SCALABLE CHIRAL PLASMONIC STRUCTURES: FABRICATION AND SENSING APPLICATIONS

by

GEORGE KEEFE LARSEN III

(Under the direction of Prof. Yiping Zhao)

ABSTRACT

As chiral metamaterials become increasingly more technologically relevant, scalable yet proficient nanofabrication methods will be needed for their production. Dynamic shadowing growth (DSG) takes advantage of the shadowing effect during physical vapor deposition and is a simple and powerful tool to produce chiral nanostructures. This dissertation describes several new DSG strategies for scalable production of chiral plasmonic thin films with significant optical activity in the visible and near-infrared wavelength region.

The helix is the prototypical chiral structure, yet fabrication of nanoscale helices is a significant technological challenge. By using metal composite (Ti/Ag) and metal/dielectric composite materials (Ag/MgF₂), it is demonstrated that nanoscale helices can be fabricated through DSG at room temperature in a scalable manner. However, these thin films have a high degree of alignment, which increases the difficulty of interpreting the optical measurements. Thus, a generalized ellipsometry measurement scheme is introduced to extract the optical parameters from aligned films. It is found that some of these DSG helical structures are among the most optically chiral films to date.

It is also shown that self-assembled colloidal monolayers of nanospheres can serve as effective templates for the production of a wide variety of highly chiral films. Furthermore, this method can be combined with chemical techniques to dynamically tune the optical response. These chiral films can have coatings with well-defined shapes that are analyzed using a continuous chirality measure. This measure of chirality allows for the quantification of chirality, providing insight into the origin of optical activity in these films.

Finally, DSG films are developed to serve as both surfaced enhanced Raman scattering (SERS) substrates and as molecular chirality sensors through chiral plasmonic sensing. A molecule's "handedness" determines its function in the body, and introduction of the wrong-handed molecule can have serious consequences. Therefore, a sensor that is sensitive to molecular chirality is highly desirable. In addition to their SERS response, the DSG films are investigated for their sensitivity to the chirality of L- and D- enantiomers of tryptophan. Notably, the results show that the measured optical response depends on both the handedness of the film and the handedness of the molecule.

INDEX WORDS: Dynamic shadowing growth, Glancing angle deposition, Chiral metamaterials, Plasmonics, Biosensors, Surface enhanced Raman scattering, Helix, Nanosphere lithography

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GEORGE KEEFE LARSEN III

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by

GEORGE KEEFE LARSEN III

Major Professor:

Yiping Zhao

Committee:

William M. Dennis Peter Kner Steven P. Lewis Susanne Ullrich

Electronic Version Approved:

Julie Coffield Interim Dean of the Graduate School The University of Georgia December 2014

DEDICATION

For my father, who would be proud even though it's the "wrong" type of doctor.

And for Brittany, for so many reasons.

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TABLE OF CONTENTS

		Page
ACKNOWL	EDGEMENTS	v
LIST OF TA	BLES	viii
LIST OF FIC	JURES	ix
CHAPTER		
1	INTRODUCTION	1
	1.1 Optical Activity – Discovery and Phenomena	1
	1.2 Plasmonics and Chiral Plasmonics	6
	1.3 Optical Properties of Chiral Molecules, Nanostructures, and Materials	11
	1.4 Brief Review of Current Fabrication Methods	17
	1.5 Dynamic Shadowing Growth	20
	1.6 Organization of the Dissertation	25
2	PLASMONIC HELICES	27
	2.1 Introduction	27
	2.2 Composite Ti/Ag Helical Structures	30
	2.3 Composite Ag/MgF ₂ Helices	52
3	THREE-DIMENSIONAL CHIRAL SHAPES FROM COLLOID	
	TEMPLATES	58
	3.1 Introduction	58
	3.2 Chiral Patchy Particles	58

	3.3 Stretched Chiral Patchy Particles	80
	3.4 Oligomers	82
	3.5 Patchy Staircase	
	3.6 Spectral Tuning Through Galvanic Replacement Reaction	86
4	CHIRAL SENSORS	
	4.1 Introduction	94
	4.2 Stretched SiO ₂ Patchy Particles + Ag Thin Film	
	4.3 Tryptophan Sensing	102
	4.4 Conclusion	107
5	CONCLUSIONS AND FUTURE WORK	108
REFERENCE	ES	110
APPENDIX .		127
А	JONES AND MUELLER DESCRIPTIONS OF LIGHT PROPAGATION	N 127

LIST OF TABLES

Page

Table 2.2.1: Morphological parameters of the individual chiral nanostructures	42
Table 2.2.2: Retardances and absorbances: notation and definitions	44
Table 3.2.1: Chirality index, <i>K</i> , for different simulated patch morphologies	75

LIST OF FIGURES

	Pa	ge
Figure 1.1.1:	Schematic showing the behavior of the electric field vector of circular polarized	
	light	. 2
Figure 1.1.2:	a) The electric field vector of linearly polarized light decomposed into circular	
	components. (b) The rotated electric field vector at some further point in an	
	optically active medium. The propagation direction is out of the page	. 3
Figure 1.2.1:	Pictorial description of a localized surface plasmon resonance of metal sphere.	
	The incident electric field couples with the free electrons, causing them to	
	oscillate	. 6
Figure 1.2.2:	Diagram of a split ring resonator showing the equivalent <i>LC</i> circuit	. 8
Figure 1.2.3:	(a) chiral objects, like hands, do not exhibit reflective symmetry. (b) achiral	
	objects can be superimposed on their reflection	. 9
Figure 1.2.4:	(a) Diagram of the oscillation of the electron cloud in a spherical metal	
	nanoparticle under linearly polarized light. In (b), the rotating electric field of	
	circularly polarized light causes the electron cloud to rotate around the	
	nanoparticle. In the case of chiral nanoparticles, the rotation of the electron clou	d
	under illumination with circularly polarized light can be favored or hindered	
	depending on the combination of chiral geometry and direction of circularly	
	polarized light, as it is shown in (c) and (d)	10

- Figure 2.3.1: (a) Representative TEM image of an Ag/MgF₂ composite helix. (b) ΔT spectra for Ag/MgF₂ helical films with the same composition but with different handedness, helical pitch *p*, and pitch number *N*. (c) ΔT spectra for Ag/MgF₂ helical films with the same handedness, *p*, and *N* but different compositions 53

- Figure 3.2.7: The labeling convention for the triangle used in the chiral index calculation 69

Figure 3.3.1:	SEM images of stretched chiral patchy films on 350 nm-diameter SACM
	substrates where the thickness for Depositions 1, 2, and 3, respectively are (a)
	180, 120, 60 nm; (b) 160, 120, 80 nm; and (c) 140, 120, 100 nm. (d) Circular
	polarization ΔT spectra for the stretched chiral patchy films shown in the SEM
	images
Figure 3.4.1:	(a) Schematic of the fabrication process for the CW oligomer structure. (b)
	Unpolarized UV-visible absorbance spectra and the (c) circular polarization ΔT
	spectra for CW and CCW oligomer films on 500 nm-diameter SACM substrates
Figure 3.5.1:	Simple simulation of the patch morphology on a bead where the original
	orientation of the monolayer domain is described by $\theta = 86^{\circ}$ and $\varphi_0 = 5^{\circ}$. Three
	depositions of different thicknesses are performed at the same polar angle but at
	different azimuthal angles: 90 nm at φ_0 , 60 nm at φ_0 + 120°, and 30 nm at φ_0 +
	240°
Figure 3.5.2:	CD spectra for the (a) 30-20-10, 60-40-20, 90-60-30 patchy staircases, Deposition
	1, 2, 3, respectively and for the (b) 40-20-10, 90-30-10, and 160-40-10 patchy
	staircases, Deposition 4, 5, 6, respectively
Figure 3.6.1:	Schematic of the GRR process. The major steps include the following: (a)
	initiation of replacement reaction at a specific spot with relatively high surface
	energy; (b) continuation of the replacement reaction between Ag and $HAuCl_4$ and
	the formation of a partially hollow nanostructure; (c) formation of nanoboxes with
	a uniform, smooth, homogeneous wall composed of Au-Ag alloy; (d) initiation of

dealloying and morphological reconstruction of the Au-Ag nanobox; (e, f)

Figure 3.6.3: (a) Peak location and (b) CD intensity of Peaks 1 and 2 as function of time 89

- Figure 4.1.1: Changes induced in the chiral plasmonic resonances of the PCM are readily detected using CD spectroscopy. (a) CD spectra collected from LH/RH PCMs immersed in distilled water. The three modes that show the largest sensitivity to changes in the local refractive index of the surrounding medium have been labeled I, II and III. Shown to the right of each spectrum is an electron micrograph of the PCM displaying the gammadion structure and periodicity. (b) Influence of the adsorbed proteins haemoglobin, β-lactoglobulin and thermally denatured β-lactoglobulin on the CD spectra of the PCMs. Red spectra were collected in Tris buffer before protein adsorption (solid line, LH PCM; dashed line, RH PCM), and black spectra were collected after protein adsorption.

	Magnitudes and directions of DIRH/LH values of mode II for β -lactoglobulin
Figure 4.1.2:	adsorption have been highlighted
	Schematics for PCR assembly of Au NRs. (a) PCR replication procedure in which
	a DNA strand can be amplified using primer, template DNA, taq plus polymerase
	and four different DNA bases. (b) PCR-based gold NRs ETE assembly. (c) PCR-
Figure 4.2.1:	based gold NRs SBS assembly with inter-NR gap d; in the bottom part of the
	panel the DNA chains were removed for clarity
	SEM micrographs of the 90-60-30 SiO ₂ + 10 nm Ag structure on (a) – (c) $D =$
	200, 350, and 500 nm SACM substrates, respectively. (d) 90-60-30 SiO ₂ +20 nm
	Ag structure on $d = 200$ nm SACM substrates (e) 90-60-30 SiO ₂ +50 nm Ag

layers on d = 200 nm SACM substrates. The scale bars are 0.5 μ m, unless

- Figure 4.2.3: m_{14} spectra for the 90-60-30 SiO₂ + Ag structure on (a) (c) D = 200, 350, and500 nm SACM substrates, respectively. The Ag layer thickness varies from $t_{Ag} = 0 - 50$ nm. Note that the $t_{Ag} = 50$ nm film has the ordinate axis to the right 102

- Figure 4.3.3: SERS spectra for D- and L-Trp and the background using a 90-30-60 film 106

CHAPTER 1

INTRODUCTION

1.1 Optical Activity - Discovery and Phenomena

The discovery of the phenomena collectively referred to as optical activity can be traced back to experiments performed by François Arago in 1811 and Jean-Baptiste Biot in 1812.[1] Arago observed that a spectrum of colored images was formed when a specific type of quartz crystal was placed between two crossed polarizers, and the crystal was rotated about its optical axis. Biot went further and established that this resulting spectrum of colors arose from optical rotation (*i.e.*, an azimuthal rotation in the plane of polarization of linearly polarized light) and from optical rotary dispersion (*i.e.* the wavelength dependence of optical rotation).[2] He also proposed an approximate inverse square law between the angle of optical rotation, α , and the wavelength of incident radiation, λ ,

$$\alpha = C/\lambda^2, \tag{1.1.1}$$

where C is a constant specific to the optically active substance. Notably, this marked the beginning of the convention where a clockwise rotation of the plane of polarization, as seen from observer looking *into* the radiation source, is taken as positive, while a counter-clockwise rotation is taken as negative. As Biot continued his investigations, he observed optical rotation in various liquids, such as turpentine and in solutions of camphor, sugar, and tartaric acid.[3] Given the random orientations of molecules in these fluids, this led to the conclusion that optical



Figure 1.1.1 Schematic showing the behavior of the electric field vector of circular polarized light. Ref.[4]

activity is related to the structure of the dissolved molecules. That is, the molecules exhibit a fundamental asymmetry or handedness, called chirality. Optical activity in quartz, on the other hand, is ascribed to a handedness in the crystal lattice because different forms of quartz can exhibit positive or negative optical rotations and molten quartz has no observable optical activity.

The phenomena associated with optical activity raised significant challenges to the Newtonian particle theory of light, and it was through applying the then nascent transverse wave theory to optical activity that Augustin-Jean Fresnel discovered circularly polarized light in 1824.[2] As shown in **Figure 1.1.1**,[4] the electric field vector of circular polarized light, E, rotates in a circle within a fixed plane that is perpendicular to the direction of propagation. For left circular polarization (LCP), the rotation sense is counter-clockwise when looking into the beam, and for right circular polarization (RCP) the rotation sense is clockwise. For a given time slice, the tips of the electric field vectors in circular polarized light trace out a helix whose handedness corresponds with definitions give above, *i.e.*, left circular polarization corresponds



Figure 1.1.2 (a) The electric field vector of linearly polarized light decomposed into circular components. (b) The rotated electric field vector at some further point in an optically active medium. The propagation direction is out of the page. Ref.[5]

with a left-handed helix. Fresnel's important insight is that both the linear and circular bases are equally valid descriptions of an electromagnetic wave and that these bases are interchangeable. Circular polarized light can be described by a superposition of coherent orthogonal linear polarized light beams of equal amplitude, while linear polarized light can be regarded as a superposition of coherent LCP and RCP light beams. Fresnel proposed that optical rotation of linearly polarized light was the result of different propagation velocities for left and right circular polarized lights in optically active material. Specifically, if the electric field vector of a linearly polarized beam of light at the surface of an optically active material (z = 0) is assumed to be parallel with the electric field vectors of the left and right circular components at a particular time, then at the same time at some point z = l within the medium, the electric field vectors of the left and right circular components have respectively rotated by angles $\theta_{LCP} = -2\pi cl / \lambda v_{LCP}$ and $\theta_{RCP} = -2\pi cl / \lambda v_{RCP}$, where *c* and λ are the speed and wavelength of light in vacuum,

respectively, and v_{LCP} and v_{RCP} are the medium's specific velocities for LCP and RCP light (Figure 1.1.2).[5] Thus, the optical rotation angle is given by

$$\alpha = \frac{1}{2} \left(\theta_{LCP} + \theta_{RCP} \right) = (\pi c l / \lambda) \left(v_{LCP}^{-1} - v_{RCP}^{-1} \right).$$
(1.1.2)

Defining the refractive indices for left and right circular polarization as $n_{LCP} = c / v_{LCP}$ and $n_{RCP} = c / v_{RCP}$, respectively, provides the following relation for the angle of rotation in radians per unit length

$$\alpha = (\pi / \lambda) (n_{LCP} - n_{RCP}). \tag{1.1.3}$$

Thus, α is determined by the medium's circular birefringence, which is the difference in the refractive indices experienced by LCP and RCP light.

All real materials exhibit both refraction and absorption, and these effects are related by the Kramers-Kronig relation. A Kramers-Kronig relation is a bidirectional mathematical relation that connects the real and imaginary parts of a complex function, as long as the function is analytic in the upper plane. For such a function, the real and imaginary parts are not independent, and the knowledge of one part allows for the determination of the full function. Specifically, for some function, $\chi(\omega) = \chi_1(\omega) + i \chi_2(\omega)$, if ω is a complex variable and $\chi_1(\omega)$ and $\chi_2(\omega)$ are both real, then the Kramers-Kronig relation is given by

$$\chi_1(\omega) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_2(\omega')}{\omega' - \omega} d\omega'$$
(1.1.4)

and

$$\chi_2(\omega) = -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi_1(\omega')}{\omega' - \omega} d\omega'$$
(1.1.5)

where \mathcal{P} is the Cauchy principal value and $\chi(\omega)$ is assumed to be analytic in the upper half of the plane and goes to zero faster than $1/|\omega|$ as $\omega \to \infty$. Thus, an optically active material will not only be circularly birefringent, but will also absorb LCP and RCP to different degrees, as described by the Kramers-Kronig relation. This difference in absorption between the two circular polarizations is called circular dichroism (CD). CD values are often expressed in values of ellipticity, ψ . The use of ellipticity in describing CD is related to the observation that linear polarized light becomes elliptically polarized upon transmission through or reflection from an optically active material, which is due to the LCP and RCP components being absorbed differently. Ellipticity is given by the ratio of the minor and major axes of the polarization ellipse. Since elliptically polarized light can be decomposed into circular components, ellipticity is related to the LCP and RCP field amplitudes,

$$\tan \psi = (E_{RCP} - E_{LCP}) / (E_{RCP} + E_{LCP}).$$
(1.1.6)

It can be found that the relation between ellipticity and the absorption indices for left and right circular polarization, k_{LCP} and k_{RCP} , is given by

$$\tan \psi = \tanh[(\pi l / \lambda) \ (k_{LCP} - k_{RCP})], \qquad (1.1.7)$$

where the complex refractive indices are given by $\tilde{n}_{LCP,RCP} = n_{LCP,RCP} + i k_{LCP,RCP}$ Since ellipticity values are generally small, this relation can be approximated and given in radians per unit length,

$$\psi = (\pi / \lambda) \left(k_{LCP} - k_{RCP} \right). \tag{1.1.8}$$

Values for circular dichroism described in the literature are given most often in the form of ellipticities in units of degrees, so a unit conversion factor of $180/\pi$ along with an assumed optical path length of 1 cm is often applied to Equation 1.1.8.

Circular dichroism and the corresponding anomalous optical rotary dispersion that occurs in absorption region are collectively known as the Cotton effect, after Aimé Cotton who is credited with the discovery in 1895.[6] While other manifestations of optical activity have been observed in materials through effects such as magnetic circular dichroism, vibrational optical activity, and Raman optical activity, this dissertation will focus mostly on circular dichroism and to a lesser extent, circular birefringence, due to their ease of measurement and relevance to specific applications.

1.2 Plasmonics and Chiral Plasmonics

Optical applications of bulk metals are generally limited to mirrors and beam splitters. However, as the dimensions of materials are reduced down to the nanoscale, new physical properties can emerge. Localized surface plasmon resonances (LSPRs) observed in metal nanoparticles are perhaps the most famous examples of these nanoscale effects.[7] LSPRs are excitations of free conduction electrons within subwavelength metal nanoparticles, where the excitation energy matches that of incident light (**Figure 1.2.1**).[8] The electromagnetic field of the incident light causes the surface electrons to coherently oscillate, resulting in a resonance that depends not only on the size of the nanostructure, but also its shape, arrangement amongst other interacting particles, and ambient environment. LSPRs typically produce strong absorption and scattering of the light and are different than the commonly encountered surface plasmon polariton (SPP) wave, in that SPPs are propagating surface waves, while LSPRs are non-propagating standing



Figure 1.2.1 Pictorial description of a localized surface plasmon resonance of metal sphere. The incident electric field couples with the free electrons, causing them to oscillate. Ref.[8]

waves constrained by the surface. Furthermore, the electromagnetic field of light is effectively confined by the LSPR within the small dimensions of the nanostructure, resulting in large local electromagnetic field enhancements. While these effects sound exotic, they are natural consequence of the Maxwell equations and the bulk optical properties of metals. Specifically, the plasmonic extinction cross-section, C_{ext} , by a small metal sphere of volume, V, and dielectric function, $\varepsilon = \varepsilon_1 + i \varepsilon_2$, is given by the well-known quasi-static theory,[9]

$$C_{ext} = 9\frac{\omega}{c}\varepsilon_m^{3/2}V\frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2},$$
(1.2.1)

where ε_m is the dielectric function of the ambient medium and ε and ε_m are functions of the incident light frequency, ω .

The field of study related to the theory and application of SPPs and LSPRs is generally referred to as "plasmonics." From the discussions above, it is clear that plasmonic phenomena offer significant opportunities for interesting applications. For example, the ability of plasmonic excitations to confine and guide light at scales smaller than the diffraction limit allows for the creation of miniaturized photonic circuits and could lead to the development of an optical computer.[10] Furthermore, plasmonic resonances can generate "hotspots" of very intense local electromagnetic fields, and these hotspots have been shown to improve surface-enhanced Raman scattering (SERS),[11] promote photochemical reactions,[12] and permit the development of highly sensitive sensors.[13] Another important application of plasmonics is a class of materials known as "metamaterials."[14] Metamaterials are artificial materials whose properties are determined not by their chemical makeup, but by the specific arrangement of sub-wavelength structural elements. Through careful design of these elements, metamaterials can exhibit properties not typically exhibited by naturally occurring materials. Perhaps, the most famous examples are invisibility cloaks created by metamaterials composed of split ring resonators and



Figure 1.2.2 Diagram of a split ring resonator showing the equivalent LC circuit. Ref.[16]

conductive wires. For applications such as cloaking and perfect lensing, metamaterials must have a negative refractive index, which requires that both the electric permittivity and the magnetic permeability have negative values over the same spectral range.[14] While a negative permittivity is not uncommon in natural materials, negative permeability is exceedingly rare, and unheard of in the visible and infrared regions. Thus, the challenge for metamaterial design is to create a unit cell that can couple with magnetic field of light. Very often, this is done by creating a subwavelength plasmonic system that functions similarly to an LC circuit with inductance L and capacitance C.[15] In the split ring resonator, the incident magnetic field flux linking the ring generates inductance by coupling with the circular plasmonic mode of the ring, and the capacitance is generated by the charges that accumulate across the gap in the ring (Figure **1.2.2**.[16] While split ring resonators and similar devices work efficiently in the microwave region, it is not possible to scale such unit cells down to serve as the basis for optical metamaterials due to optical losses in materials. Consequently, the fabrication of metamaterials that exhibit negative refraction in the visible region remains a significant challenge. However, an alternative and easier method of obtaining a negative refractive index that takes advantage of chirality has recently been proposed by Sir James Pendry.



Figure 1.2.3 (a) chiral objects, like hands, do not exhibit reflective symmetry. (b) achiral objects can be superimposed on their reflection. Ref.[17]

As described in Section 1.1.1 above, the term "chirality" describes a form of asymmetry. More specifically, an object is said to be "chiral" if it cannot be made superimposable upon its mirror image solely by rotations and translations (**Figure 1.2.3**).[17] That is, chiral objects do not exhibit reflective symmetry. Right and left hands are the most familiar everyday chiral objects, and in fact, the word chirality is derived from the greek word for hand, " $\chi e i \rho$." Another familiar chiral shape is the helix. Chirality is an intrinsic property of living matter, and researchers in biochemistry have long known its relevance. More recently, chirality has emerged as an important topic among researchers interested in plasmonics, creating the subfield of chiral plasmonics.[18] This rapid growth is tied to the emergence of chiral metamaterials.[19] As mentioned above, optically chiral metamaterials can offer an easier route to negative refraction than traditional metamaterials because right circular and left circular polarized light, RCP and LCP, respectively, experience different refractive indices in chiral media. This can be described by the relation, $n_{\text{RCP, LCP}} = n \pm \xi$, where *n* is the traditionally defined refractive index and ξ is the dimensionless chirality parameter of the material (see Section 1.3.3 for further discussion). Consequently, negative refraction for one circular polarization state is possible for non-negative *n* if $|\xi| > n$. This means that researchers interested in developing metamaterials for cloaking devices and perfect lenses in the optical regime can alternatively focus on creating materials that exhibit intense optical activity, instead of trying to create materials with negative permeability. While non-metallic materials have been utilized in some cases for chiral metamaterials, most investigations in the literature rely on plasmonic materials (*i.e.*, noble metals) due to their unique optical properties and strong electromagnetic field enhancements.



Figure 1.2.4. (a) Diagram of the oscillation of the electron cloud in a spherical metal nanoparticle under linearly polarized light. In (b), the rotating electric field of circularly polarized light causes the electron cloud to rotate around the nanoparticle. In the case of chiral nanoparticles, the rotation of the electron cloud under illumination with circularly polarized light can be favored or hindered depending on the combination of chiral geometry and direction of circularly polarized light, as it is shown in (c) and (d). Ref.[18]

In addition to the possibility of negative refraction through chiral metamaterials, there are also other intriguing phenomena associated with strong optical chirality that motivate interest in chiral plasmonics, such as broadband circular polarization,[20] repulsive Casimir forces,[21] unusual spin Hall effects,[22] and superchiral fields.[23] Generally, in order for these effects to be observed, the structures must have chiral features that are on the order of, or smaller than the wavelength of interest (**Figure 1.2.4**). In particular, chiral plasmonic structures must have chiral features on the nanoscale in order to exhibit optical activity in the visible wavelength region. This poses a significant fabrication challenge because nanoscale materials strongly prefer to form symmetric shapes to reduce surface energy. Thus, the fabrication of chiral nanostructures is challenging, requiring precise control of material arrangement at exceedingly small dimensions, especially for three-dimensional (3D) chiral nanostructures, which are highly desirable due to their strong chirality.[24] The current fabrication methods for chiral plasmonic structures are described in Sections 1.4 and 1.5.

1.3 Optical Properties of Chiral Molecules, Nanostructures, and Materials

1.3.1 Optical properties of chiral molecules

Qualitatively, a light induced electronic transition in a molecule occurs because the fields of the electromagnetic radiation physically rearrange electrons such that they match the conditions of an alternate stationary state.[25] During such a transition, the electric field linearly displaces electrons from the background of positively charged atomic nuclei, and this net movement of charge is quantified by the vector $\boldsymbol{\mu}$ known as the electric dipole transition moment. Note, do not confuse this vector $\boldsymbol{\mu}$ with the magnetic permeability, μ , which is generally a scalar but may be a rank 3 tensor in some materials (*e.g.*, gyromagnetic). The vector $\boldsymbol{\mu}$ points in the direction of the

net linear displacement of the electron density. On the other hand, the magnetic component of the electromagnetic field induces a circular rearrangement of the electron density. This net circulation of electrons is an axial vector, m, called the magnetic dipole transition moment. Importantly, the electron rearrangement is always helical in a chiral molecule during a light-induced transition. This helicity is imparted by μ and m having parallel components. This alignment of the electric and magnetic dipole transition moments is the basis for the famous Rosenfeld equation, [26]

$$R = \operatorname{Im}[\boldsymbol{\mu} \cdot \boldsymbol{m}], \tag{1.3.1}$$

which describes the CD intensity (or CD strength or rotational strength), R, of a transition for a collection of randomly oriented chiral molecules.

The Rosenfeld equation is not just valid for chiral molecules, and the equation derived for a single electron confined to a helix has been used to describe the optical properties of copper helices in the microwave region.[27, 28] Furthermore, it was demonstrated that this derivation is a reasonable approximation for metal helices where the helical pitch and radius are on the order of the wavelength or smaller.[28] Recent studies of plasmonic helices with optical activity in the visible region show that predictions based on a Rosenfeld approximation give qualitatively similar results as the experimentally obtained data.[29] Specifically, the sign of the CD strength matched the analytical predictions, so did the relationship between the relative CD strength and the helical radius and pitch.

1.3.2 Optical properties of chiral nanostructures

In general, most chiral nanostructures have optical responses that are too complicated for analytical analyses. Thus, many studies rely on the use of computational methods for theoretical investigations. The popular methods include finite-difference-time-domain (FDTD),[30] finite element analysis (FEM or FEA),[31] and the discrete dipole approximation (DDA).[32] These methods are not only able to reproduce experimentally measured spectra, they can also provide detailed information regarding the nature of plasmonic resonances through modeling and visualization of current distributions at the excitation energies. Furthermore, computational methods can provide maps of electromagnetic field intensities, which can be used to determine field hotspots and can describe regions of "superchirality."

Computational electromagnetic methods are certainly powerful tools in the theoretical analyses of chiral plasmonic structures. However, from a design standpoint it is often helpful to analyze or predict experimental results from (quasi-) first principles, especially through analytical methods. In this way the response can be optimized or tuned to a specific application. Optical chirality in nanostructures generally arises from one or more distinct effects. These effects, along with their molecular analogues, are shown in Figure 1.3.1 and include shape chirality, chiral coupling, supramolecular chirality, pseudo/extrinsic chirality, and chiral scaffolds. For nanoparticles with an intrinsic chiral shape and that are much smaller than the incident wavelength, there exists an analytical method to calculate their chiral optical properties.[33] This method, developed by Zhiyuan Fan and Alexander O. Govorov, follows the general formalism for calculating absorption for a nanoparticle, except in this case the chiral surface is defined by a function, $R_{NC}(\theta, \varphi)$. By enforcing the standard boundary conditions defined by $R_{NC}(\theta, \varphi)$, the coefficients for the spherical harmonic expansion of the individual electromagnetic fields, both inside and outside the nanoparticle, incorporate the chirality of the surface. In their calculations, they noted that chiral shapes, in contrast to spheres, have nondegenerate orders, m, $(-l \le m \le l)$ within each degree, l, for spherical harmonic $Y_{l,m}(\theta, \varphi)$. These

plasmonic multiplets arise from the chiral surface distortion. Further analysis showed that the CD signal only appeared for calculations using expansions with l > 1. Therefore, they concluded that the CD mechanism originates from the mixing between the different plasmonic multiplets (*e.g.*, dipolar) and modes (*e.g.*, dipolar and quadrupolar) in chiral nanoparticles.



Figure 1.3.1 Different origins of optical activity in plasmonic nanostructures and their molecular analogs, including (a) – (f) chiral shapes, (g) – (i) chiral coupling, (j) –(l) extrinsic chirality, (p) – (r) chiral scaffolds. Ref.[18]

Fan and Govorov have also developed an analytical method for calculating the chiral optical response of chiral assemblies of nanoparticles (**Figure 1.3.1q**).[34] The physical mechanism for chiral nanoparticle assemblies has some similarity with the optical chirality due to the Coulomb dipole-dipole interaction in a large chiral molecule (*e.g.*, α -helix or DNA).[25] However, there is an important difference between the plasmonic CD effect and the CD effect in biomolecules. The elementary building blocks of a complex biomolecule are interacting chromophores, which are generally described as single dipoles. On the other hand, in chiral complexes of nanoparticles, the elementary building blocks, individual spherical nanoparticles,

have three plasmonic dipoles. This analytical method will be further discussed and utilized in Section 2.3.

Additional analytical solutions to various chiral phenomena are available in the literature. For example, Govorov has also developed a theory to describe the remarkable phenomenon where an achiral nanoparticle with plasmonic resonances in the visible region is coupled with a chiral molecule that has optical activity in the UV range, and produces new plasmonic optical activity in the visible range.[35] Another notable example is the plasmonic Born-Kuhn model for chiral nanophotonic spectra.[36] In this case, the optical activity of layered plasmonic structures is interpreted in a classical manner by using the coupled oscillator model of Born and Kuhn, which consists of two identical, vertically displaced, coupled oscillators.[37] Finally, for mesoscopic laminar structures with a helical arrangement (*e.g.*, liquid crystals or sculptured thin films), transfer matrices have been employed to accurately describe experimentally obtained chiral spectra.[38]

1.3.3 Chiral materials and negative refraction

The coupling between the effects of the incident electric field and magnetic field, as described in the Rosenfeld equation, is generally at the origin of observable optical activity. For example, in bulk chiral materials or films, these effects are represented by introducing a material specific 6×6 tensor (note that the individual components of χ are themselves 3×3 tensors),

$$\chi = \begin{bmatrix} \chi_{\text{EE}} & \chi_{\text{EH}} \\ \chi_{\text{HE}} & \chi_{\text{HH}} \end{bmatrix}, \qquad (1.3.2)$$

which defines the response of the medium to the electromagnetic field through the electromagnetic constitutive relations,

$$\boldsymbol{D} = \boldsymbol{\chi}_{\text{EE}} \boldsymbol{E} + \boldsymbol{\chi}_{\text{EH}} \boldsymbol{H}, \qquad (1.3.3)$$

$$\boldsymbol{B} = \boldsymbol{\chi}_{\text{HE}} \boldsymbol{E} + \boldsymbol{\chi}_{\text{HH}} \boldsymbol{H}, \qquad (1.3.4)$$

where D is the electric displacement vector, E is the electric field intensity, B is the magnetic induction field, and H is the magnetic field intensity.[19] For the achiral materials the offdiagonal elements of χ vanish, leaving the more familiar form of the constitutive relations. For bianisotropic materials, including chiral materials, these elements do not vanish, and the electric and magnetic fields are coupled.

For the slightly less general case of bi-isotropic materials, Equations 1.3.3 and 1.3.4 can be written as,

$$\boldsymbol{D} = \varepsilon_0 \,\varepsilon \, \boldsymbol{E} + \left(\chi + i \, \boldsymbol{\zeta} \right) \left(\varepsilon_0 \, \mu_0 \right)^{1/2} \boldsymbol{H}, \tag{1.3.5}$$

$$\boldsymbol{B} = \mu_0 \,\boldsymbol{\mu} \, \boldsymbol{H} + (\boldsymbol{\chi} - i \,\boldsymbol{\zeta}) \, (\varepsilon_0 \,\mu_0)^{1/2} \, \boldsymbol{E}, \qquad (1.3.6)$$

where ε and ε_0 are, respectively, the relative and vacuum permittivities, μ and μ_0 are, respectively, the relative and vacuum permeabilities, χ is the magneto-electric parameter that describes the material's reciprocity, and ξ is the dimensionless chirality parameter. For the case of a plane wave traveling in an isotropic chiral medium, Maxwell's curl equations in the frequency-domain with no sources can be obtained using Equations 1.3.5 and 1.3.6,

$$\boldsymbol{k} \times \boldsymbol{E} = \omega \,\mu_0 \,\mu \,\boldsymbol{H} - i \,\omega \,\xi \left(\varepsilon_0 \,\mu_0\right)^{1/2} \boldsymbol{E}, \qquad (1.3.7)$$

$$\boldsymbol{k} \times \boldsymbol{H} = -\omega \,\varepsilon_0 \,\varepsilon \, \boldsymbol{E} - i \,\omega \,\xi \,(\varepsilon_0 \,\mu_0)^{1/2} \,\boldsymbol{H}, \qquad (1.3.8)$$

where *k* is the wavevector in the chiral medium. The wavevector in the medium is related to the refractive index, *n*, by $\mathbf{k} = (\omega / c) n \hat{\mathbf{s}}$, where $\hat{\mathbf{s}}$ is a unit vector that points in the direction of the wave propagation. Combining Equations 1.3.7 and 1.3.8, the wave equation for the electric field is obtained

$$\boldsymbol{k} \times (\boldsymbol{k} \times \boldsymbol{E}) = -k_0^2 \left(\varepsilon \,\mu - \zeta^2\right) \boldsymbol{E} - 2 \, i \, \zeta \, k_0 \, (\boldsymbol{k} \times \boldsymbol{E}), \tag{1.3.9}$$
where $k_0 = \omega / c$ and $c = (\varepsilon_0 \mu_0)^{-1/2}$. If we consider the case of circular polarized light (RCP, LCP) propagating in the z-direction, $k_{RCP, LCP} = \{0, 0, k_{RCP, LCP}\}$ and $E_{RCP, LCP} = \{1, \pm i, 0\}E(r, \omega)$. Inserting $k_{RCP, LCP}$ and $E_{RCP, LCP}$ into Equation 1.3.9 and writing them as column vectors we obtain

$$\begin{bmatrix} -k_{RCP, LCP}^{2} \\ \mp i \, k_{RCP, LCP}^{2} \\ 0 \end{bmatrix} = \begin{bmatrix} -k_{0}^{2} (\varepsilon \, \mu \, - \, \zeta^{2}) \, \mp 2 \, \zeta \, k_{0} \, k_{RCP, LCP} \\ -k_{0}^{2} (\varepsilon \, \mu \, - \, \zeta^{2}) \, - 2 \, \zeta \, k_{0} \, k_{RCP, LCP} \\ 0 \end{bmatrix}.$$
(1.3.10)

Equating the *x*-components in Equation 1.3.10 and solving for $k_{RCP, LCP}$, we can obtain the refractive indices for RCP and LCP,

$$n_{\rm RCP, \, LCP} = n \pm \xi, \tag{1.3.11}$$

where we have used $k_0 = \omega / c$, $k_{RCP, LCP} = (\omega / c) n_{RCP, LCP}$ and $n = (\varepsilon \mu)^{1/2}$ (*i.e.*, *n* is the nonchiral refractive index of the material). Thus, negative refraction for one circular polarization state, RCP or LCP, is possible for non-negative *n* if $|\xi| > n$.

1.4 Brief Review of Current Fabrication Methods

A variety of innovative techniques have been used in the literature to try and meet the challenge of fabricating chiral plasmonic structures with optical activity in the visible region. These techniques can be divided into top-down and bottom-up methods. Top-down methods are generally template-free, while bottom-up methods typically require chiral templates or chiral constituent elements to fabricate the desired chiral structures (**Figure 1.4.1**).

Electron beam lithography (EBL) is a common top-down method for the creation of chiral patterns at the nanometer scale.[39-41] EBL uses a focused beam of electrons to write patterns into an electron sensitive material referred to as "resist." After the writing step, the resist is developed by immersing in a solvent, which, depending on the resist type, selectively



Figure 1.4.1. Examples of bottom-up and top-down preparation of chiral nanostructures. In the first case, the material preparation proceeds from the self-assembly of a block copolymer. In (a), the three different colors (red, blue, and grey) correspond to the different blocks of the copolymer. The isoprene block (blue) is removed in (b) and is then back-filled with gold (yellow) in (c). The final structure is obtained by plasma etching the two remaining polymer blocks, revealing a 3D continuous gold network in air, in (d). In the case of top-down material preparation, the nanostructure pattern is drawn on a resist layer with electron beam lithography, in (e). Subsequently, the resist within the pattern is removed in a solvent bath, producing a mask, which is shown in (f). The mask is then subjected to metal evaporation, in (g). Next, all the resist is removed in a solvent bath producing (h). Ref.[18]

keeps or removes the portion of the resist that had been exposed to the electron beam. The EBL method is capable of creating arbitrary and complex shapes in two dimensions (2D) at high-resolution, making it ideally suited for laboratory investigations of fundamental principles of chiral metamaterials.[42, 43] However, the top-down writing of resist is a planar patterning method, which makes the formation of 3D structures very difficult. This is because the formation of a 3D structure requires multiple steps of EBL, etchings, and material depositions with carefully designed and aligned layers. For example, a true 3D chiral plasmonic metamaterial composed of loop-wire meta-atoms has been demonstrated using EBL,[44] but the fabrication requires three separate EBLs and many other fabrication processing steps, including



Figure 1.4.2. (*A*) Focused-ion-beam cut of a DLW polymer structure partially filled with gold by electroplating. (B) Oblique view and (C) top-view of a left-handed helix structure after removal of the polymer by plasma etching. (D) DLW fabrication process: a positive-tone photoresist (blue) is spun onto a glass substrate covered with a 25-nm thin film of conductive indium-tin oxide (ITO) shown in green. After 3D DLW and development, an array of air helices in a block of polymer results. After plating with gold in an electrolyte, the polymer is removed by plasma etching, leading to a square array of 3D gold helices. Ref.[20]

metal lift-offs and dry-etchings. These additional processes reduce fabrication throughput, increase costs, and are not suitable for large-scale production. Direct laser writing (DLW) is another top-down method exist for the production of 3D chiral plasmonic structures. For example, DLW of helical cavities in positive tone photoresist, followed by development and electrochemical deposition of gold, has been used to produce square-lattice arrays of plasmonic helices that show a broadband response in the infrared region (**Figure 1.4.2**).[20] Unfortunately, DLW lacks the high resolution of EBL and cannot produce chiral structure with feature sizes small enough to show optical activity in the visible region. Furthermore, it suffers from the same drawbacks of EBL, low throughput and poor scalability.

Bottom-up methods, such as chemical synthesis and self-assembly, offer scalable routes to 3D chiral structures.[45, 46] For example, surface modification of achiral metal nanoparticles

in solution with chiral molecules leads to induced optical activity in the plasmonic resonances of the nanoparticles (**Figure 1.4.3.a**).[47] More exotic self-assembled structures, like helical superstructures of noble metal nanoparticles on macromolecular scaffolds (*e.g.*, DNA, peptides, and proteins), have also shown appreciable plasmonic optical activity (**Figure 1.4.3.b**).[48-50] These solution-based methods are certainly interesting, but the obtained chiral optical properties are generally much weaker than those of structures fabricated using top-down methods. Promising exceptions to this assessment are 3D metamaterials fabricated by selectively etching and metal-filling the gyroid networks of block copolymers, which show strong optical activity in the visible wavelength region (**Figures 1.4.1a – 1.4.1d**).[51, 52] Similar to other bottom-up methods, the parameters of such gyroid structures are defined by the available chiral templates.



Figure 1.4.3. (a) surface modification of achiral metal nanoparticles in solution with chiral molecules leads to induced optical activity in the plasmonic resonances of the nanoparticles. Ref.[47] (b) Self-assembled helical arrangements of Au nanoparticles fabricated using DNA scaffolds. Ref.[49]

1.5 Dynamic Shadowing Growth

Dynamic shadowing growth (DSG) is another promising bottom-up method for the fabrication of chiral plasmonic structures. DSG is a well-known physical vapor deposition method that is scalable and simple to implement,[53-56] and has been used in the production of broadband

antireflection coatings,[57] helical organic light-emitting diodes,[58] surface-enhanced Raman scattering substrates,[59] and scaffolds for chiral nematic liquid crystals,[60] among many other applications. Due to their high sensitivity and reproducibility, SERS substrates fabricated by DSG have been investigated for commercial production.[61] Additionally, a recent investigation demonstrated the feasibility of integrating DSG with roll-to-roll processing,[62] confirming the industrial scalability of the method. The geometric shadowing effect underpins the DSG method and is straightforward to understand; the ballistic travel of vapor atoms can be blocked by existing structures (*e.g.*, previously deposited material, templates, etc.) on a substrate, leading to material accumulating only in the regions that are not situated within these shadows.[63] By precisely orienting the substrate's azimuthal and polar angles with respect to the incoming vapor flux, the shadowed area can be dynamically controlled, and various nanostructures with controlled morphologies can be sculptured in free space.[64]



Figure 1.5.1 (a) Diagram of the oblique angle deposition setup. (b) Diagram of initial nuclei formation and (c) subsequent nanorod growth. Ref.[65]

Tilted nanorods are one of the basic structures fabricated by DSG and serve as an illustrative example. As shown in Figure 1.5.1,[65] the DSG process for tilted nanorods, called oblique angle deposition (OAD), depends upon a collimated vapor flux that is incident on a bare substrate at large angle with respect to the surface normal. Initially, the arriving material accumulates into islands or nuclei that are randomly distributed along the surface of the substrate. The size of these nuclei depends on the adatom mobility; faster adatoms create nuclei with larger diameters, while less mobile adatoms result in smaller nuclei. As the deposition proceeds, the taller islands act as the shadowing centers due to the geometric shadowing effect and block material accumulation on the smaller islands. If the surface adatom mobility is sufficiently low, material will only accumulate in the regions that are not shadowed by other structures, enabling growth of the taller structures at the expense of the shorter ones. This random and competitive process will eventually produce nanorod arrays that are tilted toward the vapor source at an angle that is material dependent.[66] The OAD process only requires a static oblique vapor incident angle. However, DSG considers dynamic positioning of both the vapor incident angle (polar angle, θ) and substrate rotation (azimuthal angle, φ). Thus, DSG can be used to fabricate tilted nanorods, straight nanorods, chevrons, beaded rods, and chiral nanostructures, like helices (Figure 1.5.2).

For chiral nanostructure assembly, DSG distinguishes itself from other bottom-up methods because it does not need to rely on the asymmetry of existing templates or constituents to generate structural chirality. Instead it uses static or dynamic substrate positioning to create asymmetric shadows and chiral structures. DSG fabrication of micro-/nanoscale helices on smooth surfaces, such as bare silicon or glass substrates, is a good example (**Figure 1.4.2f**).[67-69] The fabrication process for these helices begins by tilting the substrate at a large angle θ

22



Figure 1.5.2. Examples of electron micrographs of typical nanorods prepared by DSG: (a) vertically aligned Si nanorod array; (b) nanorods with different shapes; (c) Si nanospring array; (d) bead-like multilayer Si array; (e) multilayer array of nanosprings and nanorods; (f) a regular array of Si nanosprings grown on W-plugs; (g) bundle of Si/Ni multilayer nanosprings; (h) Ag nanoparticle decorated MgF₂ nanorod; and (i) Ag nanorod array deposited onto a tapered fiber where the inset shows the tapered fiber. Ref.[64]

with respect to the vapor flux ($\theta > 75^{\circ}$), causing the initially-nucleated material islands to cast large vapor shadows. While tilted at a large θ , the substrate is also rotated azimuthally at a slow rate ($d\varphi/dt$, for azimuthal angle, φ) such that the dynamically changing vapor shadow from previously deposited material carves out a helical shape in free space, which is concurrently filled in by the incoming vapor atoms. The morphological parameters of the obtained helices can be controlled by selecting specific values for θ , $d\varphi/dt$, and the deposition rate. This process works for any material so long as it can be evaporated under high vacuum and the surface mobility of its adatoms is slow.[70] For materials with high surface mobilities, the surface diffusion of adatoms will overcome the shadowing effect and prevent 3D sculpturing. Unfortunately, noble metal adatoms typically exhibit fast surface diffusion, making them incapable of forming helices at room temperature using DSG. However, as will be described below, this problem has been overcome, and DSG fabrication of chiral plasmonic helices has been demonstrated (**Figure 1.5.3**).[29, 71, 72] The DSG process is spontaneous, and therefore, the obtained helical nanostructures will normally be randomly distributed on the surface of a smooth substrate with an average inter-helix spacing. Thus, DSG is often used in conjunction with patterned substrates or templates to create well-defined lattices of nanostructures, such as helices.[68, 73]

The use of templates for DSG processes can not only provide a regular array of nucleation centers to create well-defined lattices of nanostructures, but also can provide distinctive shadowing profiles to generate unique arrays of chiral nanostructures. Such chiral nanostructures have been generated using various templates, such as lithographically produced PMMA pillars,[74] colloidal nanohole arrays,[75, 76] hydrothermally grown ZnO nanopillars,[77] and self-assembled colloidal nanosphere mononlayers.[78, 79] While each of these template methods offers intrinsic benefits, the use of self-assembled colloidal nanosphere monolayers (SACMs) is a particularly attractive method because its simplicity and scalability complement the DSG technique and the hexagonal close packed (HCP) lattice of spheres offers distinctive and desirable shadowing properties. Therefore, this dissertation describes several new strategies that use DSG and the asymmetric shadowing of SACM templates to generate 3D chiral plasmonic structures. These structures, such as chiral patchy particles, helically stacked plasmonic layers, and Swiss rolls, can be quite different geometrically from traditional helices, but similar to helices, they exhibit chirality in all three dimensions (**Figure 1.5.3**).



Figure 1.5.3. Examples of the chiral nanostructures fabricated by DSG highlighted in this dissertation, including plasmonic helices and SACM template based structures.

In this dissertation, we highlight these new DSG methods to generate films of 3D chiral micro-/nanostructures with tunable visible to near-infrared optical activities. Specifically, we describe DSG plasmonic helices and DSG chiral motifs utilizing self-assembled colloidal monolayers to generate unique chiral structures. We demonstrate that these films are not only produced in a simple and scalable manner, but that they can also exhibit significant optical activity and potential utility that are comparable to structures fabricated using cutting edge lithographic techniques.

1.6 Organization of the Dissertation

This dissertation is divided into 5 chapters. Chapter 1 serves as an introduction to this dissertation. It begins by describing the discovery and phenomena of optical activity, and then introduces the concepts of plasmonics and chiral plasmonics. Additionally, the chiral optical properties of most materials generally arise from the coupling of the electric and magnetic components of light, and there are several ways to mathematically describe these effects, depending on the type of structure. A brief review of the fabrication processes for chiral

plasmonic structures is given, and the need for simple and scalable methods of chiral nanostructure fabrication is established. Dynamic shadowing growth (DSG), the primary method used in our laboratory, is introduced along with its potential to fill this gap. Chapter 2 describes the DSG fabrication of composite plasmonic helices, their optical and structural properties, and some theoretical aspects that should be taken under consideration during the fabrication and analysis of chiral plasmonic structures. In particular, an experimental method is developed to characterize the chiral optical properties of plasmonic thin films while avoiding artifacts. Chapter 3 focuses on DSG methods that employ the use of self-assembled templates in order to fabricate novel chiral thin films. Geometric measures of chirality are introduced, and one particular method, the angular bisection method, is described in detail and used to analyze chiral patchy films. Chapter 4 addresses the topic of sensing applications of chiral plasmonic thin films by investigating the potential to use DSG films as chiral biosensors. Finally, Chapter 5 draws conclusions regarding these investigations, as well as points to future work to be done in this field.

CHAPTER 2

PLASMONIC HELICES

2.1 Introduction

The interest in the interaction of metal helices with electromagnetic radiation has a long history. Traditionally, these interactions have been primarily applied in antenna engineering in the design of end fire and polarization-insensitive receivers.[80] More recently, metal helices have been investigated for applications in chiral plasmonics or as chiral metamaterials, and have demonstrated such effects as broadband circular polarization and negative refraction.[20, 81] Optical applications of metal helices in the visible and near-infrared (NIR) region rely on effects associated with the strong resonances of localized surface plasmons of the noble metals, gold and silver in particular. However, due to the three-dimensional shape and requisite small feature sizes, the fabrication of plasmonic helices that are active in the visible and NIR regions remains challenging. Most fabrication methods to date have relied on the use of sophisticated techniques to generate passive templates or scaffolds that are metalized to achieve plasmonic activity. For example, direct laser writing of helical cavities in positive tone photoresist, followed by development and electrochemical deposition of gold, has been used to produce square arrays of plasmonic helices that show a broadband response in the infrared region.[20] Nanoparticlesensitization is another method of metalizing passive helical scaffolds in order to achieve a chiral plasmonic response, and optical activity has been demonstrated for both gold nanoparticlefunctionalized silica helices and chiral polymer fibers.[82, 83] Additionally, self-assembled helical superstructures of noble metal nanoparticles and biological macromolecules (*e.g.*, DNA, peptides, and proteins) have shown plasmonic chiral optical properties.[48, 49, 84] While these methods are certainly novel, one is consistently forced to choose between the simplicity of the method and the strength of optical activity in the production of plasmonic helices. In order to fulfill the promise of metal helices as chiral metamaterials, a scalable fabrication method capable of producing plasmonic helices with significant optical activity will need to be developed.

DSG is one method with the potential to achieve this goal, and a wide collection of different nanostructured thin films can be fabricated using this versatile method, including arrays of micro-/nanoscale helices with controllable pitch and height.[85] Dielectric helices fabricated through DSG have already demonstrated significant circular polarization effects due to the Bragg phenomenon.[86-88] Clearly, the incorporation of Ag and Au within the DSG technique is a very appealing method of fabricating plasmonic helices for chiral metamaterial applications, especially given the recent demonstrated potential for DSG roll-to-roll processing.[89] However, high mobility of surface adatoms and corresponding clusters precludes the production of helical structures of Ag and Au using conventional DSG;[90] kinetic growth processes overwhelm the shadowing effect when surface diffusion is significant, and this prevents DSG fabrication of asymmetric and non-equilibrium shapes, such as helices.[91] Square Ag helices have been achieved using oblique angle deposition (OAD),[92, 93] a variation of DSG, but the assimilation of Ag or Au within the full spectrum of DSG structures has previously eluded researchers.

Two distinct solutions to this issue can immediately be envisioned: one is to slow down the thermally induced surface mobility by lowering substrate temperatures; the other is to simply coat DSG dielectric helices with plasmonic layers.[29, 71] Recently, Mark *et al.* have demonstrated DSG noble metal helices by using a combination of liquid nitrogen substrate cooling and Au nanodot seeding, which reduces surface mobility and improves nucleation, respectively.[29] These solid metal helices can be dispersed into a solution to obtain chiral metafluids that exhibit pronounced optical activity. Furthermore, the Au nanodot seed arrays can be adjusted to achieve lattices of helices with different spacings, allowing the chiral optical response to be tuned.[94] On the other hand, the DSG template method uses ubiquitous DSG dielectric helices as scaffolds for subsequent DSG noble metal coatings to create a plasmonically-active coating on dielectric helices,[71] thereby avoiding the kinetic limitations imposed by noble metals for nanohelix formation. By changing the coating thickness and using different annealing treatments, Singh *et al.* were able to change the size and shape of the noble metal nanoparticles and vary the chiral optical response of the films.

The two types of DSG plasmonic helices described above exhibit excellent chiral optical properties, yet are still produced in scalable, multi-step manners. As an alternative to these methods, we have very recently developed a single-step method to achieve similarly remarkable plasmonic helices by taking advantage of composite materials using DSG and co-deposition.[72] Co-deposition refers to the simultaneous evaporation of two different source materials within the same DSG system.[64] By controlling the relative evaporation rates of different materials during the deposition, doped or composite materials with specific compositions can be obtained. These designed materials can be fully assimilated within the DSG technique and allow for the formation of plasmonic helices.

2.2 Composite Ti/Ag Helical Structures

This section describes the development of a room temperature DSG process to fabricate visiblyactive plasmonic helices using a composite material.[72] In particular, we use co-deposition and DSG to dope a small amount of Ti (5%/vol.) into Ag nanostructures. This method enables small noble metal helix formation using DSG because Ti atoms can effectively pin the typically fast diffusing Ag adatoms, which increases the sticking coefficient of the adatoms and improves nucleation. Six different DSG film morphologies were produced, and these are labeled STF1, STF2, STF3, STF4, STF5, and STF6 (note, sculptured thin film, STF). The morphologies range from vertical posts to complete helices to quasi-helices, where the obtained structure type depended on the deposition conditions.

2.2.1 Composite Ti/Ag helical structures: experimental methods

Ti/Ag helical films fabrication: The DSG films were fabricated using a custom designed vacuum deposition system equipped with two electron-beam evaporation sources (Pascal Technology).[64] The source materials used were Ti (99.9 %, Kurt J. Lesker) and Ag (99.995 %, Kurt J. Lesker). Prior to the deposition, the vacuum chamber was evacuated to a pressure of 1×10^{-6} Torr, and the background pressure during the deposition was maintained at less than 5×10^{-6} Torr. Pre-cleaned quartz slides and Si wafers were used as substrates, and were loaded onto a holder that was positioned at 87° with respect to the vapor incident direction. Importantly, the holder houses six different rotating pucks, which have different gear ratios (73:98; 73:28; 73:8; 73:4; 73:2; 73:1), and therefore rotate azimuthally at different rates. Furthermore, these pucks rotate in alternating directions. For example, if puck number one rotates in a clockwise sense, puck number 2 will rotate counter-clockwise, puck number 3 will

rotate clockwise, etc. By placing substrates on these separate pucks, six different DSG film morphologies can be produced during a single deposition; these are labeled STF1, STF2, STF3, STF4, STF5, and STF6, where STF1 corresponds with the holder having the fastest azimuthal rotation rate, STF2 has next fastest, and so on. The Ti/Ag ratio was controlled by the relative growth rates of Ti (0.01 nm/s) and Ag (0.19 nm/s), which were monitored independently by two separate quartz crystal microbalