Controlling Light-Matter Interactions in the Linear and Nonlinear Optical regimes

Bryson Joseph Krause

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CONTROLLING LIGHT-MATTER INTERACTIONS IN THE LINEAR AND NONLINEAR OPTICAL REGIMES

by

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A Dissertation
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Abstract

The progression of materials science has led us down a path of rich discovery in the realm of nanophotonics. Recent strides in metamaterials and plasmonics research have allowed for an unprecedented control of light-matter interactions beyond the diffraction limit of visible light. Currently, there is a great push to improve the ability and flexibility of metamaterials and nanophotonic structures to manipulate and amplify electromagnetic waves. Researchers are seeking to find efficient, scalable and cost-effective methods to produce these materials with a broad range of tunability. In these efforts, the scope of optics research has naturally begun to shift from the linear to the nonlinear regime, due to the fact that nonlinear optical phenomena inherently offer unique ways for manipulating the intensity, phase, frequency and polarization of light. Nonlinear optical materials allow for many effects such as harmonic generation and four-wave mixing that are not possible in the linear regime. These phenomena lead to the development of all-optical switching and other mechanisms which will give rise to the next generation of advanced devices. By bolstering optical phenomena in nonlinear materials with the electromagnetic field localization offered by plasmonic metamaterials, we can achieve an even greater level of control with light-matter interactions.

The aim of this dissertation is to further develop our understanding of light-matter control in both the linear and nonlinear regimes through the investigation of such optical phenomena within several novel nanoscale structures and metamaterials. Primarily, I will focus on the characterization and investigation of various novel nanomaterials, the linear photonic decay and lasing emission enhancements offered by plasmonic nanohole arrays, the nonlinear strong coupling and second harmonic generation enhancement offered by plasmonic nanopatch antennas, and the nonlinear polarization-dependent emission of chiral metastructures.
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### List of Abbreviations

- **SPR** – Surface plasmon resonance
- **LSR** – Localized surface plasmon
- **SPP** – Surface plasmon polariton
- **LH** – Left-handed (circularly polarized)
- **RH** – Right-handed (circularly polarized)
- **CD** – Circular dichroism
- **OR** – Optical rotation
- **ODoS** – Optical density of states
- **PF** – Purcell factor
- **Q** – Quality factor
- **NPA** – Nanopatch antenna
- **EBL** – Electron beam lithography
- **SNL** – Shadowing nanosphere lithography
- **EUV** – Extreme ultraviolet light
- **FIB** – Focused ion beam
- **DLW** – Direct laser writing
- **NIL** – Nanoimprint lithography
- **GLAD** – Glancing angle deposition
- **SHG** – Second harmonic generation
- **OPO** – Optical parametric oscillation
- **SRS** – Stimulated Raman scattering
- **THG** – Third-harmonic generation
- **FWM** – Four-wave mixing
- **SERS** – Surface enhanced Raman scattering
- **TENG** – Triboelectric nanogeneration
- **PDMS** - Polydimethylsiloxane
- **OSC** – Organic solar cell
- **PCE** – Power conversion efficiency
- **FP** – Fabry-Perot
- **SHE** – Spin hall effect
- **MIM** – Metal-insulator-metal
- **HHG** – Higher harmonic generation
- **SPDC** – Spontaneous parametric down-conversion
- **PL** – Photoluminescence
- **CCD** – Charge-coupled device
- **TCSPC** – Time-correlated single photon counting
- **XRD** – X-ray diffraction
- **SEM** – Scanning electron microscopy
- **AFM** – Atomic force microscopy
- **ALD** – Atomic layer deposition
- **PE** - Polyelectrolyte
- **LBL** – Layer-by-layer
- **PSS** – Poly(4-styrenesulfonic acid) Sodium
- **PAH** – Polycyclic Aromatic Hydrocarbon
DI - Deionized
NS - Nanosphere
NW - Nanowire
NT - Nanotube
NN - Nanoneedle
NR - Nanorod
PLAL – Pulsed laser ablation in liquid
TTA – Triplet-triplet annihilation
PNA – Periodic nanohole array
PEEL – Photolithography, e-beam deposition, etching and lift-off
RIE – Reactive ion etching
PS – Polystyrene
FWHM – Full width at half maximum
DCM – 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran
QD – Quantum dot
PPM – Perfect phase-matching
EM - Electromagnetic
DMSO - Dimethylsulfoxide
DOP – Degree of polarization
ADH – All-dielectric helical
PH – Plasmonic helical
1. Introduction

The technology that modern society subsists on is not efficient enough to meet the demands of an ever-expanding civilization. For instance, though the need for computing power continues to rise, the transmission speed of most modern devices is limited by the carrier mobility of an electron travelling through some material such as silicon.\(^1\) Although optical fibers are commonly employed for the transport of data between devices, the conversion between light and electricity expends power and slows down processes significantly.\(^2\) One of the solutions to this problem may be optical switching – a photonic analogue to the electrical transistor in which a signal can be toggled solely by another optical signal without the need for electronic intervention. Until now, however, there have been few breakthroughs which make this technology feasible and easily producible on a large scale.\(^2,3\) This impasse is but one example of the need for discovery in the field of photonics. Much research continues to be done to design novel tools and materials that allow for phenomena such as all-optical computation, but these tools depend on the control of light in both the linear and nonlinear regimes, which in turn requires more research on feasible materials and systems. Nonlinear light-matter interaction especially requires much attention in order to yield devices which offer high sensitivity and background-free signal processing.

The discipline of nonlinear optics, a term which describes nonlinear responses of a medium to an incident electric field, is still in its formative years, having been brought about by the experimental observation of second harmonic generation in 1961 and theoretically established by the late 1960s.\(^4,5\) Rapid advancement in the 1960s and into the 1970s introduced many nonlinear processes to the world of science such as optical parametric oscillation and ultrashort laser pulses, which in turn led to a multitude of applications in telecommunications,
sensing and spectroscopy. However, these discoveries remained confined to the realm of academia until further developments in nonlinear optics in the late 1980s and early 1990s made fiber optical communication feasible. At the end of the 1990s, the discovery of metamaterials allowed for the manipulation of electromagnetic properties based on changes in structure rather than intrinsic material properties. Carrying on with the emergence of plasmonic materials research in the early 2000s, the study of nonlinear materials benefited from the photonic enhancements offered by the strong local field confinement that plasmonic metamaterials enable.

At its onset, research on plasmonic metamaterials was focused primarily on utilizing the negative refractive index that they offer for novel optical applications such as cloaking devices. More recently, however, metamaterials have been investigated for their use in more practical applications as researchers expand on the optical properties that can be achieved by fine-tuning fabrication techniques for engineering subwavelength structures. The current state of research into light-matter interactions is defined by a strong push to explore novel photonic materials and an effort to hone these constructions for their efficient, powerful and widely producible use in various advanced applications. Given the need for innovative technologies and ideas in nanofabrication, material design, and optical manipulation techniques, it is more important now than ever that we find new ways to master light-matter interactions at the nanoscale in both the linear and nonlinear optical regimes. The aim of this dissertation is to provide specific advances in the enhancement and manipulation of light in linear and nonlinear photonic materials with emphasis on exploring the linear photonic decay and lasing emission enhancements provided by plasmonic nanohole arrays, investigating the nonlinear strong coupling and second harmonic generation enhancement facilitated by plasmonic nanopatch antennas, examining the nonlinear
polarization-dependent emission of chiral metastructures, and the characterization of Selenium nanoneedles generated through laser ablation.

1.1 Introduction to optical metamaterials

Metamaterials are manmade materials produced by engineering processes to obtain exotic properties that do not exist in naturally created materials. Though various types of metamaterials exist (optical, acoustic, electrical, thermal, structural, etc.), the primary focus of this work is optical metamaterials, which interact with light in unusual ways. Optical metamaterials are comprised of sub-wavelength structures and components designed to interact with electromagnetic waves at specific frequencies, arranged in an ordered or disordered fashion. Various classifications of optical metamaterials (referred to henceforth as metamaterials for simplicity) exist, including electromagnetic, photonic, chiral, nonlinear and tunable metamaterials.\textsuperscript{13–15} A metamaterial exhibits optical behavior that is distinct from that of the bulk material. Through the tailoring of the periodicity and shape of nanostructures, a metamaterial can be engineered to manipulate electromagnetic waves, either allowing or disallowing their propagation. This characteristic allows for optical phenomena such as superlensing, negative refraction and perfect absorption. In the realm of photonics, the term metamaterial typically indicates a 3-dimensional material whereas the term metasurface denotes a 2-dimensional surface or plane that demonstrates the properties of a metamaterial, operating at the interface between two media.

Although metamaterials only became an experimental reality in the 1990s, their theoretical existence and theoretical formulation came in 1968 when the Soviet scientist Victor Veselago postulated that a material could have both a negative dielectric constant and a negative permittivity
without violating the equation for the dispersion of an electromagnetic wave in matter. That is, the dispersion equation,

\[
\left[ \frac{\omega^2}{c^2} \varepsilon_{ij} \mu_{ij} - k^2 \delta_{ij} + k_i k_j \right] = 0
\]

Gives a relation between the wave vector, \( k \), of a monochromatic electromagnetic wave and its frequency. Here, \( \varepsilon_{ij} \) is a given material’s dielectric constant tensor, and \( \mu_{ij} \) is the magnetic permeability tensor. In the case of a simple isotropic material, eq. 2 can be simplified,

\[
k^2 = \frac{\omega^2}{c^2} n^2
\]

where \( n^2 \) is the material’s index of refraction which can be written as

\[
n^2 = \varepsilon \mu.
\]

Thus, it follows that while \( n^2 \) must return a positive value, the values of \( \varepsilon \) and \( \mu \) are allowed to both be negative. This curious characteristic yields a negative refractive index, and materials exhibiting this unique property are now known as metamaterials.

Building upon Veselago’s previous work, Sir John Pendry detailed in 1999 the theoretical formulation of how materials exhibiting a negative refraction and, more importantly, how such a phenomenon could be used in practical applications. For instance, Pendry showed that a perfect, super-resolution lens unimpeded by the diffraction limit could be engineered with the use of some isotropic material having \( \varepsilon = \mu = -1 \). The following year, the experimental realization of metamaterials was achieved when David Smith and his group at Duke University explored a constructed split-ring resonator bilayer which maintains indefinite \( \varepsilon \) and \( \mu \) tensors and nonlinear, hyperbolic dispersion relations. From that point, metamaterial research began to enter into the collective consciousness of photonics researchers everywhere, and the field of metamaterials is as
prolific as it ever has been, constantly producing a high volume of interesting physics. Metamaterials today exist in a diverse range of constructions, each having rich optical properties with various strengths and weaknesses. Examples of typical photonic metamaterial constructions include split-ring resonators, fishnet metamaterials, nanohole or nanowire arrays, photonic crystals, hyperbolic metamaterials, nanopatch antennas and topological metamaterials such as chirals, to name only a few.

1.1.1 Introduction to plasmonic metamaterials

Plasmonic phenomena have been utilized in practice for more than a millennium, with the common occurrence of silver and gold nanoparticles used for the coloration of glass in historic works of art and architecture. One such example is the Lycurgus cup made in 4th century Rome, which appears green when illuminated from the outside and red when illuminated from the inside. This plasmonic phenomenon is due to differing local surface plasmon resonances achieved in a dispersion of gold and silver nanoparticles within the glass.

While the discipline of plasmonics is a more recent development in nanophotonics, studies on plasmonic media can be traced back to Michael Faraday’s pioneering experimentation on colloidal gold solutions in 1857. Though it was not known at the time, plasmons are responsible for the optical properties that Faraday observed. Early theoretical framework came at the beginning of the 20th century with works such as Maxwell-Garnett’s theoretical explanation of the color of glasses containing small metallic particles and Gustav Mie’s analytical treatment of the interaction of light with spherical particles. Exactly one century after Faraday’s optical characterizations of colloidal gold solution, Rufus Ritchie theoretically predicted the existence of surface plasmons and a relationship between energy loss and medium thickness in thin foils. Technical applications of surface plasmons gained traction in the 1990s
after the emergence of surface plasmon resonance (SPR) sensors in 1982, which allow for real-time, label-free detection of biomolecular interactions. Throughout the early 2000s and up until the present time, the applications and fabrication techniques of plasmonic devices have evolved rapidly with the field of plasmonics branching out further into subdivisions of nanophotonics.

The realm of plasmonics deals with the interaction of electromagnetic waves and free charge carriers in metallic nanostructures. A plasmonic material is a metamaterial having an ordered or disordered distribution of such metallic nanostructures with an electromagnetically coupled conductor-dielectric interface at which it supports the collective oscillation of free electrons called surface plasmon, creating a SPR. The principle behind SPRs is the movement of free electrons in metallic nanostructures, which can be considered through discussion of polarizability. For instance, the Lorentz-Mie scattering theory can be used to derive the optical properties of a spherical particle. The polarizability of a gold nanosphere in the quasi-static limit is given as

$$\alpha = 4\pi\varepsilon_0 r^3 \frac{\varepsilon_m(\omega) - \varepsilon_h}{\varepsilon_m(\omega) + 2\varepsilon_h},$$

where $\varepsilon_0$ is the vacuum permittivity, $r$ is the radius of the particle, $\varepsilon_m(\omega)$ is the frequency-dependent complex dielectric constant of the metal, and $\varepsilon_h$ is the dielectric constant of the substrate or host material. Taking the real part of the metal’s dielectric constant to be negative, resonance can be determined using the Frolich condition, $\text{Re}[\varepsilon_m(\omega)] = -2\varepsilon_h$. By exciting this plasmonic resonance with a resonant excitation source, absorption and scattering can be greatly enhanced, leading to further interesting optical phenomena. Furthermore, by incorporating multiple plasmonic structures in close proximity to one another, their surface plasmons couple as
the free electrons on the surface of each member oscillates collectively, leading to optical properties in which the sum contribution is greater than that of its parts (meta-properties).

Plasmons allow for the extreme localization and enhancement of electromagnetic fields and can be either confined to the geometry of the system as localized surface plasmons (LSP) or allowed to propagate along the conductor-dielectric interface as surface plasmon polaritons (SPP). The density, size, shape and composition of nanostructures within a plasmonic metamaterial determine the material’s macroscopic photonic properties, which can be finely tuned to exhibit interesting effects and enhanced nonlinear optical phenomena.

For 2D metasurfaces, the collaborative diffractive modes and the resonance achieved through matched lattice spacing play a vital role in the dispersion and behavior of light. The excitation of SPPs which propagate along metal-dielectric interfaces can be instigated by either electrons or photons of a compatible frequency. For electron scattered SPPs, energy propagates through the bulk of a metal and the scattering vector parallel to the metal’s surface creates an SPP. For photonic excitation of SPPs, the electric field of impinging photons interacts with the natural frequency of the metasurface’s surface plasmons, resulting in the efficient energy transfer from light to the surface plasmons via resonance. Coupled modes of light and electron oscillations at the interface between a metal and a dielectric material naturally have a momentum mismatch between light and the SPP. This is due to the fact that the momentum of a photon is entirely wavelength-dependent, whereas SPPs gain their momentum properties from the metal and dielectric across which they exist. However, momentum conservation dictates that the total momentum before and after the photon arrives at the metal-dielectric interface should be consistent for the efficient excitation of SPPs. In order to overcome this mismatch and create efficient plasmon polariton propagation, plasmonic materials must be designed to support SPP
excitation through the engineering of specific structures. Herein lies the present challenge of plasmonic metamaterials for light-matter control in the linear and nonlinear regime: designing efficient plasmonic devices for their use in emerging advanced technologies. Throughout this dissertation, several plasmonic metamaterial constructions will be discussed and investigated for their efficient generation of photonic phenomena.

1.1.2 Introduction chirality and chiral metamaterials

Chirality refers to an object whose mirror image is non-superimposable upon itself; these two mirror images are called enantiomers. Chirality as a study has existed since the mid-19th century, when Louis Pasteur noticed the double-ammonium salt crystals of tartaric acid used in wine fermentation oriented themselves differently to the right or left due to a tiny facet on one of their edges (Figure 1). Upon separating the left and right-hemihedral crystals, Pasteur observed their solutions using Biot’s polarimeter, revealing a left or right-hand change in the plane of polarization depending on their chiral orientation. Building upon the works of Arago,
Herschel, Fresnel and Biot, Pasteur made this discovery in 1848, only 8 months after defending his PhD theses, suggesting that the passing of his defense granted by his gracious dissertation committee led directly to this monumental discovery, which could also the case for other candidates.\textsuperscript{32–35}

Pasteur's work laid the foundation for the understanding of chirality in chemistry and optics. He proposed that the optical activity of tartaric acid crystals was due to their asymmetric molecular arrangement, which is now understood as chirality. This discovery marked the beginning of the systematic exploration of the relationship between molecular asymmetry and optical effects. Subsequent research by other scientists like Pasteur’s fellow French physicists Jean-Baptiste Biot and Augustin Fresnel further contributed to the understanding of optical activity and its connection to molecular structure.\textsuperscript{36} Augustin Fresnel introduced the concept of circularly polarized light and explained how it interacts differently with chiral substances compared to achiral ones, while Jean-Baptiste Biot collaborated with Pasteur and mentored him in his early studies of chiral substances.\textsuperscript{37}

Over time, the study of chirality in optics expanded to include other fields like crystallography, spectroscopy, and the interaction of chiral molecules with light at various wavelengths. Currently, chirality in optics is a fundamental concept in fields such as chemistry, physics, materials science, and optics itself, with applications in areas such as pharmaceuticals, materials engineering, and even the design of optical devices. In the scope of plasmonics, chirality is finding traction as a tool to gain directional control of light’s polarization, a critical property which can be utilized for many emerging sensing technologies, as well as applications in directional spin-dependent waveguides and circularly polarized photon generation.\textsuperscript{38–41} The distinctive application of chiroptical materials stems from the unique way in which these
structures can alter light through their attributes of optical activity. Chiral molecules, for instance, can have the same set of physical properties such as melting point or polarity, but when illuminated, these molecules will manipulate left-hand (LH) and right-hand (RH) circularly polarized light toward opposing directions. This attribute, referred to as circular dichroism (CD), lends to many practical applications of chiral metasurfaces, the most obvious of which is the use of these platforms as powerful sensors for chiral molecular systems. Circular birefringence or optical rotation (OR) is another manifestation of optical activity in chiral structures; much like CD alters circular polarization, OR is the altering of the incoming linear polarization plane depending on the orientation of the chiral sample. CD and OR are caused by the difference in the absorption of two opposite circularly polarized lights and the difference in the propagation velocity of light within chiral media, respectively.

The precise manipulation of light-matter interactions within metamaterials can assist in attaining and enhancing polarization-dependent chiroptical reactions within optically active chiral nanostructures and metasurfaces comprised of plasmonic helical members. While the manipulation of circularly polarized light has had much attention in the past few decades, the behavior of polarized light in chiral structures is only now gaining attraction in the nonlinear regime. This regime opens up a new range of possibilities for study, including the exploration of the nonlinear dynamics of circularly polarized light transmission in chiral metasurfaces relative to the linear behavior and the examination of the enhanced second harmonic CD treatment of circularly polarized light. In this study, metasurfaces comprised of all-dielectric and metal-dielectric helical nanostructures, as well as “L-shaped” enantiomeric nanostructures, are investigated for their linear and nonlinear light manipulation capabilities.
1.1.3 Plasmon-enhanced optical properties of novel nanomaterials

In addition to the spatially coherent control of electromagnetic waves, plasmonic effects supported in novel nanostructures also allow for temporal maneuverability. The spontaneous emission rate of a quantum emitter, for instance, can be increased based on its interaction with a resonant cavity. First observed by Edward M. Purcell in 1946 and now called Purcell Effect, this phenomenon occurs when the environment surrounding an emitter experiences a change in the optical density of states (ODoS), a property indicating the available electromagnetic states for a given frequency and energy range.\(^{42}\) Plasmonic metamaterials inherently offer a high ODoS through the generation of localized surface plasmon resonances (LSPR). The degree to which the spontaneous emission rate is enhanced is called the Purcell Factor (\(P_f\)) and can be described as

\[ F_p = \frac{3}{4\pi^2} \left( \frac{\lambda_{\text{free}}}{n} \right)^3 \frac{Q}{V}, \]

where \(\lambda_{\text{free}}\) is the vacuum wavelength, \(n\) is the refractive index of the cavity medium, \(Q\) is the cavity quality factor (given as the ratio of the resonant frequency and the resonant width of the cavity) and \(V\) is the mode volume of the cavity. Since \(F_p\) is inversely proportional to the mode volume within a cavity, a smaller \(V\) value yields enhanced spontaneous emission. For plasmonic metamaterials with a high ODoS, the mode volume is effectively reduced as the probability of interaction between a quantum emitter and the available cavity modes is increased. Thus, the \(F_p\) (and spontaneous emission rate) is increased. Additionally, the \(F_p\) can be further enhanced in nanostructures through either the strengthening of the plasmon resonance (increased \(\lambda_{\text{free}}\)) or by increasing the quality factor (\(Q\)) of the cavity. Through the design of novel plasmonic nanomaterials having such temporal enhancements, the efficiency of emerging advanced devices
can be greatly improved as will be further discussed and demonstrated in the plasmonic structures investigated in Chapter 4.

In addition allowing $F_p$ enhancement, the small mode volumes and strong resonant frequencies found in plasmonic metamaterials creates favorable conditions for SPR and the strong confinement of electromagnetic fields. As will be discussed in further detail in section 1.3, intense electromagnetic field confinement and enhancement at the nanoscale is necessary for the efficient generation of nonlinear optical phenomena in plasmonic devices.

1.2 Fabrication of plasmonic metamaterials

There are several archetypical structures used in metamaterial design, each having its own benefits and limitations. Metamaterials typically involve either a random assortment or repeating pattern of nanoscale structures. The original metamaterial proposed by Pendry allowed for a non-magnetic material such as copper to imitate a magnetic one by embedding nanoscopic loops of copper in fiberglass. In theory, this would create a collective magnetic-like flow of electrons within the material. Many nuanced versions of this came after, including the split-ring resonator which involves making a cut in these small loops in order to create a switch with which the magnetic properties of the material can be changed. As the manipulation of electromagnetic properties through metastructure design and the field of metamaterials had been firmly established, many novel designs emerged. Fabrication techniques are still being developed and improved upon with the collective goal of creating low-cost, robust and efficient plasmonic metamaterials. In this section, several fabrication methods of plasmonic metamaterials are discussed briefly.
1.2.1 Bottom-up fabrication

Stemming from technological advancements in the synthesis of plasmonic nanoparticles like rods, cubes or spheres over the past few decades, several bottom-up self-assembly techniques for the fabrication of plasmonic metamaterials have been in continuous development. The formation of these structures is dependent on self-assembly due to forces stemming from mutual interactions between nanostructures and active materials including Van-der-Waals, electrostatic, molecular binding and capillary forces.

One of the simplest forms of metamaterial consists of a surface distribution of such metallic scattering structures. Such self-assembled distributions can be easily realized through the slow evaporation of solution containing suspended nanoparticles onto a substrate. The resultant surface can support plasmonic resonances with optical properties that depend on the distance between particles. There are several slightly more complicated variations of the basic bottom-up approach to plasmonic metamaterial fabrication. Nanosphere lithography, for instance, uses nanospheres suspended in solution which is slowly drained in order for the spheres to form a hexagonal close-packed monolayer on a substrate surface. If this method is carried out using nanospheres made of soft matter such as polystyrene, plasmonic material such as gold or silver can be deposited on top and the nanospheres can be stripped away to form an array of nanoholes. This tactic is discussed further in Chapter 4. Another robust construction, the nanopatch antenna (NPA) design, employs a sub-10nm dielectric spacer gap prior to the distribution of plasmonic nanoparticles on a metallic mirror film. In this way, the plasmonic surface can be designed to have a desired nanogap-mode for the enhancement of photonic phenomena as demonstrated in Chapter 5.
1.2.2 Top-down fabrication

With the improvement of nano-scale lithography and fabrication techniques such as electron beam lithography (EBL), shadow nanosphere lithography (SNL) and extreme ultraviolet lithography (EUV), the design of metasurfaces by etching intricate structures at the nanometer scale became possible. For instance, with these contemporary lithography techniques, a metasurface could be created with ordered distributions of open cavities in a layer of metal leading to the emergence of the nanohole or “fishnet” metamaterial design.\(^{45,46}\) Nanohole arrays have since been used in many applications such as on-chip lasing and biosensing.\(^{47}\) Top-down fabrication methods are capable of producing intricate plasmonic metamaterials with high precision, however, these techniques are not feasible for large-scale production as they are generally costly, time consuming and require cumbersome equipment. Several common top-down fabrication techniques for plasmonic metamaterials are briefly described in the sections below.

1.3.2.1 Electron beam lithography

Electron beam lithography (EBL) is one of the more commonly used techniques for the fabrication of metasurfaces comprised of a patterned array of nanostructures. Rather than involving the transfer of particular patterns onto a substrate through photosensitive materials and light exposure as in the case of traditional photolithography, EBL allows for fabrication on the nanometer scale by using of a beam of high energy electrons to etch patterns into a resist which provides a high spatial resolution on the scale of 10 nm.\(^{48}\) In a typical setup, a highly focused electron beam having a resolution on the nm scale is focused onto a resist-coated substrate in order to write some programmed pattern. Once the resist is chemically etched away to form an array of nanoscale structures, a thin layer of plasmonic metallic film is deposited onto the
substrate and patterned resist layer. After deposition, a lift-off procedure follows, leaving behind a plasmonic metamaterial. This procedure, depicted in Figure 2, produces a 2D metasurface, though it can be adapted to create 3D metamaterials with the multistep addition of materials.49

While EBL precisely generates robust and intricate metamaterials with high spatial resolution, there are several downsides to this technology. The detailed scanning of an electron beam required for this technique is time consuming and costly, which makes EBL not feasible for scalable metasurface fabrication.

1.3.2.2 Focused ion beam lithography

Focused ion beam (FIB) lithography employs focused ion beam sputtering to remove atoms from a material and shape nanostructures.50 This technique allows for one-step fabrication of metasurfaces, as the desired pattern is written directly into the target substrate. Depending on the ion beam used (typically gallium, helium or neon), a resolution as low as 5 nm can be achieved. While this technique is still time-consuming and not feasible for large-scale production, its simplicity makes it an ideal tactic for prototyping plasmonic metamaterial designs.

![Figure 2. Illustration of EBL technique](image)
1.3.2.3 Direct laser writing

Similar to FIB lithography, direct laser writing (DLW) is a one-tool approach to creating patterned nanostructures. DLW uses a focused laser beam to modify the local properties of a photosensitive material such as a photoresist or polymer. With this technique, the polymerization of a photoresist can be manipulated and sculpted at the nanoscale through two-photon absorption to create intricate structures and patterns. This technique can also be used to create topological structures such as chiral metasurfaces.

1.2.3 Nanoimprint lithography

Nanoimprint lithography (NIL) is a reliable nanofabrication technique capable of producing large areas of nanopatterned structures with low cost and high efficiency. Essentially, NIL mechanically transfers nanostructures with a stamp, rather than using light or electrons to manipulate a resist. With this technique, an imprint material is mechanically pressed and deformed by a stamp having a desired pattern, and the pattern is thus transferred to the target material. After the material (typically a polymer or monomer) hardens, the stamp is removed, leaving behind a mold which can be utilized for the fabrication of nanostructured materials via standard deposition and lift-off procedures. The versatility and resolution that this technique offers is limited only by the resolution of the stamp structure, which is commonly created via EBL. Additionally, if the mold is hard enough, NIL can be applied directly to plasmonic substrates without the use of resist. The main limitation of this method is that the molds can be easily damaged, and defects can arise between pressings, making NIL so far unfeasible for large-scale production.
1.2.4 Glancing angle deposition

Glancing angle deposition (GLAD) is a specialized thin-film deposition technique in which controlled nanostructured architectures can be created. A key feature of GLAD is that the deposited material forms columned nanostructures which are tilted away from the substrate surface. These structures can be tailored to exhibit a range of unique properties and optical phenomena due to their three-dimensional and anisotropic nature. GLAD is typically used for creating thin-films with specific engineered optical, electrical, magnetic and mechanical properties.

The GLAD fabrication process begins with a deposition mechanism such as a sputtering or evaporative source, which is positioned at a glancing angle relative to the target substrate surface. The angle of deposition, which can be controlled precisely to influence the growth of the material, is responsible for the topology of the formed nanocolumns. As material is

![Flow of incident particles](image)

*Figure 3. Illustration of GLAD fabrication. [66]*
deposited at a glancing angle, it arrives at the substrate preferentially along specific directions, leading to the growth of nanoscopic columns tilted away from the normal surface of the substrate. By adjusting various parameters such as the angle of incidence, deposition rate and rotation of the substrate, the dimensions, spacing and morphology of the resulting nanostructures can be controlled to create closely packed columns, helical nanostructures or other complex configurations of nanostructures. The principle behind the GLAD fabrication process and the variable setup parameters are depicted in Figure 3. In this work, GLAD is used by Ufuk et al. in the fabrication of the chiroptical helical and “L-shaped” all-dielectric and metal-dielectric metasurfaces investigated for nonlinear polarization-dependent transmission as detailed in Chapter 6.

**1.3.5 Incorporation of fluorescent emitters in plasmonic materials**

A common technique for bolstering the optical attributes and enhancements offered by active materials is their integration with photonic structures. Many techniques for incorporating fluorescent emitters exist, though the simplest involves the deposition of particles dispersed in a liquid solution onto a metamaterial surface to achieve a controlled surface distribution which is typically done through spin-coating, drop-casting or inkjet printing. In this way, fluorescent molecules are allowed to situate themselves in the near field of metastructures, allowing for their influence on the optical response of the plasmonic material at the nanometer scale. Another simple approach to combining emitters with plasmonic metamaterials is to suspend them in polymers, which can be coated onto surfaces in thin films or in multiple layers.

Alternatively, the metal-surface functionalization technique can be utilized for the attaching of molecules or nanoparticles to a metal metastructured surface. This technique involves the use of molecules with specific functional groups that can be attached to a specific
metal surface. One example is the self-assembled monolayers of thiols (which contain a sulfur group) that occurs on gold surfaces. This technique requires consideration of the surface chemistry of the target metamaterial and the molecules to be used in the monolayer. Within this criterion, there are several nuanced tactics for achieving active material integration via metal-surface functionalization.

1.3 Introduction to nonlinear photonics

Nonlinear optics is the study of light-matter interactions in materials having higher-order susceptibilities. The ability to control optical processes in nonlinear materials is crucial for the progression of optical devices, and higher-order photonic effects hold great promise for the future of technology. While new linear-based applications are being discovered daily, there is a quickly decreasing pool of novelty in linear optics. Optics has been in many ways mastered in the linear regime, and a deeper exploration of nonlinear optical phenomena, a realm which holds a great amount of opportunity for breakthroughs in physics and the potential for technological revolution, is warranted.

Nonlinear optical phenomena have been experimentally observed since 1961 when second harmonic generation (SHG), the frequency doubling of light in nonlinear materials was observed by Franken et al. shortly after the emergence of the laser. The principle behind SHG in which two photons interact with a nonlinear material and produce one frequency-doubled photon is depicted in Figure 4. However, nonlinear optical mechanisms are so far widely unutilized in practical applications, which are limited mostly to frequency doubling, imaging tactics and communication. Focus areas of research include second, third and higher-order harmonic generation, nonlinear effects in quantum optics, optical switching and the Kerr effect, to name just a few. This realm of research is in a period of rapid progression, and new photonic structures
with fascinating properties are being explored daily. The pursuit of materials that display efficient nonlinear photonic effects will fuel innovation in the years to come. Furthermore, on-chip solutions are needed to fuel the applicability of nonlinear optics to modern advanced devices. The discovery of efficient optical switching, in particular, may hold the key to the success of photonic integrated circuits. Several studies have explored this concept, but the power required to initiate an optical switch is so far inefficient.\textsuperscript{56–59} In order for it to be a viable for use in communications and lead the way to all-optical computing, optical switching should be sustained with a much smaller input power than what has been demonstrated thus far. The optical switching effect can be amplified greatly with the careful selection of materials and the use of other nonlinear optical mechanisms to create extraordinary new applications.

Nonlinear optical phenomena exist as a consequence of the nonlinear polarization experienced by materials in response to light. This effect can be described in terms of the response generated by impinging light of field strength $E(t)$ by a power series expansion of the dielectric polarization density, $P(t)$, as,\textsuperscript{60}

\begin{equation}
P(t) = \epsilon_0(\chi^{(1)}E(t) + \chi^{(2)}E(t)^2 + \chi^{(3)}E(t)^3 + \ldots)
\end{equation}

Figure 4. Left: Illustration and energy level scheme of SHG. Right: Bulk crystal materials with a nonzero value crystal, such as KTP (utilized in green laser pointers) allow for SHG.
where $\varepsilon_0$ is the vacuum permittivity and $\chi^{(i)}$ represents a nonlinear material’s $i^{th}$-order susceptibility. Naturally, higher-order susceptibilities exhibit increasingly weak responses in nonlinear materials, with typical second order susceptibilities having magnitudes on the order of $10^{-12}(\chi^{(1)})$ and third-order susceptibilities on the order of $10^{-24}(\chi^{(1)})$. The second order susceptibility is responsible for nonlinear optical effects such as SHG, frequency mixing processes and optical parametric oscillation (OPO), while third order processes include the optical Kerr effect, optical switching and third harmonic generation to name a few. The weak nature of optical effects caused by nonlinear susceptibilities creates a challenge in efficiency, as high field intensities and large light-propagation lengths are required to induce higher-order optical effects in crystals such as the frequency conversion of light in bulk Potassium Titanyl Phosphate, depicted in Figure 4.

With the invention of highly intense pulse lasers, the 1960’s saw the emergence and rapid progress of the field of nonlinear optics with Franken’s initial discovery of SHG occurring in asymmetrically structured $\chi^{(2)}$ materials, followed by Kaiser and Garrett’s observation of two-photon fluorescence in 1961.4,55 The next year, Woodbury et al. reported stimulated Raman scattering (SRS), a third-order nonlinear optical process where an incident photon interacts with a molecule, transferring energy to create a new photon with a different frequency, resulting in the excitation of molecular vibrations. Also at that time, the third-order analog of SHG, third harmonic generation (THG), was instigated in calcite by Maker and Terhune.61,62 Optical parametric amplification, a nonlinear process in which a light source is amplified though variations in frequency, was discovered nearly simultaneously in 1965 by Akhmanov et al and Girodmaine and Miller.6,63 Akhmanov’s group, along with two others, in 1967 initiated the convergence of quantum and nonlinear optics when they observed a precursor to optical
parametric amplification known as parametric down-conversion, in which a photon is divided into two lower-energy photons based on phase-matching conditions.\textsuperscript{64,65} This discovery directly led to the production and use of photon pairs, single photons, and squeezed light for quantum studies.\textsuperscript{66–68} Thus, nonlinear optics is in a big part responsible for the emergence of quantum technologies. Presently, many researchers in the realm of quantum information processing are looking to reconcile the fast propagation speeds and weak coupling to noisy environments offered by nonlinear photonic processes with their difficult-to-control nature.\textsuperscript{69} Nonlinearities are extremely useful in the control of quantum signals in photon-based quantum computing, as linear signals introduce technical challenges in producing entangling two-qubit gates. Still, the benefits of pursuing nonlinear photonics research in the field of quantum computing heavily outweighs the risk of no reward, especially considering the breakthroughs that are to come from this pursuit.

1.4 Applications of plasmonic materials and metamaterials

The functionality of metamaterials spans many fields including biosensing, energy harvesting, communications, and sub-diffraction-limited imaging. The burgeoning metamaterials market is currently valued at about USD 200 Million is projected to surpass USD 2.5 Billion by 2030.\textsuperscript{22} This explosion is due to the new routes being developed for the application of plasmonic metamaterials in emerging technologies and the efficient, scalable methods of production being developed. The use of plasmonic metamaterials in advanced device design has greatly increased in the last two decades, as there is a growing and diverse catalogue of efficient and versatile plasmonic materials.

In the linear regime, many advantageous optical phenomena exist in plasmonic metamaterials that allow for the design of robust applications in sensing, information processing
and photovoltaics, for example. While research on optical phenomena in the nonlinear regime is only recently gaining traction, there is a wealth of applications available for effects such as SHG, four-wave mixing (FWM) and optical bistability which may very well revolutionize modern technology. In many cases, nonlinear optical effects can further enhance the throughput and efficiency of existing linear effects in photonic devices through the use of plasmonic metamaterials, providing an expanded toolkit for advanced device design. In the sections following, several extensively developed and newly emerging applications of plasmonic metamaterials which utilize both linear and nonlinear phenomena will be discussed.

1.4.1 Linear optical applications

The linear optical attributes of many plasmonic metamaterials have been studied extensively and are used to bolster optical phenomena in emerging technologies. Plasmonic devices are currently used pervasively in medical, scientific and commercial applications for the enhancements and flexible manipulation they provide in the linear regime, though there is still much room for growth and exploration. Here, several impactful applications of linear phenomena in plasmonic metamaterial devices will be discussed.

1.4.1.1 Biomolecular sensing and treatment

By enhancing the fluorescent emission of nearby molecules with increased excitation rates and radiative decay rates, plasmonic metamaterials provide a platform for the highly sensitive detection of biological molecules and pathogens. In SPR, LSPR or Surface-enhanced Raman scattering (SERS) devices, this functionality stems from the strong electromagnetic resonances and electric field enhancement supported in plasmonic metamaterials and has been taken advantage of for its use in diagnostic sensing. These devices typically involve the interaction between biomolecules and their counterparts are enhanced to facilitate the detection
of molecular binding events. In the scope of medicine, this detection capability leads to the possibility of label-free detection methods in which target molecules are allowed to bind to a plasmonic surface, causing a change in the light signal’s resonance. Thus, real-time label-free detection of biomolecular bonding can be quantified in this way. Taking the use of fluorescent emission enhancement in plasmonic devices a step further, through the heat conversion of light, plasmonic nanoparticles can also be used to selectively destroy detected cancer cells or pathogens without damaging surrounding healthy tissue. One such example is the recent work by Labouta et al. in which localized plasmonic photothermal therapy was proposed as a viable treatment for patients experiencing life threatening lung failure due to COVID-19. This study lays out an approach which relies on ACE-2-functionalized gold nanorods to target SARS-CoV-2, and upon targeted irradiation, the virus is selectively eradicated. Plasmonic nanoparticles have been used in this method previously to treat illnesses

Figure 5. Potential use of plasmonic nanoparticles utilizing linear optical properties for targeted drug delivery.
like breast cancer or bacterial infections. In addition to photothermal treatment, acutely targeted chemothermal drug delivery can be facilitated by utilizing plasmonic nanoparticles as illustrated in Figure 5.74–76

1.4.1.2 Chemical sensing

Chemical detection and sensing is another common utilization of plasmonic devices. Traditionally, chemical detection techniques require cumbersome, expensive tools. The more commonly used chemical detection techniques of liquid chromatography, gas chromatography and nuclear magnetic resonance spectroscopy, for example, are not conducive to field chemical testing as they require bulky, sensitive equipment. With surface enhanced Raman scattering, outdoor in situ detection of trace chemicals is possible. Recent work by Gao et al., for instance, has demonstrated the use of plasmonic cavities in self-powered chemical detection devices based on SERS.77 These plasmonic devices are powered by triboelectric nanogeneration (TENG), a process in which the coupling of triboelectrification and electrostatic induction allows for the conversion of mechanical energy into electricity. In Gao et al.’s work, which is an excellent example of the versatility of plasmonic devices as chemical sensors, Ag nanoparticle polydimethylsiloxane (PDMS) plasmonic cavities are synthesized through a self-assembly process, and through the combined generation of TENG and SERS, a powerful electric-field boosted chemical is demonstrated.

1.4.1.3 Light harvesting and photovoltaics

Efficient solar light harvesting is investigated by researchers worldwide as the ultimate technique for clean energy generation in a world with rapidly growing energy needs, as sunlight is free, clean, and infinitely available. Through the direct conversion of sunlight into electricity or chemical energy, photocatalytic and photovoltaic devices hold great promise for the future of
energy generation. Many solutions are being explored in the field of photonics, with semiconductor metal oxides being the most prevalent thus far. However, due to the inability of semiconductors to utilize visible light and the fast recombination of electron-hole pairs, semiconductors alone are quickly losing interest as a commercially viable solar light harvesting medium.\textsuperscript{78,79} Furthermore, the silicon required for semiconductor is a limited resource. For these reasons, researchers are looking to enhance the photocatalytic efficiency of semiconductor solar cells by either incorporating plasmonic nanoparticles with semiconductors or replacing semiconductors with plasmonic-bolstered active materials to reduce recombination and harvest visible light.\textsuperscript{80,81}

Plasmonic effects have been demonstrated as a powerful technique for the increased light absorption and performance enhancement of organic solar cells (OSCs).\textsuperscript{82} In 2014, Yao et al. reported the construction of a plasmonic single junction device using metal nanoparticles with a power conversion efficiency (PCE) of 17.8\%, while more recent studies claim that a PCE of over 30\% is achievable in OSC using perovskite solar cells bolstered by plasmonic metamaterials.\textsuperscript{83,84}

\textit{1.4.1.4 Information processing}

With the emergence of computationally expensive technologies such as large language processing, there is a dire need for faster, more efficient information processing. Photonic computers have been investigated as an alternative to electronic devices, offering increased speed and efficiency. The flexibility and light manipulation capabilities supported by plasmonic materials makes them a popular candidate for achieving high efficiency in information processing components. Through the enhancement and manipulation of EM waves with plasmonic structures such as nanoparticles and waveguides, light, rather than electrons, make possible ultrafast computation.\textsuperscript{85}
Various plasmonic structures and metamaterials have been observed to support optical computing operations. One of the first groups to demonstrate metamaterial-based optical computing, Zhu et al., used a simple design employing a semi-thin layer of silver (~50 nm) on a glass prism for first-order differentiation. This technique, which achieved a minimum edge detection resolution of 7.2 μm, used the interference between the metal-glass interface and the SPPs radiation generated by a 532 nm laser in the determination of the total reflected amplitude. Through the incorporation of multiple layers, this design has been modified by Wesemann et al. to introduce performance enhancing Fabry-Perot (FP) resonances to achieve a near-perfect reflecting mirror for optical computation. Further improvements and computing capabilities were proposed and experimentally demonstrated, based on the simple multi-film coated prism design, and work is still being done to develop this approach to optical computing, including the use of Brewster angle properties, the spin hall effect (SPE) and topological charge transfer for the spatial and topological differentiation of EM waves.

1.4.1.5 On-chip lasing

Due to the currently evolving technological landscape that is shifting to nanoscale functionality, on-chip solutions are sought after by researchers for the miniaturization and efficiency enhancements required in modern advanced device design. Plasmonic nanolasers operate below diffraction limited dimensions, which makes them alluring for a wide range of scientific and societal needs. Plasmonic nanolasers have four typical configurations: metal-insulator semiconductor structures, metal-insulator-metal (MIM) waveguides, core-shell spasers and plasmonic crystal lasers, spawning from simultaneous breakthroughs made in 2009 (2012 for plasmonic crystal lasers). Over the past decade, researchers have made great strides to improve on-chip light sources. Due to their rapid development and further potential for
miniaturization, versatility, and modulation improvement plasmonic nanolasers hold great promise for the future of opto-electrical devices. Looking outside of the linear regime, nanolasers hold the potential to be useful in the nonlinear regime as well.

1.4.2 Nonlinear optical applications

Nonlinear optical phenomena for practical technological applications have been minimal up to this point. This is in part due to the specific, difficult to achieve conditions in which nonlinear phenomena are supported. Advancements in laser technology and the emergence of high-powered, ultrafast lasers have crucially influenced the practicality and accessibility of nonlinear optics research. Due to the weakness of higher order nonlinear susceptibilities relative to first-order susceptibilities, strong input signals are needed to realize nonlinear optical effects. Thus, ultrafast lasers are necessary to provide the intense and short-duration pulses of light needed to induce nonlinear optical effects.

Most devices and applications that currently rely on linear optical phenomena can benefit and gain versatility from the utilization of nonlinear phenomena, especially in the scope of plasmonic metamaterials. In this section, several practical nonlinear optical applications will be described, along with their applicability to the improvement of existing optical devices.

1.4.2.1 Plasmonic sensors

The nonlinear phenomena of SHG, THG or higher harmonic generation (HHG) are a result of the “combination” of two, three or any multiple of photons, respectively, in nonlinear optical materials. These phenomena can be incorporated into many applications to greatly enhance desired capabilities. Plasmonic sensors based on SPR, for instance, stand to gain a large amount of molecular sensing capability in detecting low concentrations of analytes through the generation of higher-frequency harmonics in incident light when plasmonic structures experience
change due to analyte binding. By using SHG, THG, or HHG in this way, smaller changes can be sensed in the environment surrounding a plasmonic sensor. Furthermore, plasmonic sensors utilizing HHG could acquire additional spectral information beyond the fundamental resonance of a single analyte, which could be useful for the parallel detection of different types of analytes.

Plasmonic waveguide sensing relies on SPPs, which also can be enhanced through the incorporation of SHG or FWM, the interaction of two or three wavelengths of light in a nonlinear material produces two or more new wavelength of light. These nonlinear effects can provide more information about the targeted analytes while expanding the detection limits of the waveguide sensor.

1.4.2.2 Nanolasers

As discussed in the previous section, plasmonic nanolasers utilize LSPR in metal nanostructures to enhance light emission and achieve lasing at the nanoscale. By incorporating nonlinear optical phenomena like FWM or SRS, the range of emitted wavelengths in nanolasers can be broadened, and tunable wavelength conversion can be achieved.

1.4.2.3 Ultrafast optical switching and communication

Optical switching is a third-order phenomenon operating on a nonlinear optical material’s bistability that allows for the manipulation of light in a medium using no inputs apart from the light source. Full control of this mechanism has long been sought by researchers hoping to create an optical analogue to the electronic transistor, making all-optical computing a practical endeavor. Plasmonic microcavities are an attractive stage for all-optical switching due to their large quality factor to mode volume ratio, which is needed for efficient nonlinear devices. Ultrafast optical switching can be achieved efficiently through the use of NPAs paired with spacer gaps having intensity-dependent refractive indices, for instance. In this case, optical
switching operates on the Kerr effect, an instantaneous, low loss optical manipulation of a material’s refractive index. Typically, the Kerr effect requires a large input power, making it too expensive for practical use, but with the proper choice of plasmonic modulator, nonlinear intensity enhancements make the use of this effect possible.

1.4.2.4 Quantum information processing

The manipulation and generation of quantum states of light is crucial for the advancement of quantum computing and information processing technologies. Nonlinear optical processes provide an invaluable set of tools that can aid in the generation and manipulation of entangled photons, squeezed states and quantum frequency combs, which are all essential for the progression of quantum technologies. Such nonlinear optical tools include FWM, parametric amplification, and spontaneous parametric down-conversion (SPDC). Photon pairs can be generated with FWM, as two pump photons are annihilated, and two photons of differing frequencies called “signal” and “idler” are simultaneously generated. Conservation of energy and momentum thus maintain that the sum of the frequencies of the generated idler and signal photons must equal the frequency of the pump photon. This requirement, along with the phase-matching condition, generates entangled photon pairs which can be exploited for quantum information processing purposes such as quantum teleportation and cryptography.

Nonlinear amplifiers based on parametric processes can also amplify weak quantum signals without introducing excessive noise, making the preservation of quantum states during signal transmission possible. This attribute is especially important for enabling long-distance quantum communication. In SPDC, a single photon interacts with a nonlinear crystal, generating two entangled photons with lower energies through a process of photon pair creation. These entangled photon pairs are essential for quantum communication and quantum
cryptography protocols, such as quantum key distribution. Additionally, SPDC enables the creation of entangled photon states that can be used for applications like Bell state measurements and quantum teleportation.

The specific device applications of quantum information technology are wide-ranging and the scope of this emerging technology is expanding rapidly. However, to make quantum technology feasible for mainstream use, more work needs to be done to develop tools such as the nonlinear optical phenomena discussed here. These capabilities are essential for the advancement of quantum technologies, which promise secure communication, enhanced measurements and powerful sensing.
2. Experimental techniques

This chapter contains the description and background of the various measurement and fabrication techniques performed in the works presented herein.

2.1 Optical spectroscopies

Optical spectroscopy is an ideal, non-destructive method for the observation of electromagnetic responses of linear and nonlinear optical materials. There are several types of methods in optical spectroscopy used in the study of light in matter. The research presented herein heavily utilizes several of these methods, namely: photoluminescence (PL), Raman, UV-Vis, reflection and polarization spectroscopies. The time resolved spectroscopy methods of time-correlated single photon counting and pump-probe spectroscopy were also used. Here I will give a brief description of the spectroscopic methods performed in this work and how they were used.

2.1.1 Photoluminescence

If a material absorbs photons with enough energy to surpass its band gap, the electrons within that material will be perturbed from their ground state to their excited state. PL spectroscopy is a powerful technique which exploits the emission of light following photon absorption of a material, which generates electron-hole pairs, or excitons, having unique energy levels and electronic structures. Upon relaxation, which typically happens in the nanosecond range, excitons emit photons corresponding to the energy difference between the ground and excited states of the material under investigation. PL spectroscopy allows for the characterization of a material by measuring the intensity of its emitted photons as a function of wavelength by way of a combined spectrometer and Charge-Coupled-Device (CCD) camera. This information
can illuminate the nature of a material’s electronic properties such as energy band structure, electronic transitions, radiative and non-radiative recombination processes, and the presence of defects or impurities within the material. In this work, PL spectroscopy is used ubiquitously to non-destructively characterize fluorescent emitters, metamaterials and 2D structures. The general setup used for all reflection PL spectroscopy performed throughout this work is shown in Figure 6.

2.1.2 Single nanostructure spectroscopy

Single nanostructure spectroscopy is a variation of any traditional form of spectroscopy that is applied to a single nanometer-scale structure. When the optical properties of a single nano-scale structure are desired and it is not feasible to fabricate a single, physically isolated nanostructure, it is necessary to optically isolate the structure of interest. This can be done using a pinhole placed at the focal point of the structure’s image in an intermediate plane between two lenses. By placing a pinhole in such a manner and using an imaging camera for selection, the spectrographic signal from a single nanostructure can be captured for analysis.

As with many other spectrographic techniques, single nanostructure spectroscopy is diffraction-limited, and the achievable resolution caps out at around 300 nm for visible light. In this work, single nanostructure spectroscopy is applied to silver nanocube-based plasmonic
nanopatch antennas, in which case the object of interest is smaller than 300 nm. Therefore, if the sample is diluted enough, the desired single nanostructure signal can be achieved. Typically, when dealing with metastructures, one must consider the amount of signal being blocked through the isolation of the nanostructure in order to accurately characterize the single structure. This tactic will be discussed further in chapter 5.

2.1.3 Dark-field scattering spectroscopy

Plasmonic nanostructures are difficult to characterize due to their poor detection under direct illumination. However, by exciting nanostructures at oblique angles, the scattered incident light can be detected for analysis where the direct transmitted light is excluded from collection. This is the basic principle behind dark-field scattering spectroscopy, which is useful for observing particles below the resolution limit (200 nm) of ordinary optical microscopes and nanoparticles otherwise displaying transparency or low contrast. The LSPR supported by plasmonic nanostructures further enhances scattering, providing further contrast in dark-field imaging.

The setup for this spectroscopic technique is identical to that shown in Figure 6 though the illumination angle of incidence is at an oblique angle rather than normal to the sample. This

*Figure 7. Illustration of dark-field microscope setup.*
can be accomplished through the use of a dark-field compatible lens in which the illumination is blocked at normal incidence and the remaining ring of light is allowed to pass through to the sample as illustrated in Figure 7. In this way, only oblique light illuminates the structure under investigation, and the resulting signal is collected for analysis. Typically, the use of a high numerical aperture lens is preferred when performing dark-field microscopy or spectroscopy for the maximum collection of scattered light. Dark-field spectroscopy is used extensively throughout this work to illuminate nanostructures and collect signals for characterization and experimentation.

2.1.4 Raman

Raman scattering is a fundamental process in which light inelastically scatters within a material, resulting in a frequency shift of the scattered light. While most scattered photons will undergo elastic scattering, a small percentage of photons in a material will experience inelastic scattering, which is also known as Raman scattering. With elastically scattered photons, the energy of the scattered photon is the same before and after scattering occurs. Raman scattering, however, shifts the frequency of the scattered photon depending on the specific vibrational modes present in a given material. This shift is represented as the Raman shift, $\Delta \nu$, given by

$$\Delta \nu = \frac{1}{\lambda_0} - \frac{1}{\lambda_1}$$

Where $\lambda_0$ is the wavelength of the excitation source, and $\lambda_1$ is the Raman spectrum wavelength of a given peak. Raman spectroscopy takes advantage of this phenomenon by which molecular structures can be probed and identified by these shifts in the spectrum. The mechanism responsible for Raman spectroscopy is depicted in Figure 8 and includes Stokes and Anti-stokes scattering. Stokes scattering corresponds to a Raman scattering in which the resulting photon is lower in energy than the excitation source, whereas anti-Stokes produces scattered light that is
higher in energy than the excitation source due to the dissipation of thermal phonons in the crystal lattice.

In this work, Raman spectroscopy (utilizing Stokes Raman scattering) is used extensively for the characterization of photonic materials, such as Selenium nanoneedles fabricated by means of laser ablation.

![Figure 8. Illustration of Raman scattering, which is responsible for Raman spectroscopy.](image)

2.1.5 UV-Vis spectroscopy

As incident light enters a material, it can be reflected, transmitted or absorbed. Thus, incident light is converted into transmitted (T), reflected (R) and absorbed (A) light within a material, and the sum of the percentage of light converted into T, R and A equals 1. UV-Vis spectroscopy is a widely used method of absorption spectroscopy that reveals what percentage of incident light in the ultraviolet and visible region of the electromagnetic spectrum is absorbed by some substance. When a beam of light enters some material, that materials molecules will selectively absorb some percentage of the photons while transmitting or scattering the remainder of photons. By exciting a material with a broad spectrum of light ranging from the ultraviolet to the visible wavelengths, photons of different frequencies will interact with the material in different ways. The absorbed photons send electrons from the ground state to an excited state
resulting in the characteristic absorption of specific frequencies in a given material. The amount of light absorbed at different frequencies in a material comprises its absorbance spectrum, which gives important information on material properties such as lattice structure and electron energy landscape.

2.1.6 Reflection spectroscopy

Reflection spectroscopy is a practical technique in which the intensity and spectral makeup of light-matter interactions are analyzed. Whereas UV-Vis spectroscopy uses the transmitted light to determine how much emitted light is absorbed in a material across a range of frequencies, reflection spectroscopy looks at the amount of light reflected. Although this type of measurement is similar in principle to UV-Vis spectroscopy, the information gained from a reflected signal differs from that of the transmitted signal. Reflection spectroscopy is commonly used for thin film characterization and surface analysis as it reveals more about the optical properties and surface characteristics, while UV-Vis spectroscopy is better used for gaining insight into the chemical composition and electronic transitions within a material. As with UV-Vis spectroscopy, a broad range of wavelengths in the form of white light is used to excite materials under reflection spectroscopic investigation. The amount of light reflected from the sample under investigation relative to the light reflected from the substrate gives the reflectance spectrum of a material which is used in this work for determining the resonances of metamaterials and tuning the modes of spacer gaps.

2.1.7 Polarization spectroscopy

Polarization is an inherent property of light which describes the orientation and direction of the electric field vector of an electromagnetic wave. When investigating the photonic properties of metamaterials, it is typically both necessary and interesting to characterize its
polarization properties. By manipulating the polarization of both the incident light and the detection signal, the polarization properties of a material can be determined. This is the principle behind polarization spectroscopy, which is used in junction with any of the spectroscopic techniques discussed herein. Rather than a standalone spectroscopic technique, polarization spectroscopy refers more to the experimental setup applied to other techniques such as photoluminescence spectroscopy or UV-Vis spectroscopy in which either the incoming signal is prepared with some polarization or the detection is limited to a specific polarized state.

Polarization spectroscopy is especially useful when investigating the photonic properties of topological nanostructures. In this work, the linear and nonlinear circular birefringence of chiral and -shaped metasurfaces are investigated using polarization spectroscopy. There are several methods by which components of the susceptibility matrix and second order susceptibility tensor of nonlinear topological optical structures can be characterized by manipulating the polarization of both the incoming excitation and resulting signal. The simplest approach, which is used in this study and will be discussed in further detail in Chapter 6, calls for the linear polarization of the incoming beam and the rotation of the sample of interest. By measuring the intensity of the transmitted beam and comparing to the intensity of the incoming beam, the orientationally dependent susceptibility properties of the material are illuminated.

2.1.8 Time resolved spectroscopy

Time resolved spectroscopy is a powerful tool for probing optical mechanisms with a temporal precision down to the attosecond time scale. This type of spectroscopy provides insights into the structural changes and electron dynamics that occur in chemical reactions and other photonic events. While many types of time resolved spectroscopy exist, this work mainly
utilizes time correlated single photon counting (TCSPC) and pump-probe spectroscopy to probe picosecond photon decay and femtosecond electron dynamics, respectively.

2.1.7.1 **Time correlated single photon counting**

Time correlated single photon counting is a sophisticated technique used to precisely measure the timed arrival of individual photons, which allows for the observation of dynamic processes such as fluorescent decay in novel photonic materials. The basic principle behind TCSPC involves the detection and timing of single photons emitted from a sample excited by a pulsed laser beam. The setup used in this work is shown in Figure 9 and is described as follows: First, a material is excited with a light source emitting short and well-defined light pulses (in our lab an 80MHz, 150fs ultrafast Coherent laser is used) which is also directed to a trigger diode near the laser output. Once the sample is excited, the emitted photons are routed to a fast-timing avalanche photodiode for temporal analysis. The signals collected by the avalanche photodiode are then fed into a single photon counting module (PicoQuant PicoHarp 300) for analysis. When

![Figure 9. Illustration of TCSPC experimental setup taken from Picoquant](https://www.picoquant.com/images/uploads/page/files/7253/technote_tcs.png)
a photon is detected, the timing of travel between the trigger and the PicoHarp is recorded and binned accordingly. From this timing data, a histogram of photon arrival times is created; this histogram represents the fluorescence lifetime of the material under investigation. From the distribution of lifetimes, the fluorescent decay is extracted, providing valuable information about the excited state dynamics of a sample.

2.1.7.2 Pump-probe spectroscopy

Pump-probe spectroscopy is another advanced technique used to probe excitation dynamics at extremely small timescales. The capabilities used in this study allowed for a precision of around 50 femtoseconds, though attosecond-scale pump-probe spectroscopy has been achieved.\textsuperscript{104} Pump-probe spectroscopy relies on the use of synchronized \textit{pump} and \textit{probe} laser pulses. The pump pulse acts to excite the sample under investigation inducing a change in the sample’s material properties. Following the pump pulse, the weaker, time-delayed probe

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{pump_probe_setup.png}
\caption{Illustration of the pump-probe setup for ultrafast spectroscopy.}
\end{figure}
pulse arrives shortly after the pump to further excite the sample (alternatively, the probe can be fixed and the pump can be delayed as shown in Figure 11). The signal resulting from the probe pulse shows how the sample responds to the initial excitation caused by the pump pulse.

The principle of detection follows from the control of the delay between the pump and probe pulse. In a typical pump-probe setup, a single pulse laser beam is split into two paths with a beam splitter, and the probe path is directed to a time delay stage which dictates the time of separation based on the physical difference in length of the probe path in relation to the pump path. The setup employed in this research is shown in Figure 10. Precisely controlling the physical length of the probe path allows for the observation of the evolution of the photonic response in the sample on very small time scales. In the case of the work presented herein, the stage used for time delay was capable of movement on the scale of 10 micrometers, which resulted in a temporal delay precision of around 50 femtoseconds.

2.2 X-ray diffraction spectroscopy

X-ray diffraction spectroscopy (XRD) is an analytical chemical and molecular analysis technique used extensively in materials sciences. With this method, the resultant diffraction pattern from the scattering of an x-ray beam on a sample is analyzed to give information about the sample’s molecular structure. The principle behind this technique comes from Bragg’s Law, which states that the constructive interference of reflected X-rays from the crystal lattice of some material will cause a diffraction pattern that differs with the incident angle and wavelength of the X-ray beam. By analyzing the angles and intensities of the diffracted X-rays, the three-dimensional arrangement of atoms within a crystalline material can be deduced. This information helps determine the crystal structure, which includes unit cell dimensions, atom positions, and
bond lengths. In this work, XRD is used to better understand the morphology of various photonic materials.

2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) allows for the reliable imaging of a materials surface morphology and topography at extremely high magnification. Using a beam of electrons (which have a much shorter wavelength than photons) focused onto a sample of interest through electromagnetic lensing and operating under vacuum conditions to prevent electron scattering, SEM produces detailed images with resolutions down to the nanometer level. The scanning process involves systematically moving the focused electron beam across the sample in a raster pattern. As the primary electrons from the beam impact the sample's surface, several interactions occur, each yielding distinct types of information. Low-energy (secondary) electrons that are emitted from the sample's surface due to the impact of the electron beam carry data about the surface topography and structure of the specimen. Another interaction involves backscattered electrons, which are initial electrons that are deflected backward upon encountering atomic nuclei. The intensity of the backscattered electrons depends on the sample's atomic composition, allowing for compositional contrast in the images.

This technique has wide-ranging applications due to its ability to construct very detailed images of materials with high precision. In this work, SEM is used in tandem with other techniques to explore and further understand the surface characteristics of plasmonic nanostructures. In this way, it is possible to paint a more complete picture of how material composition on the nanoscale influences the photonic properties that are recorded for bulk excitation.
2.4 Atomic force microscopy

Atomic force microscopy (AFM) is a high-definition imaging technique used to visualize surfaces at the nanoscale. AFM can also be used to manipulate surfaces at this scale, though for the purposes of this work, only imaging capabilities are used. Rather than light, AFM uses a mechanical cantilever to interact with the surface of the sample, which provides topographical information from a reflected laser aimed at the backside of the cantilever tip as shown in Figure 11. Weak attractive forces existing between atoms and molecules, Van der waals forces, are responsible for the deflection of the microscopic cantilever, and this deflection is recorded and subsequently converted to a physical distance. The cantilever can operate in a continuous contact, no contact or tapping mode to record topographical changes in a sample’s surface. Additionally, force microscopy can be performed by measuring the forces between the tip and the sample as the tip is brought into close proximity to or direct contact with the sample.

![Figure 11. Depiction of AFM signal detection. (open source image)](image)

Throughout this work, AFM is especially useful in determining the thickness of thin films in order to produce accurate predictions of resonant modes in gap mode plasmonic materials. In this case, heat resistant tape is applied to a test sample before thin film fabrication. Once the film
is adhered to the substrate, the tape is removed, leaving a pristine edge on which AFM microscopy analysis can be performed.

2.5 Thin film fabrication

In the context of photonics, the term *thin film* typically refers to a layer of material with a thickness in the range of a few nanometers to a few micrometers. Through careful fabrication methods, these layers are engineered to have specific optical properties in order to manipulate and guide light at the nanoscale, enabling the creation of advanced optical devices and systems with enhanced performance, efficiency, and functionality.

2.5.1 Atomic layer deposition

Atomic layer deposition (ALD) is a type of chemical vapor deposition in which thin films are created through the chemical reaction and deposition of a precursor gas onto a substrate. With ALD, a substrate is sequentially exposed to alternating bursts of gaseous precursor and water, resulting in the growth of one atomic layer at a time. It involves sequentially exposing a substrate material to alternating gaseous precursors in a controlled environment. Each precursor reacts with the substrate surface to create a single atomic layer of material at a time. This process, which is illustrated in Figure 12, ensures the creation of ultra-thin, atomically smooth and uniform films which lends to robust and controllable optical responses in metastructures designed with a dielectric gap. ALD's self-limiting nature prevents excessive growth, allowing for precise control over film thickness. It finds applications in semiconductor fabrication, catalysis, energy storage, and other fields where precise and controlled thin-film deposition is crucial. In this work, ALD is used extensively to produce sub-10 nm films of ZnO in the fabrication of plasmonic nanopatch antennas as discussed in Chapter 5.
2.5.2 Layer-by-layer method

In this method of thin film fabrication, a substrate is alternately immersed in solutions containing oppositely charged molecules. With each immersion, the substrate gains a single atomically thin layer of material, and through repeated immersion a thin film of a desired thickness can be built up. The polyelectrolyte (PE) layer-by-layer (LBL) method is a useful tool for quickly building a spacer gap with a thickness that depends on the number of layers incorporated. In this work, alternating layers of polymers Poly(4-styrenesulfonic acid) sodium salt (PSS) and Polycyclic Aromatic Hydrocarbons (PAH) are used for LBL thin-film construction.

Figure 12. Illustration of ALD fabrication of thin films.\textsuperscript{101}
The LBL process, depicted in Figure 13, is utilized throughout this study to create dielectric gaps in which optical modes can exist in gap-mode metasurfaces. In addition to an NaCl solution made by mixing 29g of NaCl powder with 500 mL deionized (DI) water, the particular polymers used for LBL thin film construction in this work are the negatively charged anion PSS and positively charged cation poly PAH. The application of a PE layer using LBL begins with the preparation and cleaning of a substrate in order to rid the surface of any debris, which could impede the coating process. The substrate is immersed in solution containing the first PE (PAH) for approximately 5 minutes, followed by an immediate immersion in NaCl solution for 1 minute and gently rinsed with water afterward. Then, the substrate is immersed in PSS for 5 minutes, followed by immersion in NaCl for 1 minute and a gentle rinse following. This cycle continues for the desired number of layers, with each full cycle (as shown in Figure 13) contributing 3-5 nm of PE layering. The NaCl acts to neutralize the surface charge of the previous polymer to facilitate layer homogeneity. It should be noted that for the purposes of the work presented herein, PAH is made to be the last layer so that negatively charged Ag nanocubes can bond more readily to the final surface.

*Figure 13. Illustration of PE LBL technique.*
2.5.3 Spin coating

Spin coating is a reliable, widely used method of thin film fabrication in which a substrate is placed upon a rotating stage and exposed to a solution containing the desired deposition material. By spinning the substrate at a speed which is appropriate for the given material/solution combination, a uniform thin film can be quickly created. This method is touted as a scalable, cost-effective way to prototype thin film designs. In the works presented herein, spin coating is used prevalently as a means to homogenously distribute a wide range of solution onto various substrates.

2.5.4 Template stripping technique

Ultra-smooth substrates can be prepared by way of the template stripping technique. The template stripping technique is a fabrication method used to produce thin metal films with well-defined nanostructures or patterns on their surfaces. This technique is commonly employed in nanotechnology and nanofabrication processes. In order to create ultra-smooth metallic substrates, the general procedure begins with the cleaning of a base substrate (such as silicon or glass). Epoxy is then applied to the target substrate, which in this work is typically gold that has been deposited onto ultra-smooth silicon. Then, the base substrate is allowed to bond to the target substrate via epoxy. Once the epoxy has set, the base substrate is mechanically peeled from the sacrificial substrate which the gold was sputtered onto, resulting in a gold layer adhered to the base substrate. In this way, the smoothness of the gold layer is defined by the precision of the sputtering method used to deposit the gold onto silicon, and an atomically smooth layer can be achieved.

The template stripping technique is advantageous for producing high-quality nanostructures because it allows for precise control over the resulting patterns and geometries.
The technique is often used in applications like plasmonics, SERS, and other areas where precisely engineered nanostructures are crucial for specific functionalities. Additionally, if capabilities such as sputtering are not available or feasible, pre-sputtered gold wafers can be purchased and used in this way.
3. Characterization of novel nanostructures

3.1 Introduction

In the scope of photonics, the characterization of novel nanostructures is crucial and necessary for the advancement of materials science. Novel nanomaterials typically behave in more complex ways than their bulk counterparts due to quantum confinement and surface effects. For nanostructures to be tailored for specific photonic applications, their intrinsic optical properties such as their PL spectra and plasmonic behavior must be fully considered. Furthermore, accurate characterization informs the use of novel nanomaterials and structures within plasmonic devices.

In general, a thorough characterization of a nanomaterial involves observations on its growth, composition, and morphology. Nanostructures exhibit unique properties that do not exist in their bulk counterparts, and various imaging and spectroscopy techniques are required for characterization in addition to thermal, chemical and other analyses. Through proper characterization, the unique attributes of emerging materials can be identified, and their practical uses can be explored. In practice, the choice of characterization methods used usually depends on the intended application of a nanostructure or material. While characterization is a crucial early phase in all of the works presented in this dissertation, this chapter will detail two instances of intensive characterization to elucidate the properties of novel nanomaterials and nanostructure systems. In particular, the growth, morphology and decay of Se nanoneedles fabricated by varying degrees of laser ablation were spectrally characterized, and the characterization of varying blends of 2-D perovskite and rubrene was performed via spectroscopic methods.
3.2 Laser-ablated Se Raman characterization

Selenium (Se) belongs to a host of rare but vital semiconductors with an energy-critical element classification by both the Materials Research society and the American Physical Society.\textsuperscript{107,108} The development of many highly technical applications are dependent on the availability of Se, which can only be recovered as a byproduct of copper refining and not mined directly. Technologies such as sensors, solar cells and rectifiers rely on Se, which has a large flexibility and versatility owing to its relatively wide 1.79 eV bandgap, high photoconductivity ($\sim 8 \times 10^4 \text{ S cm}^{-1}$) and low melting point ($\sim 490 \text{ K}$). By tuning the composition and morphology of Se-containing materials and structures, optical properties can be controlled, allowing for the tailoring of advanced materials and metastructures.

Various morphologies of one-dimensional Se nanostructures (NS) have been investigated for their potential use in the sciences, and several different fabrication techniques have been utilized in their making.\textsuperscript{109} Se nanowires (NW), nanotubes (NTs), nanoneedles (NNs), and nanorods (NRs) have all been synthesized and investigated in the past. Typically, chemical-based methods are implemented for fabricating Se NSs, such as in the case of Li et al’s production of high-quality trigonal Se or Jiang et al’s demonstrated use of silver to induce the growth of t-Se NWs.\textsuperscript{110,111} Each of these fabrication methods and their resultant products rely on proper characterization for their progression in research, which is also true for the work presented here.

In this work, Se NNs are produced by collaborators at the University of Arkansas Little Rock through a non-chemical-based method known as pulsed laser ablation in liquids (PLAL) which is a materials processing technique that involves the use of high-intensity laser pulses to remove material from a solid target immersed in a liquid medium. The variable parameters
within this study are the liquid in which bulk Se is dispersed and the power, irradiation time, wavelength and repetition rate of the laser used for ablation.

The characterization of the novel Se NNs began with SEM imaging. Comparison of the various solvents used in the PLAL fabrication of Se NNs shows a clear influence on the final product (Figure 14). In DI water, Se formed spherical NPs, while NPs formed in the other solvents investigated had an elongated NN morphology of varying quality. Initial Raman spectroscopic measurements of the particles in each of the colloids shown in Figure 15 revealed two resonant peaks at 234 cm\(^{-1}\) (trigonal Se or t-Se) and 251 cm\(^{-1}\) (amorphous Se or a-Se). Based on the SEM and Raman measurements, it can be assumed that the spherical NPs produced in DI water are amorphous while the needles produced in the other solvents are trigonal.

\textbf{Figure 14. Influence of solvent on PLAL Se structuring shown through SEM images.}\(^{108}\)
Acetone was selected to be used for the rest of the study as the most favorable solution for the synthesis of Se NNs by PLAL.

The next step in characterizing Se NNs was to better understand the growth mechanisms of Se NNs by varying the synthesis time of the PLAL fabrication process from 30 s to 300 s of irradiation. From the solutions synthesized using these irradiation times, two drop-cast Si wafer samples were prepared with freshly-made Se and two more were made 30 minutes after synthesis to further understand the growth mechanism. Visual and SEM images show that immediately after 30 s of irradiation, the Se solution appears pink and largely amorphous, while after 300 s of irradiation, the Se solution appears light gray and mostly trigonal (Figure 15). The samples made with 30 min-old synthesized Se solution both appeared gray and trigonal. Initially, the Se NPs created with the PLAL method were spherical, but the acetone solvent promoted the conversion of a-Se NPs into t-Se NNs over time. This conversion can be considered as a three-pronged process. First, a-Se spherical NPs are produced by the laser-target interaction in acetone

Figure 15. Left: Raman spectra of particles/needles present in each colloid. Right: SEM images of colloids on Si wafer for 30 s and 300 s (a,b) irradiation immediately after synthesis and 30 minutes after synthesis (c,d). 108
due to the melting of Se in the irradiated zone, injection into the solvent and its quenching into an amorphous structure. Then, the a-Se NPs sacrificially transform into t-Se NPs, which have a lower surface energy compared to a-Se. Lastly, the t-se NPs act as seeds for NNs and consequently support 1D growth due to the anisotropy of t-Se, which has a crystalline structure consisting of helically chained Se atoms with three atoms per turn. Through electrical and van der Waals forces, these chains form a hexagonal lattice, resulting in a strong inclination for t-Se to grow 1-dimensionally along the c-axis direction.

Going further into the characterization of the growth of morphological Se nanostructures, the repetition rate of the pulsed laser beam used in PLAL fabrication was varied in order to investigate the control the sharpness of the NNs. An increase in the pulse repetition rate caused a decrease in the resulting NN’s diameter, which is visible in the SEM images of the Se NNs produced using a range of repetition rates in Figure 16. The optical properties of the Se NNs

![Figure 16. SEM images of Se NNs produced using a repetition rate of (a) 0.1 kHz, (b) 1 kHz, (c) 5 kHz, (d) 10 kHz, (e) 15 kHz, (f) 19.9 kHz.](image)

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fabricated using various repetition rates were thus investigated by room-temperature PL and Raman spectroscopy. Different PL characteristics exist for Se needles at room temperature depending on the parameters used in synthesis. Low repetition rates in the 0.1 – 10 kHz range result in Se NNs with broad PL emissions having a maximum around 550 nm (Figure 16a) and a FWHM of roughly 0.6 eV (140 nm), which is quite blue-shifted from the bulk Se bandgap of 1.76 eV (705 nm).\textsuperscript{114} This difference is likely due to the fact that the a-Se crystal phase is produced with the low laser repetition rates. As shown in Figure 16, low repetition rates yield a mixture of Se NSs having both small NPs and NNs. Similar to the Se NPs that were produced within ~30 s of irradiation, the smaller-sized Se NPs are in the a-Se phase and remain there rather than forming into NNs, which can explain the blue-shifted PL emission as has been shown in previous studies of Se NP optical properties.\textsuperscript{115,116} The blue shift of the PL emission under a

![PL emission spectra from Se NNs synthesized at a repetition rate of 1 kHz at various laser excitation powers. Red dashed line indicates blue shift of peak resonance at different powers.\textsuperscript{108}](image)
Figure 18. Temperature-dependent optical properties of Se NNs synthesized by PLAL in acetone. (a) PL emission spectra at room temperature PLAL-produced Se NNs for varying repetition rates. (b) Decay dynamics of PL emission at 525 and 700 nm from PLAL produced Se NNs in acetone using 10 kHz repetition rate. (c) PL emission at varying temperatures and (d) decay dynamics of PL emission at 8K of Se NNs synthesized at 19.9 kHz in acetone.  

range of laser excitation powers from 2.5 uW to 1 mW (or 2.5 to 100 kW/cm2) is shown in Figure 17, indicating a shift from 2.26 to 2.38 eV (548 to 521 nm). One explanation for this blue shifted emission wavelength is the band filling due to the increased occurrence of free carriers. The PL emission spectra of Se NNs synthesized at higher laser repetition rates in the range of 10 to 19.9 kHz are characterized by an emission band near 1.74 eV (710 nm) as shown in Figure 18a. This emission band energy is very close to the bandgap energy of bulk Se and is due to the near-band-edge emission. This is in line with how the SEM characterization shows higher
repetition rates resulting in larger Se NNs and more prevalent t-Se phase particles than the lower repetition rates produced (Figure 16). Time-resolved PL measurements are performed in order to further analyze the optical attributes of Se needles at room temperature. Figure 18b shows the decay curves measured from Se NN clusters synthesized at 10kHz at 525 nm and 700 nm emission wavelengths with an excitation power of 500 uW. These PL emission decay times, which are analyzed and obtained using a fitting of the instrument response function-deconvoluted data, show a slower decay time of around 1.21 ns at 525 nm emission and a shorter decay time of approximately 0.03 ns at 700 nm emission. The decay time for the near-band-edge emission at 700 nm has a much shorter decay time than solid-state Se quantum dots having an intrinsic decay time of the photoexcited excitonic states which is comparable to the decay time at 525 nm emission.\textsuperscript{117} This shorter decay time for PL emission at 700 nm may be partly due to the unpassivated surface of Se NNs, which causes rapid quenching of photoexcited carriers.

In the low temperature regime (8 K), the near-band emission from Se needles exhibit a PL emission peak around 1.85 eV (660 nm) with an additional peak at 1.70 eV (730 nm) as displayed in Figure 18c. The second peak at 1.70 eV stems from the defect-related emission, which rapidly quenches at temperatures around and above 50 K, indicating a weak binding between the involved defects such as surface states and the photoexcited carriers. The near-band-edge low temperature emission at 1.85 eV persists independent of temperature and blends into the 1.74 eV (710 nm) emission band at room temperature as a result of the bandgap shrinkage. Figure 18d shows the decay dynamics of the emissions at 1.85 and 1.70 eV at 8K. The near-band-edge emission at 1.85 eV shows a very fast decay time of around 30 ps, similar to the room-temperature measurements. The decay dynamics of the defect-related emission show a longer decay of approximately 100 ps. Once again, the unpassivated surface of the Se NNs may
be responsible for the very fast time components of their PL emission, which indicates a significant degree of nonradiative decay channels. Surface passivation of these needles has the potential to improve overall optical efficiency, as demonstrated in studies involving analogous nanostructures like semiconductor NWs.\textsuperscript{118–120} For instance, the application of surface passivation to individual GaAsP NWs resulted in the achievement of solar cells with efficiency exceeding 10%.\textsuperscript{121} Considering the substantial surface-to-volume ratio inherent in these needles (\(\sim 108 \text{ m}^{-1}\)), modifying the synthesis conditions to achieve surface passivation could significantly reduce the nonradiative recombination rate of charge carriers at the surface associated with surface states. In such scenarios, the radiative emission rate (or charge collection efficiency) can be markedly enhanced, a property of utmost importance for applications such as photovoltaics and photocells.

Overall, this study characterized the morphology of Se NNs synthesized using various parameters. Se NNs are thus presented as a versatile structure with tunable aspect ratios and morphological components such as needle tip thickness which can reach nanoscale dimensions. Overall, as the characterization of Se NNs reveals both photovoltaic action in which light is directly converted into electricity and photoconductive action in which electrical resistance decreases with an increase in illumination, Se NNs could be utilized as photoanodes in the production of new, advanced dye-sensitized photocells and solar cells.\textsuperscript{122}

3.3 Energy upconversion in blended 2D perovskite and rubrene

Hybrid inorganic-organic perovskites have garnered interest in light harvesting research as a strong candidate for replacing silicon in next-generation solar cells due to their efficiency, manufacturability, flexibility and lower cost. There exist many variations of perovskite, which can consist of CaTiO3 or any compound having this \(\text{A}^{2+}\text{B}^{4+}(\text{X}^{2-})\) (or ABX\(_3\)) crystalline structure.
Perovskites have only recently entered the photonics research landscape when in 2009, Miyasaka and his group at the University of Tokyo demonstrated the potential of MAPbX$_3$-type perovskites in efficient solar cells. Naturally, several challenges still exist for perovskites as a practical alternative to silicon solar cells, including poor durability and stability. Additionally, while perovskites are more tunable than silicon, there still exists limitations in design. Structurally, perovskites of the ABX$_3$ class are limited in their possible compositions which can contain only three possible structure stabilizing A-site cations, rendering them limited in their spectral and temporal properties and often forming only metastable compounds. Despite these limitations, 3D perovskites offer a greater charge transport efficiency than more tunable alternatives such as 2D perovskites. In specially engineered devices, this property can give rise to a multitude of possibilities within the realm of photonics such as triplet sensitization and triplet-triplet annihilation, which can yield higher degrees of freedom and increased efficiency in the next generation of solar cells.

Triplet sensitization can occur in any compound that can be excited to the triplet excited state, which influences photochemical catalysis. Rubrene, a chemiluminescent organic sensitizer, is susceptible to triplet sensitization in the presence of various lead-halide perovskites. This pairing has recently resulted in the efficient infrared to visible photon upconversion through the phenomenon of triplet-triplet annihilation. Triplet-triplet annihilation (TTA) begins with the absorption of a low-energy photon and generation of a singlet exciton by a triplet sensitizer. Through intersystem crossing, the singlet exciton is quickly converted to a triplet exciton which is transferred to an emitter having low-lying triplet and high-lying singlet state energies. After random diffusion, the triplet exciton self-annihilates as it collides with an emitter triplet, forms a high-energy emitter singlet and finally produces an upconverted photon as it deactivates to the
Mechanisms such as TTA are desirable in emerging photovoltaics technologies as they allow for the efficient conversion of infrared-to-visible light, aiding in the harvesting efficiency of solar cell devices. In this study, various blends of Rubrene and 2D perovskite are characterized for their photoluminescent spectral and temporal properties in order to demonstrate upconversion via triplet-triplet annihilation.

The four various blends consisted of 100% MAPI perovskite, 100% rubrene, 2% rubrene/98%MAPI or 50% rubrene/50% MAPI on glass substrate. Each of these samples was characterized by PL spectroscopy and TCSPC decay at varying excitation powers and wavelengths (400 nm, 705 nm tunable pulsed laser and 633 CW laser). Rubrene has an excitation peak around 450 nm with peak emission around 530 nm, while MAPI perovskite has a peak emission around 770 nm. Thus, the idea in this study was that upconversion could be observed by illuminating perovskite with an excitation below the bandgap of rubrene and detecting PL signal near rubrene’s peak emission. In order to ensure the excitation laser was not collected with the resultant signal from the sample, various filters were utilized. For the 400 nm pulsed laser excitation, a 550 short-pass filter is used from the excitation side, and 410 nm and 700 nm long-pass filters are used from the detection side. Figure 19 shows the PL spectra of Rubrene/MAPI blends under 400 nm laser excitation, with the left panel showing the region of interest and the right panel showing the broad spectra.

Figure 19. PL spectra of Rubrene/MAPI blends showing region of interest (left) and broad spectra (right) under 400 nm laser excitation.
488 nm long-pass filters are used from the collection side. For the 705 nm pulsed laser excitation, a 700 long-pass filter is used from the excitation side, while 650 and 600 nm short-pass filters are used from the collection side. For the 633 nm cw laser, a 633 nm band-pass filter is used from the excitation side, and a 633 long pass filter is used from the collection side.

To begin, the PL of each sample was collected upon excitation by the 400 nm laser. The resulting PL signal of each sample excited by the 400 nm pulse laser is shown in Figure 19, which shows the full PL taken on the right and the magnified region of interest in which upconversion can be detected to the left. It is clear that MAPI alone does not emit in the 550 nm region, while the samples with any amount of rubrene shows a peak when illuminated above rubrene’s bandgap. When illuminated with either the 633 nm CW or 705 nm pulsed laser, upconversion is evident in the 550 nm signal that appears in the PL spectra of samples containing rubrene as shown in Figure 20a and b. Furthermore, the relative amount of rubrene within the blend appears to have a direct correlation with upconversion efficiency, as the 550 nm peak is more apparent in the 50% rubrene blend than in the 2% rubrene blend. The 100% rubrene and

![Figure 20. PL spectra under 633 nm (left) and 705 nm (right) excitation rubrene perovskite blend.](image-url)
100% MAPI samples do not show any PL around 550 nm, further supporting the evidence for upconversion.

The decay of pure rubrene, MAPI perovskite and the various blends of the two were also investigated in an attempt to detect nonradiative transfer, which would support the likely existence of triplet-triplet annihilation. Using the pulse laser at either 400 nm or 705 nm, it was observed that rubrene alone had a decay of $\tau \approx 9.17$ ns while illuminated by a 400 nm laser. Under this excitation, the 2% rubrene blend displayed a fast decay of $\tau_{\text{fast}} \approx 0.045$ ns with a slow decay of $\tau_{\text{slow}} \approx 0.39$ ns, while the 50% rubrene blend displayed a fast decay of $\tau_{\text{fast}} \approx 0.11$ ns with a slow decay of $\tau_{\text{slow}} \approx 1.65$ ns. Under 705 nm excitation, the 2% rubrene blend showed no signs of multiple decay components, rather showing a single decay of $\tau \approx 0.056$ ns, while the 50% rubrene blend displayed a fast decay of $\tau_{\text{fast}} \approx 0.11$ ns with a slow decay of $\tau_{\text{slow}} \approx 1.73$ ns, consistent with the decay under 400 nm excitation. These results show that the decay lifetime of rubrene is significantly shortened when blended with MAPI perovskite. However, one cannot conclude from this evidence alone that nonradiative transfer such as FRET is occurring, due to the influence of MAPI on the decay. It should be noted that the decay of MAPI under 400 nm

![Figure 21. Decay dynamics (left) and XRD signature (right) of Rubrene/MAPI blends.](image-url)
excitation is rather slow ($\tau \approx 5$ ns) compared to the decays of the MAPI/rubrene blends presented in Figure 21a, which do suggest the presence of nonradiative transfer.
4 Linear control of light-matter interactions: plasmonic nanohole arrays

4.1 Introduction

The control of light in the linear regime has been integral to the progression of optical devices and technologies. Though there is an imminent need for enhanced nonlinear optical control in emerging advanced devices, linear optics has great potential still. For instance, there still exists avenues of improvement in the linear optical regime for on-chip lasing, sensing and light harvesting. As the plasmonic mechanisms employed in linear optical metamaterial devices are improved and enhanced, there is also a great interest in designing them to be more cost effective, scalable, and easy to produce. One such plasmonic metastructure that offers these improvements is the plasmonic nanohole array (PNA), an array of air nanoholes in thin film metals arranged periodically which possesses exceptional capabilities for ultra-sensitive detection and can achieve high spectral resolution on the nanoscale. By supporting surface plasmon resonances, PNAs can greatly enhance nanoscale light-matter interactions and provide a robust platform for applications in photonics and optoelectronics. Whereas singular nanostructures can only offer LSPs having a limited range, PNAs have a greater range in controlling light-matter interactions through their ability to strongly confine light via surface lattice plasmons.

Over the past two decades, NPAs have been researched thoroughly and many fabrications methods exist which yield a large variety of nanoarrays. Conventional methods of fabrication such as the EBL and PEEL (photolithography, e-beam deposition, etching and lift-off) techniques are costly and impractical for large-scale fabrication, requiring heavy equipment and an involved process. In this work, PNAs are constructed with a novel combination of the shadowing nanosphere lithography technique and reactive ion etching (RIE), which allows for
the rapid, scalable fabrication of nanohole arrays. Furthermore, the effectiveness of this design is shown through its capability to enhance lasing intensity and decrease the lasing threshold in fluorescent organic emitters and its ability to accelerate the photonic decay of quantum dots.

4.2 Methods

4.2.1 Fabrication

The production of the NPAs utilized in this investigation begins with the application of a colloidal polystyrene (PS) nanosphere monolayer on a glass substrate using the air-water interface technique, as previously outlined. To summarize this methodology, PS beads are initially dissolved in a solution comprising water and ethanol, which is gradually and incrementally dripped onto a glass Petri dish containing a small volume of water. The surface area of the resulting PS nanosphere monolayer spans a few centimeters, as defined by the size of the glass substrates used in this study. Over time, the PS beads spontaneously assemble into a hexagonally close-packed monolayer at the water-air interface, and to preserve this arrangement, a Teflon ring is placed around the surface to prevent adhesion to the side of the Petri dish. Next, the water level is raised, and a glass substrate is slowly slid beneath the PS monolayer film. Subsequently, the water is slowly pumped out, and the PS monolayer film is gently lowered onto the glass substrate. Once the monolayer is entirely placed, the PS beads undergo RIE, resulting in a reduction in their size. Following RIE, a 5 nm adhesive layer of titanium (Ti) is deposited on the glass/PS array, followed by a 100 nm layer of silver (Ag), through the process of electron-beam evaporation, carried out under a base pressure of $10^{-6}$ mbar. The Ti layer serves as a bonding agent between the glass substrate and the Ag layer. After deposition, the PS beads are
removed from the assembly using Scotch tape, leaving behind a periodic hexagonal nanohole array in the Ag layer. This fabrication process is depicted in Figure 22.47.

In this configuration, silver coating was preferred over gold (Au) due to its superior surface plasmon resonance properties, in contrast to the substantial losses observed in Au at optical frequencies. An alternative approach could utilize Au or an Au/Ag hybrid coating instead of Ag to enhance the degradation lifetime of the PNA. However, such an approach may result in weaker plasmonic responses compared to those offered by Ag-coated PNAs.

![Figure 22. PNA fabrication process via shadowing nanosphere lithography: (1) PS beads are deposited on a glass substrate. (2) RIE is applied to reduce bead size and nanohole diameter. (3) 5 nm Ti and 100 nm Ag are deposited onto PS/glass. (4) The PS layer is lifted, forming a hexagonal nanohole array. In the center is an SEM image of the finished product.](image-url)
The controllable parameters in this process are the lattice spacing and nanohole size, which can be adjusted by varying the size of PS beads and the exposure time to RIE, respectively. A longer etching time yields smaller PS beads, which in turn leads to smaller holes and larger hole separation in the final product. For the nanohole array samples presented in this study, two different sets of interparticle spacings of 500 and 750 nm were utilized, along with respective RIE times of either 300 or 450 s that yielded different hole radii of approximately 350 nm or 325 nm for 500 nm spacing and 650 nm or 600 nm for 750 nm spacing, respectively. Figure 22e displays an SEM image of one of the PNA samples utilized in this research.

It should be noted that this method of nanohole array fabrication does have several shortcomings that should be addressed. While these results show the impressive lasing and decay rate enhancement attributes of the PNAs used in this study, the fabrication process could be improved. The mechanical exfoliation of the PS balls, for instance, tends to cause widespread defects as shown in Figure 23. One possible solution to this problem is to employ chemical
exfoliation with a solvent such as acetone to rid the finished PNA of PS nanospheres rather than mechanical exfoliation.

4.2.2 Characterization

To ascertain the resonant modes of each nanoarray, they were first mounted onto a controllable turntable, and an angle-dependent white light transmission scan was performed at 45° relative to normal incidence. Illustrates the peak resonances observed at normal incidence for arrays with lattice spacings of 500 nm and 750 nm, resulting from two distinct particle sizes and RIE etching times of 300 s and 450 s, respectively.

Within this spectral range, the transmission spectrum for the 500 nm (750 nm) lattice spacing array exhibited well-defined transmission minima at approximately 450 nm and 660 nm (700 nm). These minima were attributed to the (0, 1) Wood-Rayleigh anomaly modes, originating from surface plasmon waves at the interfaces of metal/glass and metal/air, respectively. The presence of these transmission minima aligns with the plasmonic-grating theory and aligns well with recent studies involving similar structures. Importantly, the light coupled to these resonant modes propagates perpendicularly to the sample surface. This property holds great significance as it governs the directionality of photons emitted by an embedded emissive nanomaterial, guided by the directional resonance. The full width at half-maximum (FWHM) of these transmission curves, at the transmission minimum (around 660 nm for the Ag/glass mode of the 500-nm spacing PNA or around 700 nm for the Ag/air mode of the 750-nm spacing PNA), was found to be approximately 40 nm. The quality factor $Q$ is calculated using $Q = \frac{\lambda}{\Delta\lambda}$ where $\lambda$ corresponds to the wavelength of lasing and $\Delta\lambda$ corresponds to the FWHM of lasing, resulting in an estimated quality factor of around 16. Though the lasing quality factor of
the PNA alone is not considerably high, lasing can be induced in fluorescent emitters using these PNA, resulting in a much higher quality lasing as will be shown in the following section.

Figure 24b depicts a false-color image, constructed using transmission spectra collected incrementally around normal incidence for a 500 nm lattice array with an RIE etching time of 300 s. The dashed curves represent the position of the (0, ±1) Wood-Rayleigh anomaly metal/glass mode with respect to the incident angle. The observation of this anomaly, which is caused by the interference of scattered light waves from the periodic metal/glass interface and the resulting variation in local absorption/transmission enhancements, is consistent with resonant modes reported in several previous studies.

4.2.3 Active material integration

In order to fully investigate the lasing and emission enhancements offered by the PNAs, several different types of active medium were prepared on glass slides as well as on the 500 nm-
spaced, 150 nm-radius nanohole array. This particular set of PNA parameters was chosen based on the robustness of the transmission minima relative to that of the other PNAs (Figure 24a). For this study, the fluorescent emitters were also chosen based on the transmission minima of the PNA, which appeared at approximately 660 nm. As such, for observations of PNA-bolstered stimulated lasing, the active medium selected for study was an organic fluorescent DCM dye [4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran] suspended in dimethyl sulfoxide (DMSO). DCM dye was selected due to its resonant emission at around 663 nm overlapping the transmission minima of the PNA as shown in Figure 25a. The DCM dye was prepared in varying concentrations through mixing with a vortexer and 5 minutes of sonication to break up persistent clusters of dye. After mixing, a pipette was used to transfer ~15 uL of each concentration onto either a glass slide or a piece of PNA. For PNAs, the dye molecules are assumed to situate themselves above the nanoholes in the liquid gain medium. The ideal situation would be for the molecules to situate themselves fully within the nanoholes, but this was not feasible with the methods used in this study.

The demonstration of spontaneous emission enhancement in the PNAs requires the observation of shortened decay times of some emitter integrated into the nanoarrays. Once again, CdSe QDs were selected for observing spontaneous emission enhancements due to the proximity of their specified peak emission (655 nm) to the 500 nm gap, 150 nm radius PNA resonance (660 nm). Before analysis, the CdSe QDs purchased from Sigma-Aldrich were prepared in a diffuse concentration (0.01 mg/mL) suspended in toluene and spin coated for 30 s at 1500 revolutions per minute onto pieces of PNAs as well as pieces of clean glass before being cleaned with DI water and flushed with nitrogen gas. By performing spectral analysis of the
QDs, the manufacturer’s specified peak emission of 655 nm was confirmed. Additionally, the baseline decay rate of CdSe QDs on glass was measured.

All optical measurements were conducted under standard atmospheric pressure and at ambient temperature. PL signals were acquired using a CCD camera and subjected to analysis.

Figure 25. Enhanced lasing emission by PNAs. (a) Experimental setup consisting of a 2 kHz at 515 nm and 2 ns pulse laser transmitted through a 5× objective onto a DCM dye drop placed onto a 300 nm diameter nanohole array with a 500 nm lattice spacing. Power-dependent PL spectra of the 0.5 mg/mL dye on the (b) nanoarray and (c) glass. (d) Comparison between the integrated PL peak intensities of the 0.25 mg/mL DCM dye on the nanohole array and the average peak intensity of the DCM dye points, and solid lines between dots are a guide to the eye.
with a HORIBA iHR550 spectrometer. Decay time measurements of the Quantum Dots (QDs) were performed using a time-correlated single photon counting setup. An ultrafast Coherent laser operating at 475 nm (80 MHz, 150 fs) was employed to excite the QDs through a 10× objective lens. The PL emission from the QDs was collected using the same objective lens and directed either to the spectrometer for spectral analysis or to a side exit, where it was guided into a fast-timing avalanche photodiode for temporal analysis. The signals gathered by the photodiode underwent analysis utilizing a single photon counting module (PicoQuant PicoHarp 300).

For observations of lasing enhancements in PNAs, the DCM dye was excited using a different Coherent laser at 515 nm (2 kHz, 2 ns pulse width) with a 5× objective lens set at a normal incident angle. The PL emission from the dye was collected by the same lens, subsequently dispersed, and analyzed using the spectrometer and CCD camera. As these observations stem from the metamaterial nature of the PNAs, it is pertinent to note that the objective lenses used in our experiments had an excitation and collection spot size of approximately 100 μm in diameter, encompassing an area of numerous lattice periods.

4.3 Results

The unique plasmonic capabilities of these nanohole arrays allow for lasing action as well as spontaneous emission enhancement in PNA-integrated quantum emitters. PNAs with surface lattice plasmon resonances near 660 nm were selected for these observations, and the organic DCM dye and the colloidal CdSe QDs were selected accordingly as active materials for their peak emissions around 660 nm. Though such phenomena have been reported on in previous studies involving periodic nanohole arrays, the capabilities demonstrated in this study were showcased using PNAs having a novel, cheap and simple design.
4.3.1 Room temperature lasing enhancement

By harnessing the surface lattice plasmon resonance in nanohole arrays, their potential applications can be demonstrated. This can be shown through the PNA’s ability to enhance the lasing behavior of the embedded organic DCM dye. This attribute opens avenues for the advancement of plasmonic chips with integrated, directional, and efficient coherent light sources.

In order to investigate the magnitude of the lasing enhancement offered by the PNAs, the power-dependent PL spectra were recorded and compared for both the DCM dye-covered glass and 500 nm-spaced, 150 nm-radius PNA for a range of excitation power densities starting from 11.3 W/cm² (which corresponds to around 3.5 mW incident power) up to the point at which the lasing response caused CCD saturation in either sample which occurred at a power density of around 59.7 W/cm² for dye-coated glass.

The effect of dye density on lasing was compared at various densities in DMSO ranging from 0.1 mg/mL to 5 mg/mL. In principle, the ideal concentration of dye is high enough for lasing to be physically viable (critical population inversion less than 1) while being low enough for an optimal, low lasing threshold to exist. In this study, various concentrations of dye drop-cast onto PNA and glass, and the lasing action threshold for each dye density was recorded for both.

The power dependent PL spectra of the DCM dye having a 0.5 mg/mL concentration on glass and on PNA are compared in Figure 25b,c. On the nanohole array sample, the dye showed a more prominent lasing action at a lower excitation power as compared to the dye on glass for a range of dye concentrations. The nonlinearity in the integrated peak intensity shown in Figure 25d, which compares the power-dependent integrated peak PL response of dye on nanoarray and glass, signifies that lasing began at an excitation power density of about 18.9 W/cm² for dye on
nanoarray. In comparison, the dye on glass does not show any clear indication of lasing before CCD saturation was reached. For dye on nanoarray, a robust plasmon-supported lasing mode exists at an excitation power density of 22.0 W/m$^2$ with a fwhm of 4.2 nm and a lasing quality Q greater than 150. This value is in agreement with those obtained in similar studies which incorporate fluorescent emitters into comparable arrays of nanostructures. For dye on glass, only spontaneous emission occurred in dyes with a range of densities under excitation as indicated by the broad PL bands observed having a minimum fwhm of 50 nm and the lack of nonlinearity for the blue trend on Figure 25d, which shows the average emission intensity of DCM dye on glass for dye concentrations ranging from 0.1mg/mL to 5mg/mL.

Though the higher concentrations of dye yielded lasing on glass as well as on the PNA, lasing occurred at a much lower power in the dye on NPA. For example, a dye concentration of 1 mg/mL yielded lasing on glass at an excitation power density of 69.0 W/cm$^2$ whereas on nanoarray this concentration of dye began to lase at 19.7 W/cm$^2$, which indicates a lasing threshold reduction factor of 3.5 for the dye on PNA. It should also be emphasized that until now previous studies demonstrating lasing action in open-cavity systems have been achieved only at low temperature whereas the work presented here demonstrates room-temperature lasing. In practice, this is inconvenient and introduces additional energy requirements for devices.

The lasing emission observed in PNAs holds promising implications for on-chip coherent light sources, offering a potential to surpass the constraints imposed by the optical diffraction limit on conventional lasers. These findings present opportunities for innovative applications in integrated photonics. Furthermore, the utilization of organic dye as a liquid gain medium demonstrates a favorable approach for achieving dynamic tunability in these plasmonic nanostructures. This method opens avenues for tailoring and adjusting the lasing properties of
PNAs, enhancing their versatility and adaptability for diverse technological and scientific endeavors.

As was done with organic DCM dye, room-temperature lasing was attempted for PNAs with incorporated CdSe QDs of varying concentrations in solution. By spin-coating dense concentrations of CdSe QDs suspended in toluene onto PNAs, the creation of lasing action was attempted. However, it is exceedingly difficult to achieve room-temperature lasing in colloidal CdSe quantum dots due to the Auger recombination process. Despite the advantageous alignment of the absorption and emission spectra of CdSe QDs with the plasmonic resonance of the PNA, the overall optical gain exhibited by CdSe QDs remains considerably limited when contrasted with that of organic emitters such as DCM dye. For future investigation of these PNAs for use with lasing enhancements, it may be more fruitful to consider utilizing solid-state materials characterized by superior quantum efficiency, such as perovskite QDs or 2D materials, whose potential for enhancing lasing action via PNA interaction could be a more feasible proposition for future research.

4.3.2 Emission rate enhancement

As of yet, photonic devices based on novel plasmonic materials are limited by the properties of their constituents. Materials used in advanced devices such as nanowires or semiconductors QDs are still limited in their slow temporal emission speed (10-20 ns) and low efficiencies (10-15%). Through the integration of these nanomaterials with plasmonic nanocavities, the efficiency of these devices can be significantly improved (50%), and operating frequencies over 110 GHz have been realized in such devices. Much research has been done on the optical properties offered by plasmonic devices, and many photonic enhancements have been demonstrated in various plasmonic systems. The novelty in this research comes from the
integration of colloidal CdSe QDs with these novel PNAs and the exploration of optical enhancements that such a pairing makes possible. In particular, the enhanced spontaneous emission of PNA-integrated CdSe QDs is explored and demonstrated.

![Figure 26](image)

**Figure 26.** Enhanced spontaneous emission by PNAs. (a) Schematic of the experimental setup for measuring CdSe QD-covered PNA. (b) Frequency matching between the PNA’s transmission (black) and PL emission of CdSe QDs on PNA (red). (c) Average measured decay curves of CdSe QDs on glass (black) and on a 500 nm lattice PNA (red). (d) Wavelength-dependent decay times of QDs on the glass and on the array (fast component). Square dots are data points, while solid lines between dots are a guide to the eye. 47
In this work, CdSe QDs are integrated into a 500 nm lattice, 150 nm hole radius PNA, and optical compared to CdSe QDs on a glass substrate alone via decay rate and PL measurements. The CdSe QDs of various concentrations suspended in toluene were spin-coated onto the PNAs for 1 minute at 1500 rpm. In this way, the CdSe are assumed to situate themselves in the nanohole cavities. The samples were illuminated by a pulsed, frequency-doubled laser (Coherent Chameleon Ultra II, 80 MHz, 150 fs) having a power density of 3 W/cm², tuned to 475 nm and focused through a 10× objective (Figure 26a). The CdSe QDs were selected specifically for their emission energy, which spectrally overlaps with the PNA resonance. In this way, the PL emission of the QDs matches with the peak absorption of the PNAs, as shown in Figure 26b. The decay dynamics of the CdSe QD excitonic states were investigated with a TCSPC apparatus, and the decay curves were represented as coincident count vs arrival time. In agreement with previously reported values, CdSe QDs on glass displayed an average decay of 9.6 ns over the wavelength range spanning the bulk of the CdSe PL peak from 645 to 700 nm. On the nanohole array, however, the decay of the CdSe QDs displayed two different components at peak transmission (around 663 nm) – a fast decay of 1.35 ns and a slow decay of 6.0 ns. The faster decay component can be attributed to the boosted PL intensity provided by the plasmonic enhancements of the electric field in the PNA. The slow decay can be attributed to the response from QDs that did not couple with the nanohole array. In the fast decay case, the spontaneous emission rate is enhanced by a factor of 7, which agrees with previous reports of emission rate enhancement for quantum emitters integrated with plasmonic nanoparticle array structures. In Figure 26d the decay times of QD on glass and on PNA (the fast component) are plotted at a 5 nm interval from 645 to 700 nm, following the bounds of each sample’s PL curves. Based on these results and the fact that the PNA-incorporated QDs display a
consistently fast decay time across the emission spectrum, one can conclude that the QDs couple
efficiently with the PNA’s plasmon resonance, further demonstrating the technological merits of
this PNA design.

The findings from the measurements conducted to enhance lasing and spontaneous
emission in this study suggest a range of practical applications. These include the potential
utilization of the straightforward and economical periodic PNA design in ultrafast light-emitting
diodes, optical sensing, and quantum information processing systems. For instance, it is feasible
to integrate the PNAs with innovative 2D nanomaterials like WSe2 or tailored perovskite
crystals featuring controlled defects. This integration could lead to the creation of a quantum
plasmonic device capable of serving as a bright source of single photons. Furthermore, it's worth
highlighting that the technique employed to manufacture PNAs could be adapted to generate
arrays of diverse geometries, such as arrays of square-shaped apertures. This can be achieved by
employing suitably sized nanocubes as seed particles in lieu of spherical beads. Specifically, by
using seed nanoparticles with specific shapes like nanowires or nanorods, individual rectangular
or groove-shaped nanowaveguides can also be produced. These nanostructures could be further
explored in studies focusing on phenomena such as superradiance and quantum entanglement
effects. Controlling the spontaneous emission rate of photonic materials is pivotal for the
effective generation of photons, and the design of nanoscale devices can be approached with this
fundamental consideration.

The outcomes of the measurements carried out to enhance lasing and augment
spontaneous emission, as detailed in this study, suggest numerous pragmatic applications. These
encompass possibilities like employing the uncomplicated and economical periodic PNA design
in diverse fields such as ultrafast light-emitting diodes, optical sensing, and quantum information
processing systems. To illustrate, a promising avenue involves the integration of pioneering 2D nanomaterials like WSe2 or purposely engineered perovskite crystals with defects into the PNAs. This integration holds potential for showcasing a quantum plasmonic device tailored for emitting brilliant single photons.

Equally noteworthy is the technique delineated for crafting PNAs, which can be extrapolated to manufacture arrays of various shapes – for instance, arrays featuring square-shaped apertures. This can be achieved by employing appropriately sized nanocubes as seed particles instead of spherical beads. Specifically, when employing seed nanoparticles with distinct shapes such as nanowires or nanorods, it becomes conceivable to fashion individual nanowaveguides with rectangular or groove-like configurations. These nanostructures offer a canvas for further exploration, particularly in studies delving into phenomena like superradiance and the effects of quantum entanglement. In recognizing the significant role that the control of a photonic material's spontaneous emission rate plays in the efficient production of photons, there is a strategic opportunity to devise nanoscale-based devices with this principle at their core.

4.2.3 Conclusion

To conclude this portion of this report, PNAs were designed and fabricated utilizing a straightforward pairing of the shadowing nanosphere lithography method and electron beam deposition. In stark contrast to the customary EBL approach, the method introduced in this study stands out for its simplicity and cost-effectiveness. Most notably, it enables the rapid fabrication of expansive, high-quality metasurfaces. These arrays, when paired with an organic dye in a liquid gain medium, demonstrated remarkable enhancements in lasing capabilities. Furthermore, the integration of CdSe QDs onto the arrays resulted in a significant augmentation of the spontaneous emission rate. Notably, this enhancement was approximately seven times faster
compared to QDs placed on a glass slide. In a departure from previous instances of highly deterministic emitter-cavity integration, the PNAs presented here function as open-cavity systems. This design simplification eliminates spatial discrepancies between emitters and optical modes of the cavity. As a consequence, these simplistic nanohole arrays hold the potential to propel emerging technologies and production capabilities forward to contribute to the industrialization of efficient plasmonic devices. Applications span a wide spectrum, including parts per million-level gas detectors, advancements in biomedical imaging and point-of-care devices, stimulated amplification devices, and the realization of ultrafast on-chip coherent light sources. Novel applications of existing robust constructions of light enhancing plasmonic arrangements such as this are crucial for progress in linear optical applications. In the next section, a novel example of the nonlinear tools needed to progress modern advanced photonic device technology will be detailed.
5. Nonlinear control of light-matter interaction: plasmonic nanopatch antennas

5.1 Introduction

There has been a shift in recent years in the field of optics towards the investigation of making nonlinear processes (such as SHG, THG, FWM, etc.) more efficient with the aim of making these phenomena feasible for use in affordable, easily producible technologies. The conversion of low frequency light to higher frequencies can have a major impact on applications from quantum cryptography to laser technology. Until recently, nonlinear processes for use in devices have been confined to bulky crystal materials having either centrosymmetric or noncentrosymmetric properties. Traditionally, perfect phase-matching (PPM) conditions must be satisfied, and a high intensity input is required for efficient nonlinear mechanisms to be supported in these materials. Progression in the field of plasmonics has revealed significant enhancements in the generation of nonlinear phenomena through the use of nanoscale metallic structures, which can localize strong electromagnetic (EM) fields to a scale smaller than the diffraction limit. This confinement of EM fields and intensity increase can be further boosted through PPM, which can be engineered to have desired resonances in plasmonic nanostructures to meet specific needs. Different variations of individual and arrays of plasmonic cavities exist that have previously demonstrated enhanced nonlinear frequency conversion. Plasmonic metasurfaces comprised of arrays of metallic nanoparticles have been shown to offer a flexible approach to nonlinear generation enhancement.

Generally, plasmonic nanocavities are constructed from gold, which in bulk only supports third-order processes due to its centrosymmetry. At the nanometer scale, however, Au can be made to have a large surface to volume ratio, allowing for a broken symmetry and the support of second-order processes as well. By also incorporating an overlap of the fundamental
input wave and the plasmon resonance, the absorption rate of the input field is significantly increased. Taking this approach a step further, the resonance of plasmonic nanocavities can be matched to the nonlinear signal frequencies as well as the frequencies of other modes such as Fabry-Perot resonances supported in a gap layer. The results following in this chapter show that robust resonance matching for nonlinear generation enhancements can be accomplished quite nicely through the use of nanocube-film coupled NPAs, which can be made to generate a powerful SHG signal. So far, this functionality of NPAs has been scarcely explored. Furthermore, strong coupling has not yet been demonstrated in NPA structures. This phenomenon in which multiple resonant systems interact with enough strength to form polaritons is a crucial and powerful tool in advanced modern optoelectronics design, and efficient devices that support strong coupling are crucial for the progression of quantum computing technologies.129

In this study, the enhancement of SHG is demonstrated through the utilization of a gap-mode plasmonic nanocavity built upon the NPA design framework. The gap-mode plasmon resonance frequency inherent to the film-coupled nanocube NPA is strategically tailored to overlap with the fundamental input frequency, resulting in an amplified photonic density of states within the confined sub-10 nm gap volume sandwiched between the nanocube and film. Additionally, the alignment of the SHG frequency with the resonance frequency of one of the NPA higher-order waveguide cavity modes is established, thereby contributing to a heightened conversion efficiency. In comparison to alternative plasmonic platforms previously recognized for their SHG enhancement capabilities, the NPAs exhibit unparalleled field enhancement via the generation of FP or gap-plasmon resonances, giving rise to localized intensity enhancements within the narrow gap layer.100–102
5.2 Methods

5.2.1 Plasmonic NPA fabrication

The plasmonic NPAs engineered in this study are comprised of 100 nm silver (Ag) nanocubes situated on a sub-10nm spacer layer (made of either ALD-coated ZnO or LBL-coated PE layers) bonded to an atomically smooth gold layer of 100 nm thickness. The fabrication process begins with the deposition of Au on a polished silicon (Si) wafer via electron beam evaporation. By using the template stripping technique, the Au was removed from the Si substrate and transferred to glass, creating an atomically flat Au surface which is dependent only on the polished Si surface smoothness. A thin film of ZnO was deposited by ALD, and its thickness was confirmed with AFM to be between 3 and 5 nm (Figure 27a). In an alternate version of this configuration illustrated in Figure 27b, the gap layer was constructed through LBL assembly using a dip-coating technique. The Ag nanocubes, purchased from Nanocomposix with a concentration of 1 mg mL\(^{-1}\) and suspended in solution, were drop-cast onto the spacer gap and allowed to bond to the surface with random orientation. Displayed in Figure 27a is the SEM image of a finished NPA sample used for single NPA measurements, which shows a nice separation of Ag nanocubes on the surface of the gap. The surface coverage

![Figure 27 (a) SEM image and (b) illustration of NPAs](image-url)
of the nanocubes was statistically determined to account for approximately 5% of the sample surface area. In the case of ensemble NPA measurements, before drop-casting, the solution was concentrated by centrifuging the stock solution and subsequently skimming the excess sparsely populated solution to create a concentration of approximately 100 mg mL⁻¹.

In order to further explore the photonic capabilities of this construction, an organic quantum emitting dye (IR-1048) directly purchased from Sigma Aldrich and suspended in Dimethyl Sulfoxide (DMSO) was incorporated into the NPAs via drop-casting. DMSO was selected as the solvent for the IR-1048 due to its slow evaporation and its compatibility with the optical properties of IR-1048. Various concentrations of dye were tested in order to determine the optimal density for maximum photonic output. When the dye was made too dense, the laser was unable to break through the organic matter to reach the plasmonic structure beneath, and photonic response was minimal. However, for investigations of strong coupling in the linear regime, it is desirable to maintain a consistent but powerful signal. Therefore, low concentrations of dye are also problematic, as the high laser power necessary to induce strong coupling quenched the organic molecules quickly. Ultimately, the dye was made to have a high density of 50 mg/mL in order for a thorough coverage of dye molecules near the bottom edges and corners of the NPAs where the electric field is most strongly confined. Due to the rapid quenching of the dye under the heavy excitation necessary to induce SHG, the suspension of these molecules in solution paired with the optimally dense concentration of dye molecules provides a useful automatic replenishing of photonically spent dye. Using the dispersed NPA samples with integrated organic quantum emitting IR-1048 dye, the fundamental and SHG signals of the dye/NPA combinations were investigated for evidence of strong coupling.
5.2.2 NPA Characterization

The determination of the spacer gap thickness in the NPA assembly is crucial for fine-tuning resonance parameters and achieving phase matching between fluorescent emitters and NPA. To verify the gap thickness upon ALD application of ZNO onto the Au-coated Si substrate at 200 °C for 150 and 300 cycles, an AFM microscope was used prior to nanocube deposition. Heat resistant tape was applied to the substrate prior to ALD, and an edge was formed once the tape was removed after ZnO deposition. Figure 28 shows the resultant AFM thickness data acquired.

![AFM characterization of ZnO thin film for PNA assembly.](image)

For the experimental characterization of plasmonic NPAs, a Nikon LV-150 bright/dark field microscope is used. The microscope used here is modified such that either the white light or excitation laser both excites the sample and collects the resulting white light or SHG reflection signal from above, which is achieved through a series of interchangeable objective lenses. For SHG enhancement measurements, the excitation laser, having a tunable wavelength (Coherent Chameleon, 80MHz, 150 fs) spanning 680-1080 nm, is tuned to be in resonance with the NPA mode as revealed from the white light reflectance data (Figure 29). The SHG signal is subsequently dispersed by a Horiba iHR550 spectrometer to be detected by a Horiba Synapse charge coupled device. A 700 nm long-pass filter is applied to spectrally filter the laser excitation input, while a 550 nm short-pass filter is employed to filter the SHG signal. For measurements
involving an ensemble of NPAs, a 20X (0.4 NA) objective lens is employed for both excitation and collection. In single NPA measurements, a 100X (0.9 NA) lens is utilized, and the selective extraction of signal from individual NPAs is achieved by employing a pinhole aperture positioned at a confocal image plane.

White light reflection measurement was performed on a large ensemble of NPAs in order to determine the fundamental plasmonic mode of the NPA metasurface. The fundamental plasmonic resonant mode of the single NPAs is also analyzed through white light reflection measurements. Subtle variations in the NPA geometry, including differences in nanocube size and ZnO gap thickness, may result in disparities in the fundamental resonance wavelength. This phenomenon is evidenced by the scattering spectra of multiple individual NPAs, which are depicted in Figure 29 and originate from the same sample. Evidently, discernible fluctuations in

Figure 29. Scattering spectra of several individual NPAs.\textsuperscript{129}
the fundamental resonant wavelength are observed among the individual NPAs, spanning approximately 950 nm to 1050 nm.

5.3. Results

5.3.1 SHG Enhancement with NPAs

With the spacer gap in the NPAs was engineered to have a strong absorption band around 960 nm, as indicated by the dip in the reflectance in Figure 29. A ZnO gap thickness of 3 nm was required to achieve this strong localized gap-plasmon resonance at this wavelength. From the plot shown in Figure 30a, it is clear that the SHG from a bare gold sample without ZnO or Ag nanocubes presents a much lower intensity signal than the ultimate NPA configuration. The second-order nature of the signal is confirmed by the slope of the fitted power dependence line shown in the inset of Figure 30, which is very close to 2. The role of the NPA plasmonic gap-mode resonance in the SHG process is further verified through the systematic variation of the input laser wavelength across the resonance peak. The data acquired from this excitation wavelength-dependent SHG intensity scan for an ensemble of NPAs characterized by a 3 nm ZnO spacer gap layer is demonstrated in Figure 30b. While the input laser's intensity remains constant, the SHG peak intensity reaches its zenith when the fundamental wavelength coincides with the reflectance curve's minimum, as expected. This alignment corresponds to the point of least reflection for the NPAs, at which wavelength input laser absorption is maximized and optimal conditions for heightened SHG efficiency are supported. There is also a strong plasmon resonance evident within the NPA system at approximately 485 nm (Figure 30a). This resonance is related to the higher order waveguide cavity modes intrinsic to the metal-insulator-metal configuration, along with the quadrupolar modes exhibited by isolated nanocubes. Consequently,
the SHG frequency at 480 nm falls within the full-width-at-half-maximum range of the NPA's higher resonant modes, providing an additional boost to the SHG output intensity.

The SHG intensities of the various configurations of the NPA that exist during construction are excited with the same laser power and compared in Figure 31a. All configurations have a fundamental resonance at 960 nm, and although nary a peak is noticeable for the SHG signal of a 3 nm ZnO layer on glass, there are similar miniscule SHG peaks evident in the intensity plots of bare Au and bare Au coated with a 3 nm ZnO layer. However, these SHG peaks pale in comparison to the ultimate configuration upon which NPAs are deposited. Clearly, the addition of Ag nanocubes significantly enhances the SHG signal. These measurements thusly support the evidence that the plasmonic gap mode plays an important role.
in bolstering the efficiency of the SHG process. Care was taken to account for the normalization of the area covered by the nanocubes for the accurate calculation of the SHG enhancement factor. Based on an estimated 5% average nanocube surface coverage and a laser spot size of approximately 5µm, an enhancement factor of 10700 was extracted for the broad NPA metasurface, which is in line with enhancements demonstrated by Zeng et al. using a more tediously tailored structure of periodic NPA arrays utilizing polymer shell encapsulated nanocubes. The NPA design utilized in this study, however, is superior to that used by Zeng et al., as a ZnO spacer gap is utilized rather than a polymer shell, which could potentially be damaged by the required laser intensity for highly efficient SHG. The alternative NPA design used in this study utilizes a PE spacer gap, though results for these structures show a smaller SHG intensity (Figure 31b). One explanation of this difference in response may involve the difference in metal-dielectric interfaces and corresponding nonlocal bulk responses. More apparently, this difference in SHG efficiency is to be expected, as the second-order susceptibility of ZnO (≈10.2 pm V\(^{-1}\)) is greater than that of the PE polymer (≈6.5 pm V\(^{-1}\)). Thus, it may be possible to increase the SHG enhancement factor of this construction by using another semiconductor gap layer having a higher second-order susceptibility such as Al\(_{1-x}\)Sc\(_x\)N thin films, which can have a X2 of up to ≈10.2 pm V\(^{-1}\) depending on relative concentrations of Al and Sc.

The results presented herein are supported by COMSOL Multiphysics nonlinear simulations which investigate the SHG from various combinations of the NPA constituents, as well as the finished NPA (100 nm Au film, 3 nm ZnO on glass, 3 nm ZnO on 100 nm Au film, and the proposed NPA structure). These simulated results shown in Figure 31c were obtained by multiplying the continuous wave simulation acquired in the frequency domain, with a frequency-
domain Gaussian profile that emulates the envelope of the pulsed laser illumination applied to the investigated structures. These results mirror those achieved experimentally as shown in Figure 31a, verifying the crucial role of the NPA in SHG enhancement. The increase in field intensity along the structure caused by the incoming wave is computed using the maximum ratio $E/E_0$. Here, $E_0$ signifies the amplitude of the incident electric field of the input wave, while $E$ corresponds to the highest induced electric field within the nanogap. The outcome at the

Figure 31. Substrate dependent SHG intensities. a) Comparison of measured SHG spectra from NPAs, ZnO, Au, and ZnO/Au. The vertical axis is slightly offset for clarity. b) Comparison of the SHG spectra from NPAs with ZnO and PE spacer gaps. c) Computational study of the SHG spectra from NPA using a ZnO spacer gap, ZnO, Au, and ZnO/Au. d) Computed field distribution at the fundamental frequency of NPAs by using ZnO as the spacer layer. \(^{129}\)
fundamental resonance is illustrated in Figure 31d, which depicts the strong electric field localization at the bottom corners of the NPA.

5.3.2 Enhancement of SHG from single NPAs

Single NPAs were examined as described in section [single nanostructure spectroscopy], and the measured SHG spectra was recorded at various excitation powers (Figure 32a). Figure 32b shows the dark-field scattering spectrum of the same singular NPA having a maximum near 993 nm. By tuning the laser and exciting the NPA at this wavelength, the SHG power dependence is plotted as shown in the inset of Figure 32a, indicating the expected second-order power dependence ($\approx 1.924$) and providing further evidence to backup the nonlinear nature of the observed phenomena.

Accounting for the normalization factor due to the laser spot size (5µm) against the nanocube size (100 nm) and comparing the integration of the single NPA peak intensity with that of a bare Au film reveals a single NPA SHG enhancement factor of 2070. It should be noted that

Figure 32. SHG of single NPAs. a) Power dependent SHG spectra from a single NPA. The inset shows the excitation power dependent SHG intensity. b) Dark-field linear scattering spectrum of the NPA measured in (a). 129
this is representative of one isolated single NPA, which is somewhat significantly smaller than the enhancement factor due to an ensemble of NPAs. The variation observed between a single NPA and an ensemble of NPAs can be attributed to the localized variation in gap thickness, as well as the minute differences in the NPA structures and orientations. The variation in gap thickness due to ZnO surface roughness and the up to 10% size variation in the 100 nm nanocubes can account for a large change in the fundamental frequency (and thus the SHG response at a given fundamental input) of an individual NPA as evidenced previously in Figure 32b.

5.3.3 Nonlinear strong coupling of organic dye using NPAs

The examination of nonlinear light-matter interactions in this NPA design continues with the incorporation of quantum emitters in order to investigate the strong coupling response supported in the linear and nonlinear regimes. The design of the NPAs, which have a strong gap-

![Figure 33](image)  
**Figure 33.** SH exciton-polaritons and strong coupling in the nonlinear regime. a) Linear NPA reflection (without dye, red) and the IR-1048 dye absorption (cyan, without NPA). b) SHG nonlinear signal with and without dye. Substantial resonance splitting in SHG is obtained only in the case of strong coupling (with dye curve). The inset shows a schematic of the dye/NPA structure.¹²⁹
mode resonance in the 900-1050 nm range, is tuned to be optically compatible with an IR-1048 dye suspended in DMSO, which has a strong absorption band in this region. The linear response of NPA reflection without dye (red curve) and the absorption of IR-1048 dye (without NPA, cyan curve) is presented in Figure 33a. Also shown on Figure 33a is the frequency of the pump laser, which was selected to be at the higher dye absorption band near 930 nm. Thus, the NPA fundamental mode is designed to clearly overlap spectrally with the dye absorption band from around 930 nm to 940 nm in order to facilitate exciton-plasmon coupling. The SHG measurements from an NPA sample with and without dye molecules excited with the same input pump laser power of ~6 mW is shown in Figure 33b. In this case, the IR-1048 dye was made to have a high dye concentration (∼65 × 10⁻³ m) that can be unstable under high excitation due to the quenching effect. The observed behavior of the IR-1048-incorporated NPA showed a broadened SHG peak which eventually split into two distinguished peaks. These peaks are the upper and lower nonlinear second-order polaritonic states. Remarkably, this indicates that the strong exciton-plasmon coupling at the fundamental frequency of the NPAs leads to the formation of polaritons, which are up-converted to SH nonlinear polaritons with an observed Rabi splitting of ΔE = 19 meV. It should be noted that previous reports have shown large Rabi splitting in emitters incorporated into various other metasurface constructions. For instance, Drobnyh and Sukharev recently showcased a Rabi splitting of up to 68 meV at the SH frequency through the integration of emitters exhibiting an absorption band aligned with the fundamental frequency of nanohole arrays. More recently, Li et al. empirically displayed a substantial Rabi splitting at the SH frequency within a strongly coupled system involving a plasmonic nanorod and a monolayer of WSe₂. However, the observed Rabi splitting of ΔE = 19 meV is significant, as such nonlinear polaritonic behavior has until this study not been observed using
the NPA structure. In principle, a more narrow resonance bandwidth than the NPAs designed in this study could lend to a wider energy splitting with a more pronounced nonlinear polariton generation.

Though the potential exists to observe exciton-plasmon coupling at the fundamental frequency by examining the energy splitting within the reflectance spectrum of a hybrid structure that involves NPAs and dye, or by analyzing the scattering reactions from individual NPAs, the resonance band exhibited by the NPAs is comparatively broad (≈200 meV), which is roughly 20 times wider than the expected energy splitting (roughly equivalent to ΔE/2) at the fundamental frequency. Given the broad resonance band characteristic of single NPAs, as revealed from the white light reflection spectrum, detecting the energy splitting spectrum signature of exciton-plasmon coupling becomes quite difficult. To capture a small energy splitting at the fundamental frequency, an alternative approach was adopted by analyzing the reflection of the pump laser while it was incrementally scanned across the fundamental frequency. In this case, an NPA sample with a resonance peak at around 970 nm (Figure 34) exhibited a discernible

![Image](image.png)

*Figure 34. Rabi splitting at the fundamental frequency of NPA with a PE LBL-fabricated spacer layer.*

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widening and splitting of the laser line. The calculated energy separation amounts to 9 meV, closely approximating $\Delta E/2$, where $\Delta E$ equals 19 meV—equivalent to the splitting identified at the SHG. In comparison to the energy splitting witnessed in the reflected laser at the pump frequency, the division observed in the SHG peak displays greater breadth and increased prominence.

In future studies on nonlinear polaritonic states supported by emitters integrated with NPAs, alternative robust quantum materials such as quantum dots or 2D materials could be utilized. The energy splitting value is directly related to the laser intensity and emitter density, so more robust emitters should in principle widen the Rabi splitting. Additionally, the parameters of the ZnO gap thickness or Ag nanocube size utilized in the NPA could be tweaked so that the fundamental frequency could be tuned across the dye absorption band in order to further verify strong coupling by showing anti-crossing behavior. Such a set of measurements would require some degree of flexibility in the experimental setup limitations, as small changes in NPA parameters result in large shifts of their fundamental frequency in the 950 to 1050 nm range, greatly reducing the detection efficiency at the fundamental and SH frequencies. Due to the range limitations of the camera-detection efficiency utilized in this study, there was not enough flexibility to demonstrate anti-crossing behavior. However, the results presented here are sufficient to conclude the existence of both linear and nonlinear strong coupling of the dye/NPA configuration at the fundamental and SH frequencies, respectively.

5.4 Conclusion

Through the application of SHG signal measurements from both ensembles of NPAs and individual NPAs, an SHG enhancement factor of $10^4$ is observed for the ensemble of NPA structures relative to the bare gold (Au) film. Furthermore, the incorporation of organic dye
molecules possessing pronounced absorption characteristics aligned with the fundamental resonance of the NPAs yields the observation of SH polaritons, revealing a Rabi splitting of 19 meV. This intriguing phenomenon stems from the robust exciton-plasmon coupling operating at the fundamental resonance of the NPAs, an interaction that is markedly amplified and coherently transferred to the SH frequency via the up-conversion process. Notably, it is important to acknowledge that while nonlinear effects have been investigated for their capacity to heighten the sensitivity of plasmonic sensors, limited prior research has demonstrated the manifestation of nonlinear-mediated strong coupling. The work presented in this chapter prominently addresses this gap in the literature by conclusively illustrating such coupling effects. Furthermore, these results pave the way for the future of quantum information technologies by providing an optical design capable of supporting nonlinear polaritonic states and perhaps nonlocal polariton condensates in NPA metasurfaces.
6. Nonlinear control: chiral metasurfaces

6.1 Introduction

Chiral and topologically complex metasurfaces are interesting due to their anisotropic response to circularly polarized light between left-handed and right-handed turning structures as well as their ability to alter the plane of polarization of an incoming signal, which could also have important implications in quantum optics. Due to their directional nature, dielectric chiral structures have the ability to lock-in local polarizations, leading to emission behavior that depends on the direction of light propagation. These structures can also exhibit tunable emission, powerful confinement and strong plasmonic enhancements. These effects can be further amplified by employing sophisticated materials and designs, such as in the case of dielectric-metallic plasmonic chiral structures. Advances in chiral nanofabrication techniques such as direct laser writing, multilayer lithography and self-assembly via scaffolds have allowed for an increased flexibility in applications and photonic responses. Apart from their pertinence in photonic device research, the absence of mirror symmetry has generated interest in chiral structures for their use in nanorobotics and chemical sensing. Currently, work is underway to characterize the nonlinear properties of chiral metastructures and to increase SHG efficiency. It is likely that the next decade will see much progress in the ease of fabrication and overall applicability of plasmonic chiroptical metamaterials.

The primary important parameter in the usefulness of chiroptic metastructures is their efficiency in selectively transmitting broadband circularly polarized light. Variance in this transmission amount based on their orientation is also an interesting parameter. Experimentation is crucial in revealing these attributes of chiral photonic 3D structures, especially for nonlinear optical effects, as their complicated architectures yield complex 2nd order susceptibility tensors.
which are exceedingly difficult to predict. However, experimentation comes with its own challenges, as different modes may exist depending on the specific three-dimensional incidence of illumination on complex three-dimensional structures. While this makes full characterization difficult, this versatility can be made into a strength in practical devices with a broad range of tunability. It should be noted that in this study, all measurements were taken at normal incidence to the samples’ surface due to limitations in the available tools, which does not eliminate all unknowns of the chirals’ second order susceptibility tensors. Thus, there are inherent future improvements to be made to this study, which will be discussed at the end of this chapter.

Indeed, chiral metasurfaces hold great potential in both their practical applications in modern advanced devices, as well as their use as a tool for exploring fundamentals in the physics of nonlinear optical activity. This chapter deals with the investigation of CD and OR in metasurfaces of nanoscale helical and “L-shaped” chiral structures fabricated by GLAD.

6.2 Methods

Considering the circular nature of chiral metastructures, it is necessary to use multiple methods of examination in order to fully characterize their optical capabilities. In particular, the behavior of transmitted circularly polarized light must be examined at different excitation wavelengths, varying powers and along a range of rotation of the chiral sample. The whitelight absorption of the chiral metasurfaces was carried out with by exciting the samples, which were mounted vertically on a rotational stage, with a broadband white light generator (ThorLabs SLS210L), focusing and collecting the signal with an Ocean Optics HR4000 spectrometer. By dividing the background-subtracted white-light transmission signal of the samples of interest by that of the bare substrate, and absorption spectrum can be created. This absorption spectrum shows the resonance of the samples. By also rotating the sample holder to the left and right,
Information on the absorption degree of polarization (DOP) can be obtained using the general equation for the determination of DOP:

$$DOP(\%) = 100 \times \frac{(LH - RH)}{(LH + RH)}.$$

where LH and RH are the collected whit-light absorption spectra (or alternatively the integrated peak values of the spectra in the case of laser transmission) from LH-circular and RH-circular polarized light impinging on the sample, respectively.

The setup utilized for the investigation of coherently excited chiral metasurfaces in this study is shown in Figure 35, in which a tunable-frequency laser (Coherent Chameleon II) in the wavelength range of 790 – 1040 nm is used as an excitation source either at the fundamental wavelength or allowed to pass through a frequency doubling box to convert the beam into the

*Figure 35. Setup for investigation of CD and OR phenomena in chiral metasurfaces at the fundamental and second harmonic transmitted signal.*
second harmonic in the range of 395 nm – 520 nm. Then, to ensure that the light is properly circularly polarized, a Glan-Thompson linear polarizer first prepares the light with a linear polarization. Once the excitation beam is prepared with perfect linear polarization, the light enters a quarter wave-plate alternating between left-handed (-45°) and right-handed (+45°) circular polarization. After being circularly polarized, the excitation signal passes through either a 10x or 20x objective, illuminating the chiral metasurface sample, which is mounted on a rotating stage. Transmitting through the samples, which are fabricated on translucent material, the signal is then received through either a 5x or 10x objective mounted below the rotating stage. Finally, the signal is routed to the spectrometer and CCD camera (Horiba Synapse) for data collection.

Within this framework, several different types of measurements are performed on three different types of chiral metasurfaces manufactured at the University of Nebraska – Lincoln (UNL) with varying parameters: helical plasmonic nanostructures with a range of numbers of

![Figure 36. SEM image of all-dielectric (Left) and plasmonic (Right) V-shape chiral structures fabricated at UNL. Insets show illustrations of the different nanostructures.](image-url)
turns (1, 2, 3 and 4 turns), helical dielectric nanostructures with varying numbers and orientations of turns (1, 2 and 3 positive turns, as well as a 2 negative turn sample) and “L-shape” angled structures with varying GLAD angle parameters (Figure 36). Setting out on this experiment, the measurement which received the bulk effort was the SHG DOP for the different helical structures. Initially, since the rotationally symmetric helical samples were assumed to transmit signals in a rotationally symmetric way, the difference in transmission based on sample orientation was not considered, and the samples were examined with an arbitrary, unchecked orientation. Of course, these initial measurements showed that the chiral samples had a clear dependence on orientation for their CD transmission at the second harmonic due to the fact that some samples showed large DOPs while others did not, with no clear trend between them. Thus, it was determined that OR would play a critical role in the outgoing plane of polarization, and the orientationally-dependent measurement approach was adopted.

Angle-dependent SHG PL signals were detected by the CCD upon excitation of the chiral samples by the fundamental wavelength laser at various intensities and sample orientations.

Figure 37. Rotational measurement of "V-shapes" using "V" bisector as a reference of origin
Utilizing a homemade LabView program, the peak of each obtained PL intensity was integrated. By analyzing each relative LH/RH peak of a given excitation power, wavelength and sample orientation, the DOP can be determined using Equation X. For the helical samples, the origin (where the sample rotation begins and ends) were arbitrarily chosen and a scratch made on the sample substrate was used as reference. For the “L-shape” samples, artefacts were left behind periodically across the sample from the GLAD fabrication which resembled a “V” shape, as shown in the image in Figure 37. For these, the bisector of the L-shape was selected as the origin of rotation.

By exciting samples with the fundamental laser signal prepared with a circular polarization, the CD and OR of the chiral structures can be probed. Upon transmission of the sample at the frequency range of approximately 795 nm to 1040 nm with a low power, the raw signal of the laser can be analyzed at each wavelength to determine the relative raw laser absorption. This measurement could be similarly done by exciting at the SHG wavelength and sensing at the same wavelength for low powers in order to determine the raw SHG laser absorption of the sample. Taking the integrated value of the raw laser peaks for these measurements, an approximate absorption spectrum can be made.

6.3 Results

6.3.1 All-dielectric helical metasurfaces

The all-dielectric helical (ADH) chiral samples tested in this study which were fabricated by GLAD with Si on glass substrates as shown in Figure 38 varied by number and orientation of turns. In order to explore the relationship between number of turns and either fundamental or SHG transmission efficiency, OR or CD, three different ADH metasurface structures were fabricated with either 1, 2 or 3 turns. Two 2-turn ADH samples were fabricated with oppositely
spiraling helices so that the relation between turn orientation (LH or RH) and the operational parameters of interest could also be explored. The characterization of the ADH metasurfaces comprised of GLAD-fabricated Si “corkscrew” structures on glass began with determination of the white-light transmission degree of polarization. To do this, the DOP of the ADH structures based on their white-light absorption was analyzed as described in section 6.1 and is shown in

Figure 38. SEM image and illustration of helical structures fabricated at UNL on glass substrate with Si (all-dielectric, top) and Ag-doped Si (plasmonic, bottom). \textsuperscript{147}

Figure 39. The absorption spectra hint at several relationship between either the number of turns or orientation of turns on the ADH and the DOP. For the number of turns, it appears as though there is an odd parity between the number of turns and the skew of the white-light absorption DOP. For instance, in the +1 and +3-turn ADH samples, the DOP is skewed to the positive for
white-light absorption at the lower end of the spectrum, while the $+2$-turn ADH skews towards the negative. As far as helical orientation goes, the $-2$-turn ADH DOP skews towards the positive at the lower end of the absorption spectrum while the $+2$-turn ADH DOP skews towards the negative. Curiously, the $-2$-turn ADH seems to have a strong DOP skewed towards the positive.

Figure 39. (Left) Example of white-light DOP determination for 1-turn ADH sample. (Right) White-light absorption DOP for ADHs.

Figure 40. (Left) DOP of ADH SHG transmission. (Right) DOP of ADH fundamental transmission.
negative at the higher end of the absorption spectrum, while the +1, +2 and +3-turn ADH samples display a loosely positive DOP at the upper end. This could suggest that the orientation of the chiral structures on the substrate impact the directional transmission of light at specific wavelengths, which could be a profound result if confirmed through further study.

Going further, the SHG transmission from fundamental laser excitation and the SHG raw transmission from SHG laser excitation signals emitted through each of the ADH samples upon illumination were collected at varying powers, wavelengths and sample orientations. From this data, the integrated value of the PL emission peak from the LH and RH circularly polarized light at each wavelength was extracted using a homemade LabView program. All chiral samples showed a robust set of SH peaks, with the maximum peaks corresponding to fundamental excitation wavelengths which coincide with the peak SH absorption.

The DOP calculated using the SHG intensity values is shown in Figure 40. All ADH samples show a roughly inverse DOP trend between SHG transmission from fundamental excitation and raw laser transmission in the SH range. The +1-turn and -2-turn chiral go from positive in the SHG-generated transmission to negative in the raw SHG laser transmission data sets with the +3-turn ADH maintaining a positive SHG-generated DOP and a negative DOP for SHG transmission. The +2-turn ADH, however, maintains a positive DOP for SHG transmission but skews to the negative, hovering near 0 in the upper end of the raw SH transmission DOP spectrum. In general, the SHG transmission DOPs tend to be slightly stronger than the raw transmission in the SH region.
6.3.2 Plasmonic helical metasurfaces

The plasmonic helical metasurfaces were also characterized for their OR and CD attributes by white-light transmission and transmission from a range of excitations at the fundamental or SH frequencies. The plasmonic helical metasurfaces consisted of a range of Ag-doped Si helical structures having 1 to 4 turns, similar to the one shown in Figure 41. In this way, the relationship between number of turns and photonic efficiency could be tested. The LH and RH circularly polarized white-light transmission for 4x-turn plasmonic helical (PH) structures is shown in Figure 42, along with the white-light transmission DOP for all PH samples. The DOP for these structures indicates the preferential transmission of LH circularly polarized light for all PH samples.

Figure 41. (Left) Difference in white-light absorption for LH and RH circularly polarized white light transmitted through 4x-turn plasmonic helical metasurface. (Right) White-light absorption DOP for ADHs.
Again, the SHG transmission from fundamental laser excitation and the SHG raw transmission from SHG laser excitation signals emitted through each of the PH samples illuminated at different laser powers were collected along with wavelengths and sample orientations. Similar to the analysis and treatment of the ADH structures, the integrated value of the PL emission peak from the LH and RH circularly polarized light at each wavelength was extracted, and the DOP values displayed in Figure 42 were calculated. Though the white-light transmission appears consistent for all PH samples, the DOP values reveal several inconsistencies between the SHG transmission and raw fundamental transmission. These inconsistencies could be due to the OR of the chiral samples. Initially, OR was not considered, and the chirals were assumed to have rotationally symmetric optical transmission. Thus, initial measurements were taken for arbitrary sample orientation relative to other measurements. Thus, the orientational transmission was neglected, causing variation in measurements. As can be seen

![Figure 42](image-url)

*(Left) DOP of PH SHG transmission due to excitation from 800 nm to 1040 nm. (Right) DOP of PH fundamental transmission from 400 nm to 520 nm.*
from the plot in Figure 43a displaying a near 2nd-order SHG power dependence from chirals excited with circularly polarized light, the sample orientation can have a significant impact on the SHG from circularly polarized excitation even for seemingly rotationally symmetric 3D photonic structures. This could be due to the dichroic nature of the chiral structures.

Considering this behavior, the PH chirals were explored further by varying the excitation power

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**Figure 43.** Dichroic behavior of PH structures. (Left) SHG power dependence for perpendicularly oriented sample. (Right) SHG DOP for data plotted on the left.

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**Figure 44.** Left: PH chiral SHG transmission DOP average over one half sample rotation. Right: Log-log plot of 4-turn PH chiral showing near-2nd order power dependence.
and taking an average SHG signal over one half of the samples’ rotation as shown in Figure 43b. Curiously, the excitation wavelength also has a significant impact on the SHG DOP of the samples, as indicated in the polar difference between the DOP of the 4x-turn plasmonic structure as excited at 830 nm and 930 nm, which is supported by the shift in white-light absorption from negative to positive around that region. Additionally, the 2-turn PH sample showed an average negative SHG DOP from an excitation of 930 nm, which is contrary to the data taken at an arbitrary sample orientation in Figure 42; This data is also contradictory to the white-light absorption for the 2-turn PH chiral at 930 nm, which requires further investigation. In general, however, the rotationally averaged SHG DOP shows more consistent trends than data taken at a single, arbitrary orientation. indicates that the SHG transmission has small dependence on laser excitation power, with the largest dependence existing in the 2-turn PH chiral structures. Furthermore, the second-order nature of the SHG transmitted in the 4-turn PH chiral structure is supported by the

Figure 45. SEM images and illustrations of L-shaped all-dielectric Si (left) and plasmonic Ag-doped Si (right) metasurfaces manufactured via GLAD at UNL.
SHG peak integral power dependence plot having a slope of 1.76 for LH-polarized and 1.79 for RH-polarized transmission from 930 nm excitation averaged over one half sample rotation, shown on the right of Figure 44. This confirms the nonlinearity of the SH generated signal. Though difficult to characterize fully, this attribute of circular dichroism in these PH chiral structures warrants further investigation, as it may offer a wider range of versatility in chiral-based devices.

6.3.3 L-shaped chiral metasurfaces

L-shaped chiral metasurfaces composed of two linear pieces of dielectric columns with varying angles between were synthesized by the GLAD chiral fabrication technique. These structures whose SEM images are shown in Figure 45, consist of all-dielectric Si L-shapes with \( \beta = 15^\circ, 45^\circ \) and \( 90^\circ \) and Ag-doped Si plasmonic L-shapes having \( \beta = \pm 60^\circ \). These structures were assumed to have complex orientation-dependent optical properties due to their lack of rotational symmetry, and thus, careful consideration of the rotational variation was given to the samples during their characterization. To begin, the white-light transmission of each L-shape

![L-shaped topology white light transmission DOP](image)

![L-shaped enantiomer degree of polarization](image)

*Figure 46. (a) White-light SHG DOP and (b) laser-excited SHG DOP at 100mW excitation for each L-shaped chiral metasurface.*
sample was taken in the same manner as with the helical structures. However, due to the V-shaped artifacts left during the GLAD process, the reference point for the L-shapes, selected to be the bisector of the V-shapes, was easier to track and made for a consistent reference for all samples. Thus, for the white-light transmission measurements, a combination of a linear polarizer and quarter waveplate were used to prepare the white light with a circular polarization. For the white-light DOP determination for the L-shaped structures, the quarter waveplate was adjusted to create LH and RH circularly polarized light, and the L-shaped samples were positioned in the sample holder so that the V-shaped artifacts would be upright (Figure 46a). From this data, the white-light DOP shown in Figure 46b was extracted. The L-shaped metasurface fabricated with $\beta = 45^0$ showed the most prominent white-light DOP, peaking at $\sim 3.5\%$ near $\lambda = 475 \text{ nm}$. Both the L-shaped metasurface fabricated with $\beta = 15^0$ and $\beta = +60^0$ peaked around $\lambda = 460 \text{ nm}$, though the $\beta = 15^0$ L-shape had a much broader peak. As expected, the $\beta = +60^0$ and $\beta = -60^0$ L-shaped chiral metasurfaces displayed opposite white-light transmission DOP trends at the lower end of the spectrum. On the higher end of the

![Figure 47. (a) SHG PL of L-shaped metasurfaces GLAD-fabricated with varying $\beta$ values. (b) Power dependence of $\beta=+60$ degree L-shape metasurface at 30° orientation, illuminated with LH (black) and RH (red) circular polarized light having near-second order dependences.](image-url)
spectrum, however, all L-shape samples’ white-light transmission trended towards the positive. This could be due to the limitation of the spectrometer used (Ocean Optics HR4000) to accurately measure PL signals closer to the infrared region, which in turn distorts the calculated DOP values significantly.

The SHG signal achieved through the excitation of the L-shapes was generally robust and well-defined as shown in Figure 47 with a power dependence slope close to 2, which further supports the observation of a second-order phenomenon. The orientationally varying SHG signal from fundamental excitation of the L-shape chiral samples was taken both at the reference for each (upright V) and as the samples’ orientations were manipulated by $5^\circ$ between data collection points over one rotation. The reference SHG DOP is shown in Figure 46b, where the samples follow a similar SH trend as the fundamental white-light transmission in the mid-range.

![Figure 48. Polar plot of 100mW, 1030 nm laser-excited SHG transmission (top) and DOP of SHG transmission (bottom) by sample orientation at normal incidence for (a) $\beta = 15^\circ$, (b) $\beta = 45^\circ$ and (c) $\beta = 90^\circ$ L-shape samples.](image)
of the spectrum starting around $\lambda = 515\ nm$. The rotationally varying SHG response of the $\beta = 15^0$ and $\beta = 45^0$ L-shape samples are strikingly similar to one another (Figure 48), as is consistent with their white-light transmission similarities. It is interesting to note that the LH polarized SHG emission peaks around a sample orientation of $\theta = 30^0$ and $210^0$ whereas the RH polarized SHG emission peaks around $\theta = 110^0$ and $290^0$ for both the the $\beta = 15^0$ and $\beta = 45^0$ L-shape samples. This off-set, which could be due to imperfections in the

![Figure 49. Integrated SHG peak intensity for $\beta=+60$ degree (a) and $\theta=-60$ degree L-shape metasurfaces. (c) DOP for SHG signals from +60 degree (black) and -60 degree (red) L-shapes excited at 1030 nm and 790 nm (blue, +60 degree L-shapes). (d) DOP comparison of raw laser absorption for +60/-60 degree L-shape metasurfaces.](image-url)
manufacturing process, is reflected in the DOP polar plots in Figure 48. The rotationally varying SHG response of the $\beta = 90^0$ L-shape samples shown in the polar plots of Figure 48c behaves symmetrically about the selected reference with a maximum positive DOP of $\sim 15\%$ around $\theta = 0^0$ and $180^0$ with a near-zero negative DOP of approximately $-0.5\%$ around $\theta = 90^0$ and $270^0$ indicating a strong circular polarization-dependent SHG transmission with a preference for LH circularly polarized light.

The correlation between the direction of $\beta$ and the resulting directional nonlinear optical response is investigated further in the oppositely turned $\beta = \pm 60^0$ L-shaped nanostructures. Exciting these L-shape metasurface samples at 1030 nm and detecting the transmitted SHG while manipulating the sample orientation revealed a similar albeit shifted relative response between the SHG signals transmitted from LH and RH circularly polarized excitation (Figure 49). For the turned $\beta = -60^0$ sample excited at 1030 nm, the maximum SHG DOP appeared around This trend is upheld for an excitation of 790 nm for the $\beta = +60^0$ sample (Figure 49d),

![Graph](image)

**Figure 50.** (a) Polar plot of power-averaged DOP for SHG signals from $+60^0$ degree (black) and $-60^0$ degree (red) L-shapes excited at 860 nm ranging from 20 mW to 110 mW excitation. (b) Linear plot depiction of polar plot shown in (a) for clarity.
although a different trend is seen with an 860 nm excitation as shown in Figure 50. One possible explanation for this is the crossover from positive to negative and vice versa for the white-light absorption of the $\beta = \pm 60^0$ L-shapes in the 430 nm to 510 nm range, in which the SHG of 860 nm lies, but 790 nm and 1030 nm do not. The linearly transmitted raw 790 nm, 100 mW laser signal for the $\beta = \pm 60^0$ samples show the opposite trend (Figure 49d) indicating a rotation of the optical transmission axis between the fundamental and SHG activity.

6.4 Conclusion

Novel photonic metastructures having enantiomeric properties such as the arrays of chiral or L-shaped structures discussed in this chapter show great promise in controlling light in the sub-diffraction limited regime. Not only do these structures allow for polarization dependent manipulation of signals, but they also exhibit robust nonlinear photonic response as well, furthering their versatility and flexibility in advanced device applications. However, due to their complex susceptibility tensors, intricate design and nonlinear optical effects, the study of these structures is challenging. Employing a raw experimental approach in the investigation of intricate photonic enantiomers can be extensive, involving an in-depth probing of spectral, spatial and polarization dependencies for any given structure. A more thorough investigation of these structures in the future, particularly in the nonlinear regime, would necessarily involve SHG polarimetry, in which the susceptibility matrix of an enantiomeric structure could be partially or fully determined experimentally by controlling the polarization of both the incoming and the outgoing signal. This method involves the mapping of intensities resulting from different combinations of incident polarizations and outgoing SH signals. Regardless, the rigorous experimentation done in this chapter mirrors this method through the rotation of the
sample and incident polarization, revealing interesting CD and OR phenomena in chiral and L-shaped structures.

In this chapter GLAD-fabricated helical and L-shaped metastructure surfaces were analyzed for their CD and OR properties through the observation of polarization dependent transmission and the resulting degrees of polarization at fundamental and SH-generated transmission. The helical structures investigated in this chapter consisted of either metal-dielectric (plasmonic) or all-dielectric components fabricated with varying turn-number and orientation parameters. In the case of ADH metasurfaces, there appears to exist an odd parity between the number of turns and the skewness of DOP. The PH chirals also displayed an odd parity in the fundamental absorption at the second harmonic (1-turn and 3-turn chirals preferred the transmission of RH circularly polarized light whereas 2-turn and 4-turn chirals showed a preference for LH transmission), though the SHG signals apart from those for the 2-turn chirals tended to show a preference for LH circularly polarized light. Discrepancies between raw absorption of SH light and SHG light from the fundamental (frequency-halved) excitation could be due to the random orientation of the chirals at the beginning of each data set. The samples were only rotated ½ rotation, which in theory should provide an acceptable average to determine the overall DOP, though variations in the samples may skew the true DOPs. In general, the DOP skewness for the SHG signal is amplified as compared to the fundamental DOP for all helical structures.

The L-shaped structures, which consisted of all-dielectric (Si) L-shapes having varying GLAD angle parameters (β = 15°, 45°, 90°) also display a pronounced SHG DOP. Additionally, Ag-doped Si structures having the opposite parameter of β = ±60° displays an opposite OR trend between the positively and negatively-turned structures. Whitelight absorption performed on the
L-shape samples revealed consistent polarization dependencies with the \( \beta = \pm 60^\circ \) displaying opposite trends. Orientationally-varying SHG signals from several fundamental excitation wavelengths were studied and similar trends were observed for \( \beta = 15^\circ \) and \( 45^\circ \) L-shape samples while the \( \beta = 90^\circ \) sample showed a distinct response. As expected, the SHG for the \( \beta = \pm 60^\circ \) samples were opposite, supporting the correlation between \( \beta \) and the resulting directional nonlinear optical response. These results reveal interesting polarization and orientation-dependent behaviors which can be utilized in the progression of tailored nonlinear optical devices.

As of yet, the nonlinear capabilities of enantiomeric materials such as these have been scarcely explored. The path forward in the study of these chiral and L-shaped metamaterials in the nonlinear regime involves the integration of active materials to influence and bolster nonlinear phenomena such as the SH strong coupling observed in the dye-coupled- NPAs discussed in the previous chapter. By utilizing their OR and CD properties, along with the robust SHG supported in these materials, complex tools for flexible and dynamic light manipulation can be realized.
7. Conclusion and Outlook

The work presented in this dissertation serves to further progress the field of photonics and contribute to the expansion of optical technologies utilizing both linear and nonlinear optical mechanisms. The range of applications and phenomena demonstrated throughout this text lends to the collective understanding of light-matter control and will bolster further strides in photonics. Through the characterization of novel selenium nanoneedles fabricated by laser ablation, a new active material has been made readily available to be further explored and utilized in research. Additionally, by probing nonradiative mechanisms in blends of 2D perovskite and rubrene, the interesting upconversion mechanism of triplet-triplet annihilation was observed, hinting at the use of these materials in efficient next-generation light harvesting devices. Building upon the characterization of novel nanomaterials, plasmonic nanohole arrays were fabricated using simplified novel techniques and integrated with fluorescent emitters, displaying enhanced lasing in organic dye and increased spontaneous emission in quantum dots. This technology could be utilized in modern advanced devices for many applications including on-chip lasing and biomedical imaging applications.

Going further with novel engineered nanomaterials, plasmonic nanopatch antennas were designed via phase-matching for efficient second-harmonic generation. By incorporating organic dye, strong coupling was evidenced by Rabi splitting at both the fundamental and second harmonic, marking the first time that nonlinear strong coupling has been observed in these devices. The robust capability of these devices alone lends to powerful sensing applications among others. Furthermore, the discovery of nonlinear strong coupling opens the door to powerful quantum applications for these structures.
Expanding on the exploration of the nonlinear controlling of light, metasurfaces composed of enantiomeric chiral or L-shaped structures were fabricated via glancing angle deposition and their circular dichroic and optical rotation properties were investigated in both the linear and nonlinear regimes. These results showed interesting trends between structural topology and the resulting signal at the second harmonic, indicating a wealth of as-yet unexplored polarization and orientation-dependent applications for these structures.

While this work reveals several functional mechanisms for emerging advanced technologies, the research presented here does warrant further investigation to optimize these tools for practical use. For example, through the integration of active emitters with the various devices presented herein, efficient nonlinear output can be tuned through perfect phase matching and greatly improved going forward. Additionally, these nonlinear processes supported in these novel metamaterial designs can be probed more accurately using pump-probe spectroscopy to elucidate electron dynamics, building on the collective understanding of ultra-fast dynamics in nanostructures which is necessary for the realization of efficient all-optical switches and transistors.
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