) is varied from 0.6 mW to 0.7 mW and the galvo-dithering amplitude (A) is varied from 0 to 3.
For the lowest laser powers of $P = 0.60$ mW, when standard DLW is used (i.e. $A = 0$) the polymerisation is not strong enough to mechanically sustain the 3D microstructure, causing it to collapse and wash away during the rinse-out procedure. As the power is increased to $P = 0.70$ mW, the polymerisation becomes stronger and the filling fraction of the polymer is increased, leading to improved mechanical stability.

Interestingly, the use of galvo-dithering clearly shows that one can greatly improve the mechanical integrity of the srs-network by using the GD-DLW method. Even the lowest laser power of $P = 0.60$ mW can lead to a mechanically stable structure for values of $A > 2$. This allows us to improve the fabrication resolution in the $Z$ direction for two reasons. Firstly, a lower laser power can be used closer to the polymerisation threshold. Secondly, the dithering causes the shortening of the fabrication voxel as shown previously in Fig. 4.3. Note that the most important resolution for the fabrication of 3D microstructures like the srs-network is that of the longest axis of the fabrication voxel (i.e. the axial resolution). Thus the improvement of the axial resolution provides the ability to fabricate even smaller-sized srs-networks.

In order to determine if the cubic symmetry of the srs-network has been preserved during fabrication we have taken SEM images of the srs-network to determine the symmetry as shown in Fig. 4.5. The srs-network has a unit cell size of $2 \mu m$, width of 16 unit cells, height of 6 unit cells with the values of $P$ and $A$ optimised for fabrication symmetry. The SEM images viewed along $[001]$ and at an oblique angle both match excellently with a computer simulated view for an srs-network with circular rods (i.e. with cubic symmetry). This is a great improvement to the symmetry of the srs-network compared to the results obtained using standard DLW in the previous chapter.

However, in order to truly determine if we have a 3D microstructure with perfect cubic symmetry (i.e. where $\Delta X_{GD} = \Delta Y_{GD} = \Delta Z_{GD}$), SEM imaging was
not sufficient. Cubic symmetry can only be strictly proven via experimental characterisation of the optical properties of the structure without a substrate and along all three Cartesian axes. This remains a challenge as standard PC characterisation techniques such as FTIR are currently not capable of such methods and may be the topic of future work.

Figure 4.5 SEM images of an srs-network with unit cell size 2 μm fabricated using GD-DLW and a comparison with computer simulated images. a,c,d,f) SEM images of the srs-network. b,e) Computer simulated views of an srs-network consisting of circular rods and with perfect cubic symmetry.

4.5 Srs-network for telecommunications wavelengths

Here we show the experimental characterisation results of an srs-network fabricated via GD-DLW with a unit cell size $a = 1.2$ μm, a width of 40 unit cells,
and height of 6 unit cells. In Fig. 4.6a we show the experimentally measured transmission spectra. We have used the same experimental procedure for the FTIR as in Sec. 3.6, except here we used a quartz achromatic retarder (Bernhard Halle GmbH) for these near infrared wavelengths.

Figure 4.6 Optical characterisation of the polymer srs-network along [001] with a = 1.2 μm. Red and blue curves represent RCP and LCP incident light, respectively. a) Experimentally measured transmission spectra. Inset contains an SEM image of a srs-network viewed from above. The scale bar is 2μm. b) Numerically simulated transmission spectra. c) Theoretical band structure for the polymer srs-network. The size of the points are related to the coupling coefficient $b$, and the colour is given by the circular dichroism index $C$, where RCP is red, LCP is blue and unpolarised is black.
We observe a similar transmission spectra as seen for the larger 3 μm srs-network in Sec. 3.6. However, the bandgaps have been greatly reduced in wavelength due to the smaller unit cell size of 1.2 μm and the circular dichroism band now being at the wavelength 1.55 μm. This is an important wavelength regime for telecommunications applications, and marks a milestone achievement for the development of cubic chiral PCs.

In Fig. 4.6b we show numerically simulated transmission spectra along [001] for the srs-network with 35% polymer filling fraction and a polymer refractive index of 1.52. We observe a good qualitative agreement with the experimental measurement of circular dichroism at the wavelength of 1.55 μm. The experimentally measured larger transmission of RCP light relative to LCP light in the wavelength region at 1.6 μm may be attributed to minor fabrication imperfections.

In Fig. 4.6c we provide the band structure along [001] for an srs-network with unit cell size 1.2 μm with the structural parameters used in Fig. 4.6b. These theoretical results predict a circular dichroism band around 1.55 μm and are in good agreement with the experimentally measured and numerically simulated transmission spectra.

This is a significant improvement over cubic chiral PCs previously reported, such as the bi-chiral PC operating at 5 μm [90] and the srs-network operating at 3.4 μm that we demonstrated in Chapter 3 and in Ref. [175]. Most importantly, experimental excitation and imaging at these shorter optical wavelengths can be easily achieved using commonly available near-infrared optical equipment. This plays an important role in the following section where we fabricate and characterise a CBS.
4.6 Chiral beamsplitter

4.6.1 The chiral beamsplitter concept

In 1828 William Nicol invented the LPBS [185] known as the Nicol prism [186]. Today the LPBS is a standard optical component heavily used in a wide range of optical systems. These polarising beamsplitters come in many variations such as the Glan-air prism [187] and are designed using linearly birefringent crystals (e.g. calcite), which have significantly different critical reflection angles at the crystal-air interface for s and p polarised light. This leads to the transmission of one polarisation through the polarising beamsplitter and the angled reflection of the other [188]. Unfortunately, the circularly polarised analogue of the LPBS has yet to be experimentally demonstrated, due to the lack of natural materials with sufficient circular birefringence.

![Figure 4.7](image.png)

**Figure 4.7** Conceptual image of a CBS, where LCP light transmits through the beamsplitter and RCP light is reflected off it.

The development of chiral nanostructures, particularly chiral metamaterials (MMs) that have greatly enhanced optical activity (see Chapter 2 for a review),
has inspired recent theoretical investigations suggesting the possible use of these strongly chiral media for the development of a CBS [189–191]. This phenomenon arises from the chirality parameter ($\xi$), which is very weak in natural materials like quartz [188] but can be very large in chiral MMs, significantly changing the reflective and refractive properties of RCP and LCP light.

The cubic chiral srs-networks we have developed in this thesis are excellent candidates for the development of a circularly polarised analogue of the polarising beamsplitter, a CBS. The basic functionality of the CBS is the transmission of LCP light through the chiral prism whilst RCP light is reflected at the interface and vice versa. This effect, as we shall discuss later, comes from the chirality of the srs-network and is illustrated in Fig. 4.7, where light is incident along the crystallographic $[100]$ direction onto the triangle’s hypotenuse (the cleaving plane with $(110)$ inclination). The reflected (transmitted) intensity strongly depends on the circular polarisation state of the incident plane wave, due to the chirality of the internal structure of the prism (i.e. the srs-network).

4.6.2 Fabrication results

The CBS shown in Fig. 4.8, is a triangular prism with an internal microstructure corresponding to the chiral srs-network of cubic symmetry $I4_132$, with a unit cell size of $a = 1.2 \mu m$ and a polymer filling fraction approximately equal to 30%. The CBS spans 20 unit cells in height and 80 unit cells in width corresponding to an overall size of the prism of $96x96x24 \mu m^3$ corresponding to $0.5x80x80x20 = 64,000$ unit cells, which equates to 768,000 individual rods. The fabrication time for this large microstructure was 16

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$^1$We have used the Miller index notation where $(110)$ denotes a plane of the 3D PC that is normal to the vector direction $[110]$. 
hours. The CBS has been designed such that the incident boundary is cleaved along [110] so that light propagating along [100] is incident on a 45° interface. The large size of the CBS was chosen such that characterisation could be performed by using a weakly focused incident beam of approximately 10 µm in size.

A solid dielectric U-shaped frame (scattering bar) was also fabricated via GD-DLW that has been added for the characterisation experiment discussed below.

Figure 4.8 SEM images of the CBS fabricated using GD-DLW from different perspectives. a) Angled front view showing the (110) and (001) surfaces. b) View of the back corner. c) View of the exiting (100) surface. d) Zoomed in view of (a). e) Zoomed in view of (b). f) Zoomed in view of (c). The scale bars are 5 µm in (a), 10 µm in (b-c) and 2 µm in (d-f).
The cross sectional dimensions of this scattering bar are 10 \( \mu \)m wide and 10 \( \mu \)m tall. The SEM images shown in Figs. 4.8 and 4.9 show that the CBS we fabricated has excellent uniformity and almost negligible distortion is observed at the terminating surfaces.

Figure 4.9 SEM images of the CBS fabricated using GD-DLW from different perspectives. a) Angled front view showing the (110) and (001) surfaces. b) View of the back corner. c) View of the exiting (100) surface. d) Zoomed in view of (a). e) Zoomed in view of (b). f) Zoomed in view of (c). The scale bars are 5 \( \mu \)m in (a), 10 \( \mu \)m in (b-c) and 2 \( \mu \)m in (d-f).

In order to have the CBS mounted at the edge of the substrate (an 18x18 mm borosilicate coverslip), a 60 \( \mu \)m deep line was etched at the bottom surface of the substrate after DLW had been performed at the centre of the top surface. This was followed by snapping the substrate along the direction of the line by applying a small force by hand. Breaking the substrate in this manner left a clean straight cleave along the side of the microstructures, exposing the beamsplitters for illumination from the side. The etching laser was an amplified
femtosecond laser operating at a wavelength of 800 nm, a pulse width of 90 fs and average power of 1 W. The beam was focused with a Mitotoyo NIR microscope objective with a numerical aperture of 0.5 and magnification of 100x. This method provides a sharp cleave that exposes the beamsplitters for illumination from the side in our following experimental characterisation as seen in the SEM image of Fig. 4.8a.

### 4.6.3 Experimental characterisation

To characterise the CBS we built a customised experimental imaging system as shown in Fig. 4.10. The experimental characterisation of the beamsplitters was performed by illuminating the sample along $[100]$ with a supercontinuum laser (Fianium), which operates between 400-2400 nm. This is combined with an acousto-optic tunable filter, which allows us to select a single wavelength with bandwidth around 8 nm. In order to excite the CBS with circularly polarised light, we used a near-infrared polariser (Thorlabs) in conjunction with a broadband achromatic quartz quarter-wave plate (Bernhard Halle GmbH). This polarised light was then focused onto the CBS using a low numerical aperture 10x near-infrared achromatic objective (Mitotoyo). The sample was imaged using a thermo-electrically cooled InGaAs camera (Xenics), which is sensitive between 1-1.7 µm. A 100x near-infrared achromatic objective (Mitotoyo) was used for the magnification of the CBS image along $[001]$ (i.e. we are imaging from above).
The concept of this experiment is as follows. As light is incident to the CBS, a fraction of light will couple into the PC, transmitting through, and the remainder is reflected off the (110) interface. A small fraction of the light that exits the CBS (either through reflection or transmission) can propagate until hitting the scattering bar. The height of this bar is approximately 10 μm, less than half the height of the CBS, which is 24 μm tall. Thus only a small fraction of the 10 μm wide beam can hit the scattering bar. This small scattering signal can be detected by a sensitive infrared camera, providing images of the scattered reflected and transmitted beams.

An illustration of the experimental conditions that are to be recorded by the infrared camera is given in Fig. 4.11. Here LCP (blue) and RCP (red) light is incident on the CBS and different transmission and reflection properties are illustrated by the strength of the beams passing through the CBS.
In order to approximate the amount of light that is reflected and transmitted through the CBS in the characterisation experiment, we have made the following assumptions:

1. The far field radiation exiting the beamsplitter is proportional to the scattered signal the camera detects. Thus the maximum pixel intensity in the regions of interest (the black boxes in Fig. 4.11) are taken as the values $T$ and $R$.

2. Absorption and scattering loss from the structure is negligible such that we can normalise these measured signals so $T + R = 1$ at all wavelengths.

3. The size of the beam at the scattering bar for both the reflected and transmitted signals is equal.

Note in these experiments we have attenuated the laser to ensure that the
camera was far from saturation in the regions of interest and thus operating at a linear regime. Fig 4.12 contains images of the video recorded by the infrared camera. A spectral plot of the normalised T and R measured by the camera is given in Fig. 4.13a. A plot of the circular dichroism, $\Delta T$ and $\Delta R$ (where $\Delta T = T_{LCP} - T_{RCP}$ and $\Delta R = R_{LCP} - R_{RCP}$) is shown in Fig. 4.13b.

As the wavelength is scanned from 1560-1660 nm we observe three distinct regimes. At wavelengths between 1560 -1590 nm both LCP and RCP incident light is completely reflected from the CBS and no transmission can be seen (the reflection band). At wavelengths between 1640 -1660 nm nearly all of the light is transmitted through the beamsplitter (the transmission band). Note that the reflection does not go to zero since there is always a small reflection due to the lack of impedance matching.

The most interesting region (beamsplitting band) is around 1615 nm as shown in Fig. 4.12b where LCP has strong transmission and weak reflection, whereas RCP has strong reflection and weak transmission. The optimum wavelength yielding maximum degree of circularly polarised beam splitting is around 1615 nm. Here the circular polarisation extinction ratio is 5.12 dB in transmission and 3.46 dB in reflection. Note that the circular dichroism band observed along [001] for the srs-network in Sec. 4.5 was the wavelength at 1.55 $\mu$m. The difference in wavelengths for circular dichroism measured along [001] and the beam splitting region for the CBS, is due to the fact that the CBS light is incident on an angled interface. This causes the beam to refract upon entering the PC, thus exciting modes not purely along [001]. Note that the beam propagating through the CBS does not appear to attenuate and suggests the validity of our assumption of a lossless system.
The handedness of the observed circular dichroism is related to the handedness of the right-handed 4-screw axis of the srs-network along [001]. This is analogous to the circular dichroism found in dielectric helices where the strong reflection of RCP (LCP) light was observed for right-handed (left-handed)
helices [90, 94]. Note that due to the cubic symmetry of the srs-network, the identical phenomenon can be observed if light was incident from the side of the beamsplitter (i.e. along [010]).

![Figure 4.13](image)

**Figure 4.13** a) Spectral plots of the transmitted (solid) and reflected (dashed) beams from the CBS, under illumination by RCP (red) and LCP (blue) light. b) Spectral plot of the circular dichroism for the transmitted and reflected beams, respectively.

To the best of our knowledge, this is the first experimental fabrication and characterisation of a CBS, demonstrating circularly polarised beamsplitting.
4.6.4 Numerical characterisation

In this section we present the numerical simulation of the CBS. We have used the finite-element method (CST Microwave studio) in frequency domain for a srs-network with 22% filling fraction and polymer refractive index of 1.52. This CBS structure is 20 unit cells wide in the XY plane and 1 unit cell thick in the Z direction. Perfectly matched layers (open boundaries) are used for the X and Y boundaries and a periodic boundary condition is used in the Z direction. A circularly polarised plane wave in combination with an 8 μm wide aperture is used to excite the prism. The CBS was chosen to be 20 unit cells wide, which is large enough to observe the PC effects that cause the beamsplitting phenomenon.

In Fig. 4.14 we plot the Poynting vector distribution for a CBS that is excited with circularly polarised light at the three wavelengths 1570 nm, 1615 nm and 1650 nm, respectively. We observe good qualitative agreement between the experimental data shown in Fig. 4.12. Most importantly, at the wavelength of 1615 nm we observe high reflection for RCP light than that for LCP light. Note that the finite size of the aperture causes the incident light to diffract before illuminating the CBS. This can have a small effect on the coupling of light into the crystal, the refraction properties and far-field distributions.
In order to determine the exiting polarisation states of the CBS we have analysed the electric fields of these numerical simulations. In general we find that the polarisation states of both the transmitted and reflected waves become elliptical. This is caused by the partial polarisation reversal upon reflection. The numerical simulation results shown in Fig. 4.14 provide a good qualitative
description of the interaction of circularly polarised light with the CBS. We now seek to obtain quantitative values for the CBS phenomenon. By exciting the srs-network PC with a circularly polarised plane wave along [100] we have been able to calculate the transmission and reflection spectra.

An illustration of the numerical simulation conditions is shown in Fig. 4.15. The structure is infinitely periodic in two-dimensions with the input and exit boundaries of the srs-network clipped with inclination (110). Incident plane waves are angled 45˚ relative to the input surface (i.e. along [100]) to replicate the experimental excitation conditions.

![Illustration of the simulation setup for the srs-network clipped such that the input and output faces are with inclination (110).](image_url)

**Figure 4.15** Illustration of the simulation setup for the srs-network clipped such that the input and output faces are with inclination (110).

In Fig. 4.16 we show the numerically simulated transmission (solid lines) and reflection (dashed lines) spectra for RCP (red) and LCP (blue) incident light under the excitation conditions shown in Fig. 4.15. The structure has a thickness of 6 unit cells and a polymer filling fraction of 22%. We observe
a good qualitative agreement with the experiment measurements even though
the numerical simulation does not consider the prism shape of CBS and thus
neglects the back surface inclination of (100). Therefore we expect the major
contribution of the experimentally observed CBS phenomenon to be related to
the coupling of circularly polarised light to the Bloch modes of the srs-network
PC at the input surface of the CBS.

![Figure 4.16](image)

**Figure 4.16** Numerically simulated transmission (solid lines) and reflection spectra (dashed lines) for a periodic srs-network that has been clipped such that the input and output planes of the PC have inclination (110). The structure is excited with RCP (red) and LCP (blue) light along [100] (i.e. at 45° to the (110) input surface).

It is important to note that the incident beam refracts upon entering the
CBS. Thus the excitation of the Bloch mode is not along [100] but instead
at an angle between [100] and [110]. Note that this refraction property is
also strongly wavelength dependent due to the super-prism phenomenon [12,
13]. The band structure for [110] is given in Fig. 4.17, where the same
parameters used in Fig. 4.6c have been used. We see that over the entire
spectral range of interest there are two degenerate Bloch modes that are not
strongly circularly polarised. This implies that the circular dichroism along
[110] would be expected to be much weaker than that in [100]. Thus the
refraction of the beam entering the CBS may reduce the performance of the
beam splitting phenomenon.
Theoretically simulated band structure for the polymer srs-network with 35% filling fraction, for propagation along [110]. The almost black colouring of the points over the entire spectral range suggests that the Bloch modes along [110] are neither strongly LCP nor RCP.

Figure 4.17  

It should be possible to improve the extinction ratio of the CBS through further engineering of the design, and achieve an extinction ratio comparable to commercial LPBSs used today. For example a second material (possibly a PC as well) on the opposite side of the incident surface could be added to the design to achieve phase matching. This is analogous to the phase matching condition described in the theoretical investigations of CBS from chiral MMs [189–191]. When the wave-vector and impedance of this phase matching material is equal to that of the Bloch mode of the srs-network one could achieve perfect phase matching. This would remove the refraction of the beam entering the PC, such that light transmits along [100] of the PC where the circular dichroism is strongest. Further theoretical investigation of the coupling of light to these 3D chiral PCs at angled interfaces, particularly when impedance matching materials (or PCs) are introduced, will undoubtedly provide further insight to the optimisation of this phenomenon.
4.6.5 Theoretical prediction of a superior 4-srs beamsplitter

In this section we briefly propose the use of the 4-srs network, which was recently theoretically proposed as a novel chiral PC that also possesses cubic symmetry and chirality [115]. The 4-srs network consists of four identical like-handed srs-networks that are intergrown to give a strongly chiral structure with simple cubic symmetry. When constructed from materials with high refractive index such as silicon, the 4-srs PC has been shown to possess very broadband and strong circular dichroism [115].

![Figure 4.18](image)

**Figure 4.18** Numerically simulated reflection spectra for a periodic 4-srs network that has been clipped such that the input and output planes of the PC have inclination (110). The structure is excited with RCP (red) and LCP (blue) light along [100] (i.e. at 45° to the (110) input surface). a) $n = 1.5$. b) $n = 1.92$. c) $n = 2.34$. d) $n = 2.76$.

In Fig. 4.18 we present the numerically simulated reflection spectra for a the
4-srs network over a broad wavelength range. The structure has been clipped with inclination (110) and excited at 45° as in Fig. 4.16 for the single srs-network. A dielectric filling fraction of 32% was used. We have varied the refractive index of the dielectric material from 1.5 (polymer) to 2.76 (high index glass/semiconductor).

For the polymer 4-srs network we observe negligible circular dichroism. However, as the refractive index is increased the circular dichroism band becomes very strong and broadband. Most importantly, the extinction ratio is greatly improved compared to that of the polymer srs-network. Therefore the experimental development of high refractive index 4-srs networks is of great interest towards developing a CBS with even better performance.

4.7 Discussion

Here we have shown that the elongation of the fabrication voxel inherent in the standard DLW method can be detrimental when developing optical devices where the symmetry of the structure is of importance. For our srs-network, the elongation breaks the cubic symmetry and leads to the formation of linear birefringence and polarisation conversion of circularly polarised light.

These unwanted properties can be eliminated only by removing the fabrication voxel elongation, which we have achieved here by developing a novel GD-DLW method. The GD-DLW method not only improves the isotropy of the fabrication, but also greatly enhances the mechanical strength. This novel method has allowed us to scale the unit cell size of the srs-network to 1.2 μm, where a circular dichroism band at the useful telecommunications region at 1.55 μm has been demonstrated. This is a milestone achievement, compared to the circular dichroism bands of prior work, including the 3 μm srs-networks.
in Chapter 3 fabricated via standard DLW.

Using the GD-DLW method we have been able to fabricate a CBS using the single srs-network as the internal nanostructure of the chiral prism. This is the first demonstration of circular polarisation analogue of the original LPBS invented in 1828 by William Nicol. We have presented both experimental and numerical characterisation of this CBS attributing the physical mechanism to the chiral diffraction caused by the srs-network PC.

Finally, we proposed the use of the 4-srs geometry as a CBS and numerically demonstrated superior beamsplitting performance. Based on current rapid progress of the DLW technology for chalcogenide [25, 74, 182] a 4-srs chalcogenide CBS is a realistic prospect that is likely to further improve the extinction ratio over the first functional CBS demonstrated here.
Chapter 5

Numerical investigation of metallic gyroids

5.1 Introduction

In Chapters 3 and 4 we saw that dielectric photonic crystals (PCs) constructed from the cubic chiral srs-networks formed excellent templates for the development of chiral PCs with strong circular polarisation sensitivity. Metals have a much stronger light-matter interaction than dielectrics, due to the extreme negative permittivity at optical and infrared wavelengths. Thus, the aim of this chapter is to discuss the optical properties of gyroid-based microstructures made from metals like silver. Specifically we aim to address the following questions:

1. Can the circular dichroism observed in the dielectric gyroid PCs be enhanced using metals?

2. How do the geometrical parameters of a metallic srs-network affect the optical response?
3. What are the metamaterial (MM) properties of a metallic srs-network?

4. Do metallic chiral composites like the 2-srs or 4-srs networks provide other unique physical phenomena?

5. What is the difference between a metallic microstructure consisting of solid metal rods or dielectric rods with a metal coating?

This chapter has the following structure. In Sec. 5.2 we have investigated optical properties of thin slabs of metallic single srs-networks and their geometrical dependence. We compare the simulation results between a silver srs-network and perfect electric conductor (PEC) srs-network and demonstrate at which wavelengths the metallic srs-networks have a plasmonic response. In Sec. 5.3 we have investigated the optical properties of a metallic version of the 2-srs achiral composite and discuss why no transmission bands appear outside of the plasmonic regime. In Sec. 5.4 we show that the metallic 4-srs is a better choice for the construction of chiral MMs, and discuss their optical properties. In order to understand how the silver coating of polymer gyroid networks will perform in contrast to the solid metallic gyroid networks, we have performed numerical simulations using silver coated polymer rods in Sec. 5.5. Finally, in Sec. 5.6 we investigate the optical properties of inverse metallic gyroid structures that can be realised via other metallisation methods such as electro-deposition.

5.2 Metallic srs-network

5.2.1 Silver srs-network

In this section we investigate the optical properties of a srs-network consisting of solid silver rods. We used CST microwave studio to perform numerical
simulations of the metallic srs-networks, using the same simulation conditions as in Chapter 3. In the first part of this chapter we have considered solid silver rods for simplicity. A comparison using a PEC instead of silver is given in Sec. 5.2.2 and a comparison using dielectric rods that have been coated with silver is given in Sec. 5.5.

The numerical simulations of this chapter used the Drude model for the dispersive permittivity values of silver [54], using the published values of the plasma wavelength and collision frequency for silver, \( \omega_p = 1.37 \times 10^{16} \text{s}^{-1} \) and \( \omega_c = 8.5 \times 10^{13} \text{s}^{-1} \), respectively [192]. An image of the silver srs-network is shown in Fig. 5.1.

![Figure 5.1](image)

**Figure 5.1** Images of the solid silver LHD srs-network, with filling fraction 11.5% and 1 unit cell tall. a) View from the top. b) View from the side. c) View from an oblique angle.

As for the simulations in Chapter 3, the left-handed (LHD) srs-network is constructed from circular rods, where we used rods with a circular cross section that are not elongated (i.e. the cross sectional aspect ratio = 1). The geometrical parameters we have used for the first set of numerical simulations are:
• Unit cell size, \( a = 3 \, \mu\text{m} \)

• Number of unit cells thick, \( N_z = 2 \)

• Filling fraction of the metal (silver or PEC), \( \text{ff} = 11.5\% \) (this was chosen based on practical fabrication conditions)

• Light is propagating along \([001]\)

These parameters were chosen based on practically realisable microstructures via direct laser writing (DLW), followed by electroless silver plating (ESP). Details on the fabrication of these microstructures will be discussed in Chapter 6. In Fig. 5.2 we show the numerical simulation results for the silver srs-network. The spectra here have been calculated at wavelengths from 3 \( \mu\text{m} \) to 10 \( \mu\text{m} \) (i.e. from \( 0.3 < \omega a/2\pi c < 1 \), where \( c \) is the speed of light in a vacuum). We observe that at the longest wavelengths light is almost completely reflected. The reflection is mainly internal (i.e. LCP and RCP reflection is much larger than L2R and R2L reflection) at these longest wavelengths. At shorter wavelengths where PC effects occur, we observe strong external reflections.

As the wavelength becomes shorter than double the unit cell size (i.e. for wavelengths < 6 \( \mu\text{m} \)) we observe transmission bands. At most frequencies left-circularly polarised (LCP) light is able to transmit through the LHD metal srs-network more than right-circularly polarised (RCP) light. At wavelengths between 3 \( \mu\text{m} \) to 4 \( \mu\text{m} \), we see the strongest circular dichroism band. In this frequency range the metallic srs-network acts as a metallic PC, and should not be considered a MM. To be considered a MM, the wavelengths of operation are required to be much larger than the unit cell size (i.e. \( \omega a/2\pi c \ll 1 \)). Unfortunately, the transmission is very small at these longer wavelengths, thus this metallic srs-network is not a suitable candidate for a chiral MM at this size scale.
The circular dichroism observed within the dielectric PC in Chapter 3 was the opposite to these results here. For the dielectric srs-network, light was able to propagate through both the dielectric material as well as the air background. In fact at the lower fundamental bands of a PC, light preferentially locates itself within the high dielectric materials [8]. On the other hand, at these wavelengths light does not penetrate through the metal and is forced to propagate only through the air channels. Thus we see a reversed circular dichroism phenomenon between dielectric and metallic srs-networks. The reason for this swapping of the circular dichroism becomes more clear later in the chapter when we have considered inverse geometries.

Another significant difference with the dielectric PC is that the transmission conversion is much stronger. This polarisation conversion is attributed to
the lack of XY symmetry at the input and output coupling interfaces of the metallic srs-network, as we discussed in Chapter 3. This effect is stronger for the metallic srs-network compared to the dielectric srs-network. However, the transmission conversion is still relatively weak relative to the transmission of light.

5.2.2 Perfect electric conductor srs-network

At these long wavelengths the permittivity of silver is negative and has a very large value. For example at 4 μm the permittivity of silver is \( \epsilon = -818 + i147 \) (calculated using the Drude model) [27]. Therefore, at these long wavelengths light effectively sees the silver as a PEC. In Fig. 5.3 we show the numerical simulation of the srs-networks constructed from a PEC.

![Figure 5.3](image)

**Figure 5.3** Numerical simulation of the PEC LHD srs-network. a) Transmission. b) Transmission conversion. c) Reflection conversion. d) Reflection (note both L2L and R2R curves perfectly overlap).
Not surprisingly, the results are almost identical at all wavelengths, with just a small blue shift of 0.13 µm for the spectra for the PEC srs-networks. The absolute value of the transmission is also slightly increased for the PEC, as the material here is lossless. This implies that for simulations of metallic srs-networks in this frequency range, it is sufficient to assume the silver is a PEC. This is advantageous for numerical simulations as PEC objects only require surface meshing (greatly speeding up calculation times) and allows one to perform eigenmode calculations. This assumption of a PEC for silver is accurate at these wavelengths in the mid-infrared (MIR). However, when performing simulations in the near-infrared (NIR) and visible regimes, one must consider the Drude response of silver.

In order to further understand the physical properties of the metallic srs-network, we have performed eigenmode calculations for the PEC srs-network also using CST microwave studio software (note lossy materials like the Drude model for silver cannot be used for eigenmode solvers). We have used a periodic boundary condition for all X, Y and Z boundaries, and simulated a single 3D periodic unit cell with a metal filling fraction of ff = 11.5 %.

In Fig. 5.4 we plot the dispersion of the first three fundamental modes of the PEC srs-network. The colour and sizes of the points are represented by $C$ and $\beta$, respectively (see Sec. 3.4 for definitions of $C$ and $\beta$ that are derived in [115]). The fundamental band cuts on at $\omega a/2\pi c = 0.51$ and consists of three degenerate modes that are degenerate for $|k| = 0$. The lack of bands below $\omega a/2\pi c = 0.51$ explains the lack of transmission at wavelengths beyond 6 µm in Fig. 5.3. As $|k|$ increases, these modes lose their degeneracy and we observe 3 distinct eigenmodes from $0.51 < \omega a/2\pi c < 0.78$. The lowest frequency mode has weak coupling and does not contribute to the transmission of light along [001]. The second and third order modes are RCP and LCP respectively, with LCP mode having slightly stronger coupling strength (related to the size of the
points). Note that the existence of both LCP and RCP modes in this regime explains the weaker circular dichroism observed in the transmission spectra in Fig. 5.3. For frequencies above $\omega a/2\pi c = 0.78$ the RCP mode does not exist, hence the strong circular dichroism observed at higher frequencies in Fig. 5.3.

![Dispersion diagram for the PEC srs-network](image)

**Figure 5.4** Dispersion diagram for the PEC srs-network for the first three fundamental eigenmodes and the unit cell of the PEC srs-network. The metal filling fraction of the srs-network is $f = 11.5\%$. The colours of the points are directly proportional to the value of $C$ (where $C = +1$ is red and $C = -1$ is blue) and the radii of the points are directly proportional to the value of $\beta$. Black dots represent Bloch modes that have neither RCP or LCP polarisation. Crosses have been used for the fundamental eigenmode that do not couple to external plane waves, i.e. $\beta = 0$.

The 3D electric field distribution of the eigenmodes are shown in Fig. 5.5, for $|k| = 0.25$. The fundamental mode has its electric fields polarised along the direction of propagation (Z-direction) with weak coupling to incident plane waves. The second and third order modes have transverse polarisation that are predominantly LCP and RCP, respectively.
5.2.3 Dependence on the filling fraction

To investigate the effect of the filling fraction of the PEC srs-network, we have performed further numerical simulations of the PEC LHD srs-network for varying filling fraction (ff) from ff = 3.1% to ff = 38.5%. The results are given in Fig. 5.6a,b, which contain the transmission spectra for LCP and
RCP incidence, respectively. We see that there is a red shift of the spectra as the filling fraction decreases. For the smallest fraction considered here of 3.1% the fundamental transmission band is red shifted to around 6 µm. This corresponds to a wavelength double that of the unit cell size.

![Figure 5.6 Numerical simulation of the PEC LHD srs-network for varying filling fraction, ff. a) Transmission of RCP light. b) Transmission of LCP light.](image)

Decreasing the filling fraction to 3.1% causes the fundamental transmission band to red-shift to 6.5 µm, which corresponds to a normalised frequency of $\omega a/2\pi c = 0.46$. Even for this incredibly low filling fraction value, these frequency bands are within the PC regime and thus the metallic srs-
network can not be considered a MM. Further, the fabrication of such a porous structure using DLW remains almost impossible due to mechanical integrity limitations (related to the mechanical strength of the photoresist) and resolution limitations of current fabrication technology. For the 3.1% filling fraction the circular rod width would have to be 300 nm. This would pose a significant technological challenge based on our fabrication results using the galvo-dithered DLW method (GD-DLW) in Chapter 4.

5.2.4 Dependence on the number of unit cells

Here we investigate the effect of the number of unit cells on the transmission spectra of the PEC srs-network. As the number of unit cells in the propagation direction \(N_z\) increases we see a dramatic change in the observed transmission spectra shown in Fig. 5.7.

![Figure 5.7](image)

**Figure 5.7** Numerical simulated transmission spectra of the PEC LHD srs-network for varying number of unit cells \(N_z\). a) \(N_z = 1\). b) \(N_z = 2\). c) \(N_z = 3\). d) \(N_z = 4\).
For $N_z = 1$, the srs-network can hardly be considered a periodic structure. Nevertheless, we still observe strong circular dichroism at the shortest wavelengths. As $N_z$ is increased, the formation of several sharp resonances appear in the transmission bands. This is most likely due to the interaction of multiple modes in these frequency bands. Most importantly, as $N_z$ increases the circular dichroism band between 3 $\mu$m to 4 $\mu$m becomes stronger. For $N_z = 4$ the circular dichroism is much stronger than that observed for the polymer srs-network with the same thickness. In addition, unlike the dielectric srs-network, the circular dichroism band here does not contain the sharp resonances for the transmitted LCP light. Thus the circular dichroism band here is more preferable as a circular polarisation filter.

Interestingly, the transmission of LCP light still remains high for 4 unit cells thickness, with nearly 100% transmission at 3 $\mu$m. This suggests that the propagation loss through the PC is minimal, and thus high localisation of the fields in the air channels. Note that simulations for non-PEC materials such as silver give quantitatively the same transmission spectra at these long wavelengths.

### 5.2.5 Dependence on the cleaving plane

In this section we vary the cleaving plane of the srs-network to determine the effect on the transmission spectra. We have varied the thickness of the overall structure by non-integer amounts of the unit cell size. The thickness of the metallic structure for these simulations is $N_z + d$ (measured in number of unit cells, a), where $d$ is a non-integer. The results are shown in Fig. 5.8.

The position of the fundamental transmission band edge around 5.5 $\mu$m is not greatly affected by the value of $d$, and hence the cleaving plane. This is expected as changing the cleaving plane does not shift the position of the bands,
which is only dependent on the unit cell size and filling fraction of the metallic networks. However, the position and magnitude of the sharp resonances within the transmission band are significantly affected as $d$ is varied from 0.1 to 0.5. It is important to note that during DLW of the srs-networks the cleaving plane can vary over a large area due to variations in the substrate position. This may cause inhomogeneous broadening of the resonances observed in the numerical simulations.

Figure 5.8  Numerical simulation of the PEC LHD srs-network for varying cleaving plane positions. The thickness of the overall structure measured in number of unit cells is $N_z + d$. a) Transmission of LCP light. b) Transmission of RCP light.
5.2.6 Dependence on the unit cell size

Here we discuss the effect of the unit cell size of the srs-network. Note that for a PEC, the unit cell size has no effect on the optical properties, besides shifting the wavelength of operation. That means if we half the unit cell size of a PEC srs-network, the exact same spectra can be observed at exactly half the wavelength (analogous to a dielectric PC). This assumption should hold for silver at wavelengths in the MIR and NIR where silver is practically a PEC. However, in the visible spectrum, one must consider the Drude-like response of silver as plasmonic effects can exist at these shorter wavelengths.

In Fig. 5.9 we plot the transmission spectra for 4 different unit cell sizes of the silver LHD srs-network. The spectral range has been scaled along with the unit cell size, such that $0.3 < \omega a/2\pi c < 1$, in all 4 spectra. The number of unit cells thick is $N_z = 2$ and the filling fraction is $\text{ff} = 11.5\%$.

The results for $a = 3 \mu m$ and $a = 1.5 \mu m$ are almost identical, with only minor differences in the sharp spectral features at higher frequencies. Here the fundamental transmission bands for both of these spectra cuts on at $\omega a/2\pi c = 0.5$. For $a = 0.5 \mu m$ the differences in the spectra becomes more significant and the fundamental transmission band cuts on at $\omega a/2\pi c = 0.38$. The red-shift of the normalised cut-on frequency is due to the effect of the plasmonic response of the silver srs-network. As we further reduce the unit cell size to 0.3 $\mu m$ the fundamental transmission cuts on at $\omega a/2\pi c = 0.3$ and the plasmonic red-shifting of the spectra becomes stronger. Therefore, for these smaller unit cell sizes where the optical response is in the visible regime, the metallic srs-network acts as a plasmonic PC.
Figure 5.9  Numerical simulation of the transmission spectra for a silver LHD srs-network with varying unit cell size. a) $a = 3.0 \, \mu m$. b) $a = 1.5 \, \mu m$. c) $a = 0.5 \, \mu m$. d) $a = 0.3 \, \mu m$.

For the smallest unit cell size of $a = 0.3 \, \mu m$, the diameter of the circular rods is $d = 0.2 * a = 60 \, nm$ (for the 11.5% filling fraction considered in Fig. 5.9). Such a small 3D resolution is not realisable via current DLW technology. However, with super-resolution methods under development [50, 95], these metallic srs-networks may be achievable in the near future.

A different method of fabricating these metallic nanostructures based on the chiral gyroid networks has recently been theoretically and experimentally investigated using self-assembly with metallic infiltration [167, 174]. For these self-assembled structures the unit cell size is typically around 30-100 nm, and thus are ideal length scales for the development of MMs operating at visible wavelengths. Unfortunately, the current lack of control of the self-assembly of
homogeneous crystals with defined crystal orientation and unit cell size limits the application of these methods in photonics.

Note that at these extremely small length scales of 30-100 nm, the width of the network rods is much smaller than the skin depth of light. For example, at the wavelength of 1 μm, the skin depth of silver using the Drude model, is approximately 22 nm. Thus in this nanoscale regime, the optical response of these metallic gyroid networks is significantly different as shown in Fig. 5.10.

**Figure 5.10** Numerical simulation of the transmission spectra for a silver LHD srs-network with varying unit cell size. a) $a = 0.3$ μm. b) $a = 0.2$ μm. c) $a = 0.15$ μm. d) $a = 0.1$ μm.
5.3 Metallic achiral 2-srs

It has recently been theoretically shown that a gold achiral 2-srs composite with unit cell size of 100 nm (achievable via self-assembly methods) \[174\] can possess almost-isotropic negative refraction (see Sec. 2.6.4). Such a MM would be highly valuable for applications such as the perfect lens \[44\] and there is now an urgency within the self-assembly community to realise such a novel nanoscale MM. The fabrication of gold srs-networks (via co-polymer self-assembly and post-process electro-deposition) has recently been demonstrated \[167\] and shown to perform as a chiral MM at optical wavelengths. So far only the single chiral srs-network geometry has been experimentally realised but current efforts are being made to realise the achiral 2-srs geometry in the nanoscale regime.

In this section we investigate the optical properties of a metallic achiral 2-srs with a unit cell size that is practically achievable via 3D nano-lithography methods such as DLW. As in Chapter 3, the achiral 2-srs composite consists of a LHD and RHD srs-network intertwined to form a cubic structure with achiral symmetry. Our first simulation results for the metallic achiral 2-srs is for a 3 μm unit cell size, based on the successful fabrication at this length scale, as shown in Chapter 3. In Fig. 5.11 we show an image of the silver achiral 2-srs composite. Each srs-network has a filling fraction of $f_f = 3.1 \%$, such that the total filling fraction of metal is $f_f = f_f^1 + f_f^2 = 6.2 \%$. Note we have chosen a small filling fraction here as the results of Sec. 5.2 suggested that a smaller filling fraction leads to a red-shifting of the transmission bands.
Images of the silver achiral 2-srs, with filling fraction $\text{ff} = 6.2\%$ and 2 unit cells tall. a) View from the top. b) View from the side. c) View from an oblique angle.

The numerically simulated transmission spectra through the silver achiral 2-srs is shown in Fig. 5.12. The geometrical parameters used for these simulations are a unit cell size of $a = 3 \ \mu m$, the overall structure thickness measured in unit cells is $N_z = 2$ (i.e. 6 $\mu m$ thick) and the filling fraction of the total metal structure is 6.2%. Note that due to the lack of chirality, we only need to simulate the transmission of either LCP or RCP, as the results are identical for both polarisations.

The numerical simulation results in Fig. 5.12 clearly show that in the size scale regime the achiral 2-srs does not act as a MM. The transmission spectra show only significant transmission at wavelengths between 4.5 $\mu m$ to 5.2 $\mu m$ and 3 $\mu m$ to 3.5 $\mu m$. Thus the silver achiral 2-srs operates as an achiral metallic PC. Note that we have performed further numerical simulations of the metallic achiral 2-srs composite with the variation of the filling fraction and thickness of the structure (not shown here for succinctness). However, these geometrical variations do not greatly change the physical properties and more importantly
do not lead to the long wavelength negative refraction response shown in [174].

![Figure 5.12](image)

**Figure 5.12** Numerical simulation of the silver achiral 2-srs. Calculations have only been performed for LCP polarisation due to the achiral symmetry. a) Transmission. b) Transmission conversion. c) Reflection conversion. d) Reflection.

Note that the small unit cell size of the achiral 2-srs composites theoretically investigated in [174] allows the structure to perform as a MM at visible wavelengths where propagating plasmon resonances occur. This plasmonic property of the nanoscale gyroid structure is important to the formation of the observed negative refraction bands. Our results here at much longer wavelengths do not support such propagating plasmonic modes and thus we do not observe long wavelength transmission bands.
5.4 Metallic 4-srs composite

In Sec. 5.2 we observed that metallic srs-networks do not operate as chiral MMs due to the cut-off of modes at long wavelengths. This restricts these 3D chiral microstructures to PC applications. Our numerical simulations have shown that only by scaling the unit cell size to the nanoscale plasmonic regime can the transmission of these metallic srs-networks be extended to the MM regime. Unfortunately, this nanoscale size regime is currently unachievable via current state-of-the-art 3D nano-lithography.

We also discussed in Sec. 3.8 that the chiral 4-srs composite possesses an extremely broadband and very strong circular dichroism when constructed by high refractive index materials [115]. Interestingly, this 4-srs composite has a unit cell volume that is $1/8^{th}$ the volume of that of the single srs-network building block (i.e. the unit cell size of the 4-srs composite is half the size of the single srs-network). This has inspired our investigation to the question, “does a metallic 4-srs composite acts as a broadband chiral MM?” which we address in this section.

Note that the metallic 4-srs composite consists of 4 individual metallic srs-networks that intertwine with each other as shown in Fig. 5.13. It is important to note that unlike the metallic achiral 2-srs of the previous section, the 4-srs is a chiral geometry as it contains four srs-networks of the same handedness. Details of this geometry and the dielectric 4-srs PC properties have been discussed in Sec. 3.8. An important geometrical feature of the 4-srs, is that the unit cell of the 4-srs is exactly half the size of the single srs-network. Here we shall perform numerical simulations where the unit cell size of the 4-srs is 1.5 μm (i.e. it consists of four srs-networks each with a 3 μm unit cell size). In Fig. 5.14 we plot the numerical simulation results for the silver 4-srs with $N_z = 4$ (i.e. it is 6 μm thick) and metallic filling fraction $ff = 26.4\%$ (i.e.
each individual srs-network has a filling fraction of $f_f = 6.6\%$). A study of the dependence of the metallic 4-srs filling fraction is provided later in this section.

![Image](image.png)

**Figure 5.13** Image of the LHD metallic 4-srs composite consisting of four identical LHD metallic srs-networks. a) Top view along [001]. b) Oblique view.

The numerical simulation results for the metallic 4-srs has many differences to that of the single metallic srs-network. Firstly, the sign of the circular dichroism has been inverted i.e. RCP incidence has high transmission whereas LCP incidence is completely reflected. Note that in Sec. 5.2 the air channels that light propagates through were of opposite handedness to the metallic srs-network. On the other hand, the air channels within the metallic LHD 4-srs are also geometrically LHD. This results in the transmission of RCP light.
Figure 5.14 Numerical simulation of the silver LHD 4-srs, the unit cell size is $a = 1.5 \, \mu m$, $N_z = 4$ and $ff = 26.4\%$. a) Transmission. b) Transmission conversion. c) Reflection conversion. d) Reflection.

The high circular dichroism strength over a broad range of wavelengths suggest that the metallic 4-srs acts as a superior broadband circular polariser compared to the single srs-network. Note that the polarisation conversion is very small, but it has a small peak around the wavelength of $5.5 \, \mu m$ of amplitude $10\%$. As for the single metallic srs-network, this is caused by linear birefringence of the terminating boundary.

The most important difference of the transmission bands observed for the metallic 4-srs compared to the single metallic srs-network is the wavelengths of operation. The fundamental transmission band for the 4-srs cuts on at $7 \, \mu m$, which corresponds to a normalised wavelength of $\omega a / 2\pi c = 0.214$. This longer wavelength response of the metallic 4-srs makes it a promising candidate for a chiral MM.
In Fig. 5.15 we plot the transmission spectra of the silver LHD 4-srs for the varying filling fraction, ff. Note that the transmission spectra for LCP incidence has been plotted in the region from 0 - 10 %.

Figure 5.15  Numerically simulated transmission spectra of the silver LHD 4-srs for the varying filling fraction (ff). The unit cell size is $a = 1.5 \, \mu m$, and $N_z = 4$. a) LCP incidence, note the change of scale to 0 - 10 %. b) RCP incidence.

Interestingly, as ff increases from 17.6 % to 64 %, the transmission bands are weakly red-shifted. This is the opposite trend to that of the metallic srs-network, which showed a strong blue shift with increasing ff. We also observed a significant decrease in the overall transmission for increasing ff. This is expected due to the reduced air channel sizes for light to propagate through.
In Fig. 5.16 we plot the transmission spectra for a PEC 4-srs with the same geometrical parameters in Fig. 5.15. We see a close replication of the spectra obtained for the silver 4-srs and the PEC 4-srs. The only significant differences are observed in the magnitudes of the transmission peaks. Therefore, the use of a PEC in our numerical simulations of the metallic 4-srs should accurately model the physical phenomena observed for silver based srs-networks.

Using this assumption we performed eigenmode calculations of the PEC 4-srs to further investigate the optical properties of this chiral MM as shown in Fig. 5.17. We observe a cut off for modes below $\omega a/2\pi c < 0.23$. A single RCP mode
exists from \(0.23 < \omega a/2\pi c < 0.47\) explaining the extremely broadband circular dichroism observed in Fig. 5.14. The bandwidth of this circular dichroism band is \(\Delta \omega/\omega = 2 \times (0.47 - 0.23)/(0.47 + 0.23) \times 100\% = 69\%\), over twice as broad than the silicon 4-srs, which had a circular dichroism bandwidth of 30.2\% [115].

![Dispersion diagram for the PEC 4-srs with metal filling fraction, \(ff = 26.4\%\), for the first three fundamental eigenmodes and the unit cell of the PEC srs-network. The colours of the points are directly proportional to the value of \(C\) (where \(C = +1\) is red and \(C = -1\) is blue) and the radii of the points are directly proportional to the value of \(\beta\). Black dots represent Bloch modes that have neither RCP or LCP polarisation. Crosses have been used for the eigenmodes with very low coupling values, i.e. \(\beta \approx 0\).](image)

**Figure 5.17** Dispersion diagram for the PEC 4-srs with metal filling fraction, \(ff = 26.4\%\), for the first three fundamental eigenmodes and the unit cell of the PEC srs-network. The colours of the points are directly proportional to the value of \(C\) (where \(C = +1\) is red and \(C = -1\) is blue) and the radii of the points are directly proportional to the value of \(\beta\). Black dots represent Bloch modes that have neither RCP or LCP polarisation. Crosses have been used for the eigenmodes with very low coupling values, i.e. \(\beta \approx 0\).

### 5.5 Solid versus coated structures

The direct fabrication of 3D metallic microstructures has been demonstrated via photo-reduction [77, 78]. In principle this could be used to fabricate metal-
lic srs-networks constructed from solid silver rods with resolution comparable
to DLW in polymer photoresists. However, the photo-reduction method suffers
from weak mechanical properties, poor surface roughness and low conductivity
[77, 78].

In our review in Chapter 2, we discussed that the electroless silver deposition
(ESD) of dielectric templates is currently the most suitable method for the
fabrication of 3D metallic microstructures. The ESD of a dielectric template
does not result in a solid metallic structure, but a dielectric structure with thin
silver coating. In this section, we numerically investigate the optical properties
of silver coated polymer srs-networks and compare results with that of solid
silver srs-networks from previous sections of this chapter.

![Figure 5.18](image.png)

**Figure 5.18** An illustration of the silver coated dielectric srs-network. a) Cross sectional
view of the silver coated srs-network along [100]. b) Cross sectional image of the silver
coated dielectric rod, with inner dielectric diameter 2r and outer diameter 2r + 2t.

The geometry of the silver coated polymer srs-network is shown in Fig. 5.18a
and an illustration of the cross section of a silver coated rod in Fig. 5.18b.
The radius of the dielectric rod is r and the thickness of the silver coating is t.
Thus the total diameter of the silver coated rod is d = 2r + 2t. In Fig. 5.19
we have simulated the transmission of light through the silver coated polymer srs-network for varying silver thickness \( t \). We have kept \( d \) constant for these simulations such that the filling fraction of the srs-network remains at \( \text{ff} = 11.5\% \). The unit cell size is \( a = 3 \, \mu \text{m} \) and \( N_z = 2 \).

Figure 5.19 Numerical simulated transmission spectra of the silver coated polymer srs-networks for varying silver thickness, \( t \). The overall diameter of the coated rod, \( d \) is kept constant such that the total filling fraction of the silver + polymer is \( \text{ff} = 11.5\% \). The unit cell size is \( a = 3 \, \mu \text{m} \) and \( N_z = 2 \). a) RCP incidence. b) LCP incidence.

From these simulations we see that varying \( t \) has only minor effect on the transmission spectra. For silver thickness larger than the skin depth (the black and magenta curves) the transmission spectra are identical. However, as the
thickness of silver becomes smaller than the skin depth (i.e. less than 23 nm), the transmission spectra is red-shifted. Note that the ESD method that we use in Chapter 6 for achieving the silver coating on the polymer srs-networks can only produce silver thickness as small as 30-50 nm.

Note that if the unit cell size approaches the nanoscale, where propagating plasmon resonances exist, the silver thickness becomes more a significant parameter. Plasmon modes have been shown to undergo a hybridisation when their geometries are formed by thin silver shells [60, 61]. This was shown to cause localised plasmon resonances to be shifted to the NIR, when polymer woodpile microstructures were coated with thin layers of silver[193]. In Appendix A we report on the theoretical development of an extension to plasmon hybridisation theory, which allows one to accurately model plasmon modes beyond the electrostatic regime. Further details of retarded plasmon hybridisation can be found in Ref. [67].

5.6 Inverse metallic srs-networks

The metallic srs-networks considered in the previous sections of this chapter are based on solid silver rods or dielectric rods coated with a thin layer of silver. These metallic srs-networks can be realised through ESD, which is the subject of Chapter 6.

This section investigates the optical properties of variants of the srs-network inspired by the infiltration of metals via electro-deposition. While ESD can be used to form a thin layer of silver on the dielectric template, electro-deposition fills the entire void space of the template with metal. For example, if the polymer srs-networks in Chapters 3 and 4 were filled with silver via electro-deposition one would form a completely solid material of partly polymer and
partly metal. The polymer template can then be thermally removed to form a purely metallic inverse srs-network as shown in Fig. 5.20. This silver microstructure has a 30% filling fraction and is the inverse of a dielectric srs-network template with filling fraction 70%. As expected, the inverse of the srs-network looks very similar to the original srs-network, but with the opposite handedness (the dielectric template is LHD and the metallic structure is RHD).

On a practical note, higher dielectric filling fractions (i.e. greater than 50%) and thus smaller metal filling fraction may be more difficult to experimentally achieve, due to the proximity effect [26] that occurs during DLW. Thus this method would only be suitable for the fabrication of metallic srs-networks with relative large metal filling fraction.

![Figure 5.20](image)

**Figure 5.20** Images of the inverse metallic srs-network, with filling fraction 30%. a) View from the top. b) View from the side. c) View from an oblique angle.

The numerically simulated transmission spectrum through the inverse metallic srs-network is shown in Fig. 5.21a. The unit cell size \( a = 3 \, \mu\text{m} \), the number
of unit cells in height is \( N_z = 2 \) and the PEC filling fraction \( f_f = 30\% \). The dielectric template has been removed such that the structure consists of PEC and air only.

Figure 5.21 Comparison of the numerically simulated transmission spectra for the original and inverse metal srs-networks. The unit cell size is \( a = 3 \mu m \), the number of unit cells in height is \( N_z = 2 \) and the PEC filling fraction is \( f_f = 30 \% \) for both simulation results. The insets figures are images of the corresponding metallic microstructures. a) PEC inverse of a LHD srs-network. b) PEC RHD srs-network.

The results clearly show that RCP light has greater transmission at most frequencies than LCP light. This is the opposite circular dichroism effect to the results observed for the LHD metal srs-network in the previous sections.
This is not a surprise due to the change in sign of chirality that occurs due to the inversion procedure. In Fig. 5.21b, we have calculated the transmission spectra for a PEC RHD srs-network, with the same geometrical parameters (i.e. $a$, $N_z$ and $f_f$) used in Fig. 5.21a. The comparison between these two results shows that both the inverse metal srs-network and original metal srs-network have approximately the same cut-off wavelength, which is determined purely by the unit cell size and filling fraction of the metal. Both results observed the same sign in circular dichroism, i.e. RCP light has higher transmission than LCP light over the entire spectral range. However, due to the different cleaving conditions of the two structures (as well as other minor geometrical differences), we see significant differences in the features of the resonant peaks.

![Figure 5.22](image)

**Figure 5.22** Images of the achiral inverse metallic srs-network, with filling fraction 30%. a) View from the top. b) View from the side. c) View from an oblique angle.

Another interesting geometrical configuration obtainable through electrodeposition methods is an metallic inverse achiral 2-srs. This structure shown in Fig. 5.22 consists of a metallic inversion of the achiral 2-srs composite discussed in Chapter 3. Unlike the inverse of the single srs-network, the inverse
achiral 2-srs results in an achiral surface. This surface is similar to that of the gyroid surface, which is the boundary between two chiral networks of opposite handedness [150].

On a side note, one can form a chiral surface from the boundary between the two chiral 2-srs we introduced in Chapter 3. However like the chiral 2-srs, this chiral surface has strong linear birefringence due to the lack of cubic symmetry. Thus this configuration shall not be presented in this research thesis.

The transmission spectra for this achiral silver surface has been calculated and the results are shown in Fig. 5.23. The geometrical parameters used for these simulation results are $a=0.5\,\mu m$, $N_z = 2$ and $ff = 23\%$. Note that the small unit cell size of $0.5\,\mu m$ has been chosen, for operation in the plasmonic regime where transmission bands can be observed at wavelengths longer than the unit cell size (i.e. for $\omega a/2\pi c < 1$). For unit cell sizes around $1.5\,\mu m$ or $3\,\mu m$ we do not observe any significant transmission for $\omega a/2\pi c < 1$.

![Transmission spectra for the silver inverse achiral 2-srs. The unit cell size is $a = 0.5\,\mu m$, the number of unit cells in height is $N_z = 2$ and the silver filling fraction is $ff = 23\%$. Note that the LCP and RCP curves perfectly overlap due to the achiral symmetry of the surface.](image)

**Figure 5.23** Transmission spectra for the silver inverse achiral 2-srs. The unit cell size is $a = 0.5\,\mu m$, the number of unit cells in height is $N_z = 2$ and the silver filling fraction is $ff = 23\%$. Note that the LCP and RCP curves perfectly overlap due to the achiral symmetry of the surface.
The transmission properties of this achiral surface is not particularly interesting. The transmission spectra are identical for both LCP and RCP light as expected due to the achiral symmetry of the surface. Unlike the inverse single srs-network that can preferentially allow one circular polarisation to propagate through single chiral channel, the achiral surface has both RHD and LHD air channels. Thus both LCP and RCP have the same transmission spectra.

One interesting question that naturally arises is, “does LCP and RCP light propagate through different air channels?”

To answer this question, in Fig. 5.24 we analysed the electric field amplitude distribution in the XZ plane (i.e. $|E(x, y = 0, z)|$) at the peak of the transmission spectra, around 0.519 μm. Light incident from above (along the Z-axis) is able to propagate with around 75% transmission through the achiral surface for both polarisations. The two LHD and RHD 4-screw air channels are labelled 1 and 2 respectively.

An interesting feature shown in Fig. 5.24 is that LCP and RCP light preferentially propagate through the RHD and LHD air channels, respectively. This localisation selectivity between channels 1 and 2 is most prominent at this wavelength of 0.519 μm, which corresponds to the peak of the transmission band. This physical phenomenon thus causes a chiral partitioning of light. That is, if one was to shine unpolarised light through the achiral surface, the LCP and RCP components of the source would propagate through different air channels of the nanostructure.

This can be physically explained by considering the continuity conditions of Maxwell’s equations. Note that light inside the metal is approximately zero at these visible wavelengths. Due to the continuity of the parallel component of the electric field at the metal-air interface, the electric field parallel to the surface should be zero. Let us consider light at a wavelength that matches the
pitch of the channel 4-screw air channel. If circularly polarised light was to travel through the air-channel of the same handedness, the electric-field vector at the metal-air surface would always be zero. Hence light at this wavelength is rejected. Therefore, we see that LCP and RCP light propagates only through the air channel of opposite handedness. When the wavelength is detuned from the transmission peak, this phenomenon is significantly weakened.

Figure 5.24 Distribution of the electric field amplitude, for light propagating through the silver inverse achiral 2-srs at the wavelength of 0.519 μm. The RHD and LHD air channels are labelled 1 and 2, respectively. a) LCP incident light propagates through the RHD air channel. b) RCP incident light propagates through the LHD air channel.
5.7 Discussion

In this chapter we have numerically investigated the optical properties of metallic srs-networks with a broad range of geometrical configurations. We have observed that the metallic srs-network has stronger circular dichroism and of opposite handedness compared to that of the dielectric srs-network. However, these circular polarised transmission bands exist only at the shorter wavelengths where it performs as a PC and not a MM. At longer wavelengths where the metallic srs-network acts as a MM, there are no transmission bands and thus all light is completely reflected. This problem can only be avoided when the unit cell size is scaled to the nanoscale (i.e. the plasmonic regime) and the size of the silver rods become smaller than the skin depth of metal. Similarly for the achiral 2-srs in the same size regime we observe no transmission bands at longer wavelengths. Whilst current DLW technology cannot produce unit cell sizes of around 100 nm, advances in super-resolution DLW methods may make these plasmonic scale metallic srs-networks feasible designs for chiral MMs.

On the other hand, for the metallic 4-srs we have been able to observe transmission bands at wavelengths longer than four times the unit cell. These transmission bands in the MM regime, show superior circular dichroism, over a broadband wavelength region and are promising for the development of cubic chiral MMs. We have performed eigenmode simulations to analyse the physical properties of this chiral MM and attribute the strong broadband circular dichroism to the existence of a single circularly polarised mode over this wavelength range.

Our numerical simulations of the silver coated srs-networks have shown that for silver thickness larger than the skin depth we expect identical optical properties to that for the solid srs-networks. Thus our proposed experimental procedure
to produce these gyroid MMs based on the ESD method should accurately replicate these physical phenomena. We then showed that other interesting geometries can be derived from the srs-networks, based on inversion methods. Interestingly, we found that the achiral surface formed by the boundary of two srs-networks, can be used to partition LCP light and RCP light into complementary regions of the porous structure.

In the next chapter we show the experimental fabrication and characterisation of the silver coated srs-networks and 4-srs networks we have introduced here.
Chapter 6

Fabrication of metallic gyroid photonic microstructures

In this chapter we investigate the fabrication of metallic gyroid photonic microstructures for metamaterial (MM) and photonic crystal (PC) applications. Our fabrication method involves the combination of the direct laser writing (DLW) method followed by electroless silver deposition (ESD). This precise, fast and low cost method of fabricating three-dimensional (3D) metallic microstructures is suitable for the development of the metallic gyroid networks that we have numerically investigated in Chapter 5. A review on the fabrication of metallic 3D microstructures has been presented in Sec. 2.2.

This chapter has the following structure. In Sec. 6.1 we investigate the use of the ESD method to selectively silver coat gyroid microstructures. In Sec. 6.2 we report on the fabrication of polymer srs-network templates that have been coated with silver via the well-established ESD method. We then demonstrate the fabrication of polymer 4-srs templates in Sec. 6.3, which is an important step towards the development of 3D chiral metamaterials. Finally, we conclude the chapter with a discussion of these results and provide an future outlook of
6.1 Electroless silver deposition

The ESD method is a well known silver coating process for producing a compact layer of silver nanoparticles [85–88, 100, 194]. The roughness of the silver coating is related to the size of the silver nanoparticles, which are typically between of 20 nm to 100 nm (depending on ESD conditions) [194]. The procedure for ESD is based on the Tollen’s reaction and is as follows.

A solution containing silver nitrate, ammonia and sodium hydroxide is prepared. Glucose is then added to the solution as a reducing agent. The following chemical reaction then occurs [194]:

\[ 2Ag(NH_3) + RCHO + 3OH^- \rightarrow 2Ag + RCOO^- + 4NH_3 + 2H_2O. \] (6.1)

Immediately after the glucose is added to the solution the silver reduction process occurs, forming silver particles that attach to surfaces with the suitable surface bonds. During this reaction the clear aqueous silver solution becomes darker and eventually forms an opaque black solution of silver nanoparticles. During this reaction the sample to be coated with silver is immersed in the silver bath solution. It is important to place the object in the solution immediately after the glucose is added and before the solution turns opaque. This avoids the coating of larger silver nanoparticles, which would result in a greater silver surface roughness.

A scanning electron microscope (SEM) image of a silver coated glass substrate is shown in Fig. 6.1a. Details of this silver coating procedure have been given in [194]. The average particle size is around 50 nm. From the AFM measurement shown in Fig. 6.1b we observe that the average coating thickness is around 40
nm and the average surface roughness is around 20 nm.

\[\text{Figure 6.1} \ a) \text{ Scanning electron microscopy (SEM) image of a silver coated glass substrate. The scale bar is 500 nm.} b) \text{ Atomic force microscope (AFM) profile of the silver coating. Data was supplied by Alessandro Antonello.}\]

In order to improve the adhesion of the silver particles to the sample, the surface of the sample is activated before ESD. There are several methods to activate the surface of the sample, such as oxygen plasma etching [194], tin activation [88] or silver activation [195].

Due to the fast rate of reaction of the ESD method, the silver plating time can be as short as several seconds. This short reaction time can often be disadvantageous when attempting to precisely control the amount of silver deposition onto the sample. Thus there have been efforts to slow the reaction through the addition of a gum arabic solution [194]. However, recent measurements of the ohmic conductivity of these ESD coatings have shown that the addition of gum arabic can greatly reduce the ohmic conductivity [195].
6.1.1 Silver coated gyroid networks

Here we show the results of the ESD of polymer srs-networks that we have been fabricated using the standard DLW method (see Chapter 3 for experimental details). An illustration of the ESD of the srs-networks is shown in Fig. 6.2.

First, the DLW of srs-networks is performed and washed using the standard procedure of immersion in 2-propanol for 20 minutes (see Chapter 3 for experimental details). Then a silver solution was prepared by mixing 0.34 g of silver nitrate in 8 mL of water, 5 mL of 30% aqueous ammonia solution and 0.096 g of sodium hydroxide in 3 mL of water together in a 50 mL beaker. In addition, 0.2 g of arabic gum in 4 mL of water was added to slow down and control the reduction reaction to obtain smoother coatings.

![Figure 6.2 Illustration of the ESD procedure. The DLW microstructure containing polymer srs-networks on a glass substrate is placed in silver solution. After several minutes have passed, the solution is removed and rinsed. The resulting sample is a silver coating formed on both the polymer microstructure and glass substrate.](image)

Before the sample is placed in the silver bath, it is first exposed to oxygen plasma etching for 45 seconds. This essential procedure activates the surface of the sample to promote the adhesion of silver particles to the polymer and glass surfaces.

After the surface activation of the sample, 0.18 g of glucose was dissolved in 12 mL water and added to the silver plating solution. The sample is then
immediately immersed in the silver solution and mounted vertically. At this point, silver started reducing forming a homogeneous coating on the structure. Every 5 minutes the sample was removed from the solution and rinsed in water and dipped again in the solution. This is to remove unwanted large particles that are more weakly bound to the sample surface. This procedure was repeated for 1 hour.

The results of the ESD coated srs-networks are shown in Fig. 6.3. The srs-network has 3 \( \mu m \) unit cell size and a pyramid-like overall shape. The silver coating appears homogeneous and the surface roughness is much smaller than the feature sizes of the srs-network. Therefore, the silver coating does not modify the geometry of the underlying polymer template.

![Figure 6.3](image)

**Figure 6.3** a) SEM image of a silver coated srs-network. The scale bar is 10 \( \mu m \). b) Zoomed in view of (a). The scale bar is 1 \( \mu m \).

However, as observed in Fig. 6.3a, both the polymer template and the glass substrate are coated with silver. The silver coated srs-network thus stands upon a silver mirror. This is undesired as the sample becomes completely opaque, resulting in the complete reflection for all optical wavelengths.
6.1.2 Selectivity

In order to obtain a sample whose optical properties can be experimentally characterised, one must selectively coat only the polymer template leaving the glass substrate uncoated and transparent. Here we discuss two methods we have used to approach this issue, a hydrophobic surface protection method and the use of an amine activated photoresist.

6.1.2.1 Hydrophobic surface protection

The first method we have implemented to achieve a selective silver coating was the hydrophobic surface protection method [85] illustrated in Fig. 6.4.

![Figure 6.4 Illustration of the procedure for the ESD of polymer srs-networks with a hydrophobic substrate.](image)

First, a standard glass coverslip was coated with a hydrophobic sol gel. The sol gel solution contains a 30 cc of ethanol, 4.2 cc tetraethyl orthosilicate, 0.12 cc fluoroalkysilane, 3.56 cc distilled water and 0.4 cc hydrochloric acid. The hydrophobic component is the fluoroalkysilane. The hydrophobic coating was
applied to borosilicate microscope coverslips by dip coating with a rising speed of 10 mm/min at room temperature. The coated coverslips are then baked at 80°C for at least 1 hour.

DLW is then performed on the hydrophobic coverslip. Oxygen plasma etching of the sample is not performed, as this would cause activation of both the substrate and polymer structure. In order to perform a selective activation of the polymer structure, the sample is treated with a solution containing 0.45 g of SnCl₂ in 20 mL of ethanol for 5 minutes. During this stage tin ions are formed selectively on the polymer structure [88]. The hydrophobic substrate repels the ethanol based solution and thus does not get seeded with tin ions. The ESD process is then performed as outlined in the previous section.

The result is the selective coating of the polymer template, keeping the substrate uncoated and transparent. A photograph of a coverslip containing a silver coated hydrophobic substrate with DLW microstructures is shown in Fig. 6.5a.

![Figure 6.5](image)

**Figure 6.5** Results of the ESD of polymer srs-networks on a hydrophobic glass substrate. a) Photograph of the sample after ESD. b) Optical microscope image of the silver coated srs-networks.

The section of the substrate that has been protected by the sol gel hydrophobic coating appears to be completely transparent and uncoated with silver. On
the other hand, the right most section of the coverslip that did not get coated with the hydrophobic sol gel, appears to be coated with silver. Thus, the hydrophobic coating successfully inhibits the deposition of silver on the substrate where the polymer templates stand.

An optical microscope image of the srs-networks after the ESD is shown in Fig. 6.5b. Here we observe a few issues. Firstly, the array of 24 srs-networks have been mostly washed away or moved to another location due to the ESD procedure. We have attributed this to the weak adhesion of the polymer (IP-L) to the hydrophobic sol gel coating. The adhesion of the sol gel coating to the polymer structures could be improved through further chemistry developments. One example is the addition of vinyl groups to the sol gel that have good adhesion properties to the polymer photoresist. However, these developments in surface chemistry are not within the scope of this PhD thesis.

The second issue we observe in Fig. 6.5b is the aggregation of silver particles around the polymer templates. This suggests that the substrate region around and below the polymer templates may not be transparent. As the transparency of the substrate directly under the microstructures are most important, this poses a significant problem. These challenges unfortunately limit the practically of this method for producing a smooth selective coating of silver on the srs-networks, and thus our development of 3D chiral MMs.

6.1.2.2 Amine activated photoresist

Here we discuss an alternate solution to selective silver coating of DLW microstructures using a polymer photoresist that has been modified to contain metal binding amine groups [101, 195]. The details of this photoresist have been published in [195] and the photoresist has been supplied to us by the authors of [195]. This pre-activated photoresist allows one to skip the oxygen
plasma etching or tin surface activation stages of the standard ESD method, as silver will directly attach to the amine groups found in the modified photoresist (MPR). This results in the formation of silver only on the amine terminated polymer microstructure with the substrate left uncoated with silver.

The procedure for the fabrication of metallic microstructures using the MPR is as follows. DLW is performed in the MPR, followed by rinsing in a solution of 70 % 2-propanol and 30 % 1-propanol. The ESD procedure is then performed as follows:

1. **Silver seeding**: The samples were immersed in a 0.05 mol/L aqueous silver nitrate solution at room temperature for at least 38 hours. This allows the formation of small ions on the polymer microstructure. The samples were mounted vertically in order to avoid particle attachment due to gravity adsorption.

2. **Sample rinsing**: The sample was then thoroughly rinsed with distilled water to remove unwanted particles on the substrate and then left for several minutes to dry at room temperature.

3. **Silver seed reduction**: An aqueous sodium borohydride solution 6.6 M was prepared and left to settle for at least 4 hours. The solution was thoroughly stirred and kept uncovered for the removal of the oxygen bubbles. The samples were then vertically immersed in the reduction solution for 22 hours to reduce the silver ions and form silver nanoparticles.

4. **Sample rinsing**: The sample was then thoroughly washed again with distilled water to remove bubbling on the surface of the sample.

5. **Silver coating 1**: An aqueous silver nitrate solution (0.339 g AgNO₃ diluted in 10 mL of water) was mixed with 5.6 % NH₃ and 1.9 M glucose
(5.477 g of glucose in 16 mL of water) as a reducing agent, at a volumetric ratio of 5:3:8. Immediately after the silver solution is prepared, the samples were vertically immersed for a period of time. The timing of this immersion was critical. Too short an immersion time will produce a non-connected layer of silver particles. Too long and large silver particles will deposit, creating a rough silver coating. The samples were removed before the solution turns dark, which typically takes between 2-3 minutes.

6. **Silver coating 2:** During the first silver coating stage a second fresh silver solution was prepared. After the first silver coating was finished, the samples were removed and immediately placed into the second fresh silver solution.

7. **Substrate rinsing:** Finally, the sample was again thoroughly washed in distilled water.

To optimise the ESD procedure using the MPR (in particular the timing of the silver bath) we have performed ESD on thin films of the MPR. The films were spin coated and cured using a ultra-violet lamp before coating with silver. The silver coating procedure was performed for 3 minutes for the first bath and 3.5 minutes for the second bath. The sheet resistance of the silver film was measured using a 4-point probe to be $2.55 \pm 0.25 \, \Omega/\square$. Based on the SEM images of the sample we see that the particle sizes vary between 10 nm to 100 nm. This allowed us to estimate the film thickness to be around 80±40 nm. Thus the resistivity of the silver coating is estimated to be $2.05 \pm 1.3 \times 10^{-7} \Omega m$ corresponding to a conductivity of $4.88 \pm 1.9 \times 10^6 \Omega^{-1} m^{-1}$. This is comparable to the conductivity of $5.71 \pm 3 \times 10^6 \Omega^{-1} m^{-1}$ measured in [101] and is only a factor of 13 times less conductive than bulk silver ($6.3 \times 10^7 \Omega^{-1} m^{-1}$) [195].
To improve the conductivity of the silver coating, the silver coated polymer film was thermally annealed at 200°C (under nitrogen to avoid oxidisation) for 30 minutes, which has been shown to greatly improve the conductivity of ESD coatings [194]. The sheet resistance was then measured to be greatly reduced to $1.85 \pm 0.35 \ \Omega/\square$, corresponding to a conductivity of $6.76 \pm 3.0 \times 10^6 \Omega^{-1} m^{-1}$. Note longer annealing times (such as 2 hours) caused degradation of the polymer film and should be avoided.

### 6.2 Fabrication of a silver srs-network

Here we discuss the fabrication of silver coated srs-networks using the galvodither direct laser writing (GD-DLW) method with the MPR (see Chapter 4 for experimental details), followed by the ESD procedure described in Sec. 6.1.2.2. The MPR sample is prepared by first drop-casting a small amount of the polymer liquid onto a coverslip. This sample is then baked at 50°C for 30 minutes before fabrication via GD-DLW. During this baking process the MPR hardens to form a solid photoresist. Unlike the IP-L photoresist that uses a
sandwich configuration as shown in Fig. 6.7a, the MPR can be fabricated using an inverted configuration as shown in Fig. 6.7b.

Figure 6.7 Illustration of the sample configuration for the GD-DLW procedure using the IP-L photoresist and MPR. a) Sandwich configuration where fabrication is performed on the bottom surface of the IP-L photoresist. b) Inverted configuration with the solid MPR, where fabrication is performed on the top surface of the MPR.

In Fig. 6.8 we show SEM images of a polymer srs-network with 3 μm unit cell size that was fabricated within the MPR. The overall 3D microstructure is 16 unit cells wide and 2 unit cells in height. The high quality fabrication results suggest the excellent mechanical properties of the MPR.

Figure 6.8 SEM images of a polymer LHD srs-network fabricated in the MPR with unit cell size 3 μm. a) View from above, the scale bar is 10 μm. b) Zoom in view of (a), the scale bar is 2 μm.
Note that due to the inversion of the sample configuration from the bottom surface (IP-L) to the top surface (MPR) we have had to invert the Z-direction translations made by the 3D nano-translation stage. This results in the handedness of the srs-network has being switched from RHD (as in Chapters 3 and 4) to LHD. As discussed in the earlier chapters of this thesis the choice of handedness of the srs-network is arbitrary as LHD and RHD srs-networks are exact mirror images of each other.

Having established that the srs-network can be successfully fabricated in the MPR we have performed the ESD of polymer srs-networks using the procedure discussed in Sec. 6.1.2.2. It is important to note that the timing and procedure for the ESD method is critical for achieving a homogeneous and smooth silver coating on the complex 3D microstructure. If the ESD procedure is performed for too long, silver nanoparticles will grow everywhere including the glass substrate making the sample completely opaque. On the other hand, if the ESD procedure is performed for too short a time, not enough silver can deposit on the 3D microstructure, leaving the srs-network non-conductive.

In Fig. 6.9 we show SEM images of two silver coated srs-networks. This sample consists of multiple polymer srs-networks that have been immersed in three silver plating solutions each time for a period of 3-4 minutes.

Whilst a relatively smooth silver coating can be observed on the top of the srs-networks, these silver coated srs-networks contain several issues. Firstly, the silver coating that is formed on the srs-network in Figs. 6.9a,b is very different to that in Figs. 6.9c,b. This is unexpected as both srs-networks are located on the same sample and thus are exposed to the identical ESD conditions. This suggests that the homogeneity of the ESD method between one structure and another is quite poor.
Figure 6.9  SEM images of two silver coated srs-networks with unit cell size 3 \( \mu m \). a) A partially coated srs-network where the silver plating solution has only coated the top of the microstructure. b) Zoomed in view of (a). c) A coated srs-network where the silver plating solution has coated the entire microstructure and the glass substrate. d) Zoomed in view of (c). The scale bars are 20 \( \mu m \) in (a) and (c) and 2 \( \mu m \) in (b) and (d).

Secondly, in Figs. 6.9a,b, we observe that only the top 2 layers of the srs-network (i.e. the first half of the unit cell) have been coated with silver nanoparticles. On the other hand, in Figs. 6.9c,d the silver coating extends to all the way to the bottom of the sample; however there is significantly less silver attached to the bottom of the srs-network than on the top.

Thirdly, for the srs-network in Figs. 6.9c,d where silver is coated throughout the entire structure, a connected layer of silver is formed on the substrate mak-
ing this structure completely opaque. We are thus not able to experimentally measure any transmission of light through this opaque sample.

Nevertheless, we have performed experimental characterisation of the transmission of light through the partially silver coated srs-network and the characterisation results are shown in Figs. 6.10. Interestingly, we observe that even though the srs-network has been partially coated with silver, relatively strong circular dichroism exists over the entire spectral range. Note that the transmission spectra beyond 6 μm cannot be experimentally measured due to the transmission cut-off of the glass substrate at these longer wavelengths.

![Graph showing transmission spectra](image)

**Figure 6.10** The experimentally measured transmission spectra for the partially coated srs-network for left-circularly polarised (LCP) and right-circularly polarised (RCP) light in blue and red, respectively. The inset figure shows the SEM image of the partially coated structure viewed from above.

In Chapter 5 we observed that both the solid silver srs-networks and coated silver srs-networks had a short-pass transmission cut-off around 4-6 μm depending on the geometrical parameters that were used. Here we do not observe such a transmission cut-off at these wavelengths. Instead both LCP
and RCP light appears to have a relatively high transmission at 6 μm. In order to understand these experimentally measured transmission spectra we have performed the numerical simulations for a silver srs-network, which has a thickness of 1.53 μm (i.e. $N_z = 0.51$). This value of $N_z$ was found to have the best agreement with the experimentally measured transmission spectra.

The numerical transmission spectra are shown in Fig. 6.11 and include both the transmission spectra and transmission conversion spectra (i.e. $T_{RCP} = T_{R2R} + T_{R2L}$ and $T_{LCP} = T_{L2L} + T_{L2R}$). It is important to include the transmission conversion, as this very thin metallic PC contains strong linear birefringence, with a peak transmission conversion of 22%.

![Figure 6.11](image)

**Figure 6.11** Numerically simulation transmission spectra for a thin LHD silver srs-network with unit cell size 3 μm and is only 1.53 μm thick, (i.e. $N_z = 0.51$). LCP and RCP incident light are shown in blue and red, respectively. Note that the transmission spectra include both the transmission and transmission conversion. The inset figure shows the half unit cell thick silver srs-network design viewed from above.

Note that this very thin silver srs-network is a simple approximation of the experimental fabrication result, which does not include the uncoated part of the polymer srs-network or the inhomogeneity of the silver coating between the first and second layers. Nevertheless, we observe a qualitative agreement
between the numerical and experimental transmission spectra. Specifically we observe a high transmission for LCP light and lower transmission for RCP light for the entire spectral range. Importantly, we observe that due to the very thin size of the structure (less than one unit cell) the transmission cut-off has been red-shifted to beyond 6 μm, as seen in the experimental results.

To conclude, further improvement of the selectivity and homogeneity of the ESD method is required and beyond the scope of this thesis. We have shown that even a partially coated srs-network has strong circular dichroism and these results are a promising step forward towards the development of cubic chiral metallic PCs and MMs proposed in Chapter 5.

### 6.3 Fabrication of the 4-srs composite

In this section we demonstrate the experimental fabrication of the 4-srs composite that was proposed in [115] and numerically investigated in Chapters 3 and 5.

The PC properties of the dielectric 4-srs composite was discussed in Sec. 3.8. The polymer 4-srs does not possess strong circular dichroism due to the weak refractive index contrast. Only when realised in a high refractive index material such as silicon or chalcogenide glass does a strong circular dichroism band exist. However, in Sec. 5.4 we discovered that a silver 4-srs composite would perform as a chiral MM with superior broadband circular dichroism and at wavelengths much larger than the unit cell size.

We have shown in Sec. 3.7 that the fabrication of two intertwined networks is possible using the DLW method. The fabrication of the 4-srs composite is much more challenging as is consists of four independent srs-networks that intertwine with each other. Nevertheless, when the GD-DLW method is used
and optimal fabrication conditions are found, we have found it possible to fabricate the 4-srs with a unit cell size of 1.5 μm (i.e. we have four intertwined 3 μm srs-networks). SEM images of the fabrication results are as shown in Fig. 6.12.

![SEM images of a polymer 4-srs fabricated in the MPR with unit cell size 1.5 μm. a) View from above. b) A tilted view of the 4-srs showing the intertwining of the 4 individual srs-networks. The scale bars are 5 μm in both (a) and (b).](image)

The overall 4-srs microstructure is 14 unit cells wide and 4 unit cells tall. These SEM images demonstrate that the 4-srs composite can be fabricated with excellent structural quality. With further improvements in the selectivity and homogeneity of the ESD method (as discussed in Sec. 6.2) this polymer 4-srs template could be used to develop the silver 4-srs metamaterial proposed in Sec. 5.4.

### 6.4 Discussion

In this chapter we have investigated the fabrication of metallic gyroid microstructures that were proposed in Chapter 5. Our fabrication method is based on the DLW of polymer srs-network templates followed by the silver
coating of these templates via the well-established ESD method.

The selective coating of 3D complex microstructures with a smooth, conductive and thin coating of silver is a highly challenging task. We have shown that applying a hydrophobic sol-gel coating to a glass coverslip can inhibit the growth of silver and maintain the transparency of the substrate. However, this hydrophobic coating only weakly adheres to the polymer microstructures and thus most microstructures are washed away during the ESD procedure. Future work on the composition of the sol-gel coating to include polymer binding groups for stronger adhesion to the polymer microstructure could greatly improve the practicality of this method.

On the other hand, the use of a pre-activated MPR is a more practical solution to the selective silver coating. We have demonstrated the high quality fabrication of both the single srs-network and the 4-srs composite in the MPR. However, due to inhomogeneity and lack of selectivity of the current ESD method, we have not been able to produce a selective homogeneous silver coating on the polymer srs-network templates. Further advancements on the ESD method are required to achieve a selective and homogeneous coating throughout the entire 3D microstructure, which is beyond the scope of this thesis.

Nevertheless, the ESD method developed in [101, 195] can be used to partially coat a silver srs-network. This partially coated chiral microstructure was shown to possess broadband circular dichroism from 3 \( \mu \text{m} \) to 6 \( \mu \text{m} \) with high overall transmission. We have attributed these optical properties to the very small thickness of the metallic srs-network and demonstrated a qualitative comparison with a silver srs-network with around half a unit cell thickness.

These experimental results are promising developments for the realisation of the metallic chiral PCs and MMs based on gyroid microstructures. A further
discussion on other possible methods to realise this experimental milestone is given in the following chapter.
Chapter 7

Conclusions

7.1 Thesis conclusions

In this thesis we have theoretically and experimentally investigated the optical properties of biomimetic chiral gyroids for photonic applications. Our innovative nano-photonic designs are based on the cubic chiral srs-network, an excellent platform for the development of chiral photonic crystals (PCs) and chiral metamaterials (MMs) with greatly enhanced chiral-optical phenomena. This PhD thesis has made several important achievements towards the development of chiral photonic devices:

1. Design and fabrication via direct laser writing (DLW) of chiral srs-networks with unit cell size 3 μm.

2. Experimental demonstration of strong circular dichroism bands centred around the mid-infrared wavelength of 3.4 μm.

3. Theoretical investigation of chiral gyroid PCs for a variety of geometries explaining the physical mechanism behind the observed circular dichro-
ism bands.

4. Development of the galvo-dithered DLW method (GD-DLW) to correct the intrinsic elongation of the fabrication voxel, greatly improving both the optical and mechanical properties of the fabricated microstructure.

5. Reduction of the unit cell size of the srs-network to 1.2 \mu m to scale the circular dichroism band to the important telecommunications wavelength of 1.55 \mu m.

6. Fabrication of a chiral beamsplitter (CBS) consisting of a prism-shaped chiral gyroid microstructure, with the first experimental demonstration of a chiral analogue of the linearly polarising beamsplitter.

7. Theoretical investigation of a series of metallic gyroid structures, with a detailed physical analysis of the optical properties of both PC and MM wavelengths.

8. Demonstrated the feasibility of the fabrication of srs-network and 4-srs composite templates for the selective silver coating.

In this thesis we have investigated a range of 3D chiral microstructures based on the gyroid network found in the wing scales of the *Calliphrys Rubi* butterfly. The first structure we analysed was the polymer srs-network, which performs as a chiral PC at wavelengths comparable to the unit cell size. We have numerically investigated the srs-network PC and shown the existence of circular dichroism bands. The physical mechanism that causes these circular dichroism bands was attributed to the lack of coupling of light to certain Bloch modes of the chiral PC.

Using the DLW method we have successfully fabricated these srs-networks with unit cell sizes of 3 \mu m with high accuracy and excellent uniformity. We have experimentally characterised the transmission of circularly polarised light
through these polymer srs-networks, demonstrating strong circular dichroism centred around 3.4 μm. These experimental results are in excellent agreement with numerical simulations and theoretical band structure calculations. We demonstrated that chiral composites based on two srs-networks of opposite (achiral 2-srs) or equal (chiral 2-srs) handedness can be fabricated and showed that the achiral 2-srs does not possess circular dichroism whilst the chiral 2-srs does.

We have shown that the elongation of the fabrication voxel inherent in the standard DLW method can lead to unwanted linear birefringence and polarisation conversion of circularly polarised light. We have developed a novel GD-DLW method to remove the voxel elongation. The GD-DLW method not only improves the isotropy of the fabrication, but also greatly enhances the mechanical strength. This has allowed us to reduce the unit cell size of the srs-network to 1.2 μm, where a circular dichroism band at the important telecommunications wavelength at 1.55 μm has been demonstrated. Using the GD-DLW method we have been able to fabricate a CBS consisting of 64,000 unit cells (768,000 connected polymer rods) of the srs-network shaped to form a prism. To be the best of our knowledge, we have experimentally demonstrated for the first time, the chiral analogue of the original linearly polarising beamsplitter originally invented in 1828 by William Nicol. Our numerical simulations of this chiral srs-network prism are in good qualitative agreement with experimental observations and have allowed us to attribute the physical mechanism behind the chiral beamsplitting phenomenon to the diffractive properties of the chiral srs-network PC. Note that the fabrication time for the CBS was 16 hours. The scaling of these structures to larger sizes is limited by the slow serial process of the DLW method. The fabrication speed of DLW can be greatly improved through diffractive methods utilising using spatial light modulators [177] making larger designs practically realisable.
To further enhance the chiral-optical properties of the gyroid microstructures we have numerically investigated the optical properties of several metallic gyroid structures for a broad range of geometrical parameters. The metallic srs-network has a stronger and more broadband circular dichroism band than the dielectric srs-network. However, the metallic srs-network supports transmission at shorter wavelengths with total reflection observed at the longer MM wavelengths. This problem can only be avoided when the unit cell size is scaled to the nanoscale (i.e. the plasmonic regime) and the size of the silver rods become smaller than the skin depth of metal. Currently this size scale regime can only be achieved through self-assembly methods. However, ongoing developments in super-resolution optical lithography may soon provide a pathway towards the fabrication of nanoscale srs-networks.

In contrast, the metallic 4-srs was shown to possess transmission bands at wavelengths four times larger than the unit cell, i.e. within the MM regime. These transmission bands show superior circular dichroism, over a broadband wavelength region and are promising for the development of cubic chiral MMs. We have attributed the strong broadband circular dichroism to the existence of a single circularly polarised mode over this wavelength range using an eigenmode analysis.

Numerical simulations of silver coated srs-networks have shown that for silver thickness larger than the skin depth (approximately 22 nm) we expect identical optical properties to that for the solid srs-networks. We then showed that other interesting geometries such as an achiral metallic gyroid surface can be used to partition left circularly polarised and right circularly polarised light into complementary regions of the porous nanostructure.

In our final chapter of this thesis we demonstrated the fabrication of metallic gyroid microstructures via the selective electroless silver deposition of polymer srs-networks using a modified photoresist (MPR). We have demonstrated the
high quality fabrication of both the single srs-network and the 4-srs composite in the MPR, showing excellent fabrication quality. The silver coating of these gyroid microstructures via ESD has resulted in selective partial coating of the srs-network. However, even these partially coated srs-networks show strong circular dichroism. With further advancements in the homogeneity and selectivity of the the ESD method, the experimental realisation of these chiral metallic srs-networks and 4-srs composites can be achieved. This is an exciting prospect for the development of true 3D chiral metamaterials with cubic symmetry.

To conclude, this PhD thesis has focussed on developing a fundamental understanding of the chiral-optical properties of gyroid microstructures. In particular we have examined the circular dichroism properties of these 3D chiral PCs and MMs. However, the importance of these 3D cubic chiral srs-networks for nano-photonics extends beyond that of circular dichroism and polarisation filters. The CBS that we have demonstrated in this PhD thesis is just one of many possible novel chiral photonic devices that can be realised from this elegant geometry.

The integration of these chiral gyroid microstructures with active materials such as quantum-dots [15] could lead to the development of tunable circularly polarised light sources. In addition, the ability to inhibit the emission of certain circular polarisation states may also be a novel method to manipulate the emission of nitrogen-vacancy centred nano-diamonds and hence their associated quantum-spin states. The strong helicity of light within these gyroid microstructures may also be useful for the development of ultra-sensitive detectors of chiral biomolecules [129] and even optically-driven micro-motors [130].

On a final note, the ability to self-assemble nanoscale gyroid networks using co-polymers, as well as the possible extraction of the gyroid from the
*Callophrys Rubi* butterfly, makes the gyroid an amazing geometry which deserves further joint efforts between the photonics, chemistry and biological research communities.

### 7.2 Future outlook

In this section we discuss the future outlook of this research proposing several possible research projects based on the results of this PhD thesis.

The 4-srs geometry we introduced in Chapter 3, was shown to possess stronger broadband circular dichroism than the single srs-network when realised in higher dielectric index materials such as silicon [115] or chalcogenide glass (see Sec. 3.8). In Sec. 4.6.5 we provided numerical simulations of a 4-srs CBS. When constructed from high index materials such as chalcogenide, the 4-srs CBS has with greatly improved extinction ratios over the polymer single srs-network we have demonstrated in Chapter 4. The fabrication of gyroid 4-srs in chalcogenide glass is currently under development by Ben Cumming with unit cell sizes of around 2 $\mu$m. Further reduction of the unit cell size would require the development of a super-resolution optical lithography method in chalcogenide glass. Alternatively, one may be able to produce a high-index 4-srs structure by applying a double inversion of the 4-srs polymer microstructure, with materials like silicon as demonstrated for the woodpile geometry [26].

Another possible method to achieving a high extinction ratio CBS is introduction of an impedance matching material or PC to reduce the refraction of light entering the prism. This would also serve to remove unwanted Fresnel reflections from the prism-air interface. Alternatively, a huge range of different prism configurations could be implemented, using the techniques applied to
the linearly polarising beamsplitter for inspiration. Further theoretical studies
on the coupling of light at angled interfaces of the srs-network would greatly
enhance our understanding of this phenomenon and perhaps inspire further
design improvements.

We have shown the ESD of polymer gyroid networks can be used to coat the srs-
networks with silver. However, advancements in the ESD method is required
to improve the homogeneity and selectivity of the silver coating. Alternatively,
one could try the removal of the silver coated microstructure from the substrate
as was demonstrated in [88]. However, sufficient mechanical supports should
be developed to reduce any mechanical distortion of the structure during this
process.

There are many other metallisation methods such as electro-deposition that
can be used to realise other metallic gyroids geometries. One such geometry
is the inverse srs-network where the air voids of the polymer srs-network are
filled with metal. As demonstrated via numerical simulations in Sec. 5.6,
this leads to a similar performance to that of the metallic srs-network. Even
more interesting would be the development of novel 3D surfaces formed at
the boundary between multiple gyroid networks, such as the achiral gyroid
surface discussed in Sec. 5.6. At these infrared wavelengths most metals act
as perfect electric conductors, hence a variety of metals could be used for
electro-deposition.

We have seen from numerical simulations in Chapter 3 and Chapter 5
that polarisation conversion arises due to the termination of the boundary,
inducing small amounts of linear birefringence. Further study into other
forms of boundary termination that do not induce these effects would be of
great importance, particularly when designing high extinction ratio circular
polarisation filters or converters.
One way to reduce this linear birefringence is to design chiral microstructures with 4-fold rotational symmetry. The 8-srs network is one such network and as the name implies consists of 8 identical srs-networks that intertwine with each other\footnote{The 8-srs can be constructed from two identical 4-srs composites that are translated by $[1/4,1/4,1/4]$ of a unit cell relative to each other.} as shown in Fig. 7.1. As for the 4-srs geometry, the 8-srs is chiral. However, unlike the 4-srs, 2-srs and single srs-network designs, the 8-srs contains 4-fold symmetry.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig7_1.png}
\caption{Illustration of a metallic 8-srs composite consisting of eight LHD srs-networks that intertwine to form a chiral composite with 4-fold rotational symmetry.}
\end{figure}

We have performed numerical transmission calculations of a 8-srs made from a perfect electric conductor (PEC) with unit cell size 1.5 $\mu$m (i.e. each srs-network has a unit cell size of 3 $\mu$m). The total PEC filling fraction is $\text{ff} = 32\%$ and the number of unit cells thick is $N_z = 2$. The transmission and optical rotation spectra for this metallic microstructure are given in Fig. 7.2.
To our complete surprise, the transmission spectra for LCP and RCP are identical to within 0.0001% (hence the transmission spectra contains only a single blue curve). This lack of circular dichroism at all frequencies is an amazing phenomenon considering the chirality of the 8-srs geometry. We believe that this lack of circular dichroism is related to the 4-fold rotational symmetry of the 8-srs (i.e. it is too symmetric to possess circular dichroism) and is now the subject of further research efforts.

Interestingly, even though the circular dichroism is zero for this structure, the optical rotation spectra\(^2\) of the 8-srs is very large as shown in red in Fig. 7.2. This lack of circular dichroism yet strong optical activity makes the PEC 8-srs a highly broadband polarisation rotator. This is significantly different to other chiral metamaterials [119–122] which have demonstrated huge optical activity and simultaneously huge circular dichroism except at a single wavelength where the circular dichroism is zero (wavelengths where the transmission spectra for

\(^2\)The optical rotation is defined as the phase of the LCP transmitted wave relative to the RCP wave, measured in degrees.
LCP and RCP light cross-over).

In fact it has been theoretically shown that the circular dichroism and optical activity of a homogeneous material are related via the Kramers-Kronig relation [196]. Therefore the 8-srs is another gyroid-based geometry which also warrants further theoretical and experimental investigation.
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Appendix A: Retarded plasmon hybridisation

In the previous section we saw that metallic gyroid structures constructed from polymer srs-networks coated with a thin layer of silver was a practical and interesting design for development of chiral MMs. If the layer of metal coated is much thicker than the skin depth of light at the wavelength of operation, then the microstructure is optically equivalent to a structure made of solid metal rods. However, for thin coatings of metal the optical properties can be very different. This was experimentally demonstrated when the polymer woodpile PC was coated with a thin coating of silver, and plasmonic modes were shown to exist at near-infrared wavelengths[193].

In order to understand how localised resonant plasmon modes arise in silver coated nanostructures, we have developed an analytical model based on plasmon hybridization theory (PHT) [61]. PHT is an analytical model developed for understanding plasmonic interactions that has been reviewed in Chapter 1. This theory is based upon the electrostatic limit, suitable for small nanoparticles around 10 nm in size, but for our silver coated srs-networks that have metallic rods 100 nm to 500 nm in size, the electrostatic limit is certainly not valid.

Here we briefly discuss our extension of the plasmon hybridization theory
which incorporates the retardation of the Coulomb interaction and investigate the effects of plasmon retardation within metallic structures. An in depth derivation and analysis of this work has been published in Ref. [67].

A1. Retarded plasmon hybridisation theory

Like the standard PHT (derived in the electrostatic limit), the RPHT assumes that a metallic nanostructure (MN) consists of a uniform stationary positive background and a fluid of conduction electrons whose motion gives rise to plasmon oscillations [61]. The fluid is assumed to be of uniform density $n_o$, incompressible, irrotational and no damping is present. These assumptions lead to relations for the MN plasmon frequencies in terms of the bulk metal Drude frequency $\omega_B^2 = 4\pi e^2 n_o/m_e$, where $e$ and $m_e$ is the charge and mass of an electron, respectively [61].

Solutions to the fluid flow potential, $\eta(r)$ can be solved via Laplace’s equation $\nabla^2 \eta = 0$. Calculating the kinetic energy and electrical potential energy of this dynamic system leads to the plasmon eigenmodes of the MN and their corresponding modal frequencies. The kinetic energy (T) of the plasmon fluid is given by

$$T = \frac{n_o m_e}{2} \int \eta \nabla \eta \cdot \hat{n} dS.$$  \hspace{1cm} (7.1)

where $S$ is the surface of the MN with normal unit vector $\hat{n}$. This term in the Lagrangian is not affected by retardation effects. The potential energy $V$ of the system is given by

$$V = \frac{1}{2} \int \sigma(r,t) \Phi(r,t) dS,$$  \hspace{1cm} (7.2)
where \( \Phi(\mathbf{r}, t) \) is the retarded Coulomb potential and \( \sigma(\mathbf{r}, t) \) is the surface charge distribution of the plasmon which are given by

\[
\sigma(\mathbf{r}, t) = n_oe \int \nabla \eta_{\text{surface}} \cdot \hat{n} dt, \tag{7.3}
\]

and

\[
\Phi(\mathbf{r}, t) = \int \frac{\sigma(\mathbf{r}', t - |\mathbf{r} - \mathbf{r}'|/c)}{|\mathbf{r} - \mathbf{r}'|} dS'. \tag{7.4}
\]

where \( c \) is the speed of light in free space. The retarded Coulomb potential given by (7.4) is the integral of the retarded charge distribution over the surface \( S' \) of the MN. By using this definition of the Coulomb potential we consider retardation effects on plasmons within MNs. The addition of the temporal delay \( t_d = |\mathbf{r} - \mathbf{r}'|/c \), causes a spatial-temporal coupling that is ignored in the standard PHT. However, if we assume that the solutions to the Lagrangian for the retarded system has the same form as that in the electrostatic case, i.e. a harmonic oscillator of frequency \( \omega \), then the spatial and temporal terms can be separated as

\[
\sigma(\mathbf{r}, t - |\mathbf{r} - \mathbf{r}'|/c) = \sigma(\mathbf{r}, t) \cos\left(\frac{\omega}{c} |\mathbf{r} - \mathbf{r}'|\right). \tag{7.5}
\]

In the electrostatic limit \( \omega |\mathbf{r} - \mathbf{r}'|/c = 2\pi d/\lambda \ll 1 \) and thus \( \sigma(\mathbf{r}, t - |\mathbf{r} - \mathbf{r}'|/c) \approx \sigma(\mathbf{r}, t) \). However, when the size of the particle becomes significant retardation will no longer be negligible. The effect of this term on (7.2) is to decrease the Coulomb potential energy and as we shall see later cause a red-shift to plasmon resonances. The Coulomb potential energy of the system then becomes

\[
V = \frac{1}{2} \int \sigma(\mathbf{r}, t) \int \frac{\sigma(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \cos\left(\frac{\omega}{c} |\mathbf{r} - \mathbf{r}'|\right) dS' dS. \tag{7.6}
\]

We shall now use this retarded PHT to investigate plasmon modes within MNs.
Appendix A: Retarded plasmon hybridisation

for a metallic nanosphere and a metallic nanotube.

A2. Retarded metallic nanosphere

In this section we shall derive an expression for the plasmon frequencies of a metallic nanosphere with radius \( \alpha \), suspended in air using the RPHT. Spherical solutions of Laplace’s equations are given by the set of orthonormal spherical harmonics:

\[
\eta(r, \theta, \phi, t) = \sum_{l,m} a_{l,m}(t) r^l Y_{l,m}(\theta, \phi),
\]

where \( Y_{l,m} \) is the normalized real spherical harmonic function and \( a_{l,m}(t) \) is the time-oscillating amplitude of the \( l, m \) mode. Using this spherical basis set with (7.1), (7.6), (7.3) and the spherical Green’s function expansion given by [197] leads to the retarded plasmon frequency \( \omega_{sphere}^{l,m} \) given by

\[
\omega_{sphere}^{l,m} = \omega_B \sqrt{\frac{l}{2l+1}} R_{l,m},
\]

where

\[
R_{l,m}^2 = \sum_{i,j} N_{lmij}.
\]

and

\[
N_{lmij} = \int \int Y_{l,m}(\theta, \phi) Y_{i,j}(\theta', \phi') \times \cos(\frac{\omega}{c} |r - r'|) Y_{l,m}(\theta', \phi') Y_{i,j}(\theta', \phi') d\Omega d\Omega'.
\]

Thus, for the simple case of a metallic nanosphere the retarded plasmon frequency given by (7.8) is just the electrostatic frequency [61] scaled by a
retardation factor $R_{l,m}$ that depends on the overall size of the nanosphere.

We now use RPHT to calculate the retarded plasmon frequency of silver nanospheres in air and dielectric backgrounds (see Ref. [67] for more details). In the case of a metallic nanosphere in a dielectric background of permittivity $\epsilon_D$ the retarded plasmon frequency becomes red-shifted due to a layer of bound charge induced at the metal-dielectric interface. Thus the retarded plasmon frequency of a metallic nanosphere in dielectric background is given as

$$\omega_{\text{sphere}}^{l,m} = \sqrt{\frac{2l + 1}{l + \epsilon_D(l + 1)}} \omega_B \sqrt{\frac{l}{2l + 1}} R_{l,m}. \quad (7.10)$$

We assume Drude dielectric for silver with a bulk plasma frequency of $\omega_B = 1.37 \times 10^{16}\text{rad.s}^{-1}$ and a collision frequency of $\omega_c = 2.73 \times 10^{13}\text{rad.s}^{-1}$ and use published Mie scattering codes [198]. This simple spherical geometry has been chosen to clearly illustrate the effects of retardation on localized plasmons and validate the RPHT methodology introduced here. However, it is important to note that at ultraviolet and visible wavelengths the use of the Drude model is inaccurate.

Figure 7.3 contains a plot of the fundamental ($l = 1, m = 0$) plasmon wavelength of a silver nanosphere for varying diameter using Mie theory (solid), RPHT (dashed) and electrostatic PHT (dotted). The nanosphere is embedded in a dielectric with refractive indices $n = 1.0$ (blue), $n = 1.5$ (red) and $n = 2.0$ (green). We observe excellent agreement between Mie theory and RPHT over all diameters considered. For very small diameters we see that both Mie theory and RPHT converge to the electrostatic PHT, where retardation is negligible and $R_{l,m} = 1$. At larger diameters ($D$) where $D > \lambda/10$, retardation weakens the Coulomb interaction causing red-shifting of plasmon wavelengths away from the electrostatic limit.
Figure 7.3  Comparison of Mie theory (solid) with RPHT (dashed) and electrostatic PHT (dotted) for a silver nanosphere embedded in a dielectric background of refractive index $n = 1.0$ (blue), $n = 1.5$ (red) and $n = 2.0$ (green).

A3. Retarded metallic nanotube

Here we use RPHT to investigate retarded plasmons of a metallic nanotube with a dielectric core of permittivity $\epsilon_C$. This geometry is of interest to the work in this thesis where metallic srs-networks consist of polymer rods coated by a thin layer of silver. As these structures typically have rod sizes $D > \lambda/10$ retardation will be significant.

In [63] plasmon hybridization within hollow metallic nanotubes was investigated, however retardation effects were not considered. Here plasmons will be localized in two dimensions (2D), so the RPHT system reduces to 2D. There are two types of plasmons to consider: stationary plasmons with constant phase along the rod and propagating plasmons with oscillating phase with wave vector, $\mathbf{k}$ along the rod axis. Here we consider a dielectric rod of radius $\beta$, surrounded by a metallic nanotube of outer radius $\alpha$ as shown in Fig. 7.4.
Appendix A: Retarded plasmon hybridisation

By using a cylindrical basis set of modes we can derive the retarded plasmon modes (see Ref. [67] for details). The eigenmodes of the system can be solved by diagonalisation of the two-dimensional Lagrangian. This leads to a quadratic equation for the plasmon frequency, with two solutions corresponding to symmetric (low frequency) and anti-symmetric (high frequency) coupling between inner and outer surface plasmons. Here, we model the symmetric dipole \((n = 1)\) stationary retarded plasmon for a silver nanotube surrounding a rod of polymer with dielectric permittivity \(\epsilon = 2.43\). Figure 7.5 contains a plot of the plasmon wavelength with the varying rod diameter for different ratios of inner/outer radii, \(\beta/\alpha\). As \(\beta/\alpha \to 1\), the nanotube thickness decreases the hybridisation between inner and outer plasmons increases, causing a red-shift to the symmetric plasmon mode.
Figure 7.5 Plasmon hybridization and retardation within a silver nanotube with dielectric core of varying diameter. The ratios of inner/outer radii are $\beta/\alpha = 0.9$ (red), $\beta/\alpha = 0.93$ (black), $\beta/\alpha = 0.96$ (green) and $\beta/\alpha = 0.98$ (blue).

For larger rod diameters there is significant retardation that causes a further red-shifting to plasmon wavelengths. For the case of $\beta/\alpha = 0.9$ retardation causes a red-shifting of up to $\sim 20\%$ at a core diameter of 200 nm (a comparable size to the rods fabricated using DLW of the srs-networks). A comparison of the RPHT with numerical simulations (CST FIT) for the nanotube is discussed in Ref. [67] and demonstrates a good agreement for rod widths up to 150 nm.
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Journal publications


Book chapters


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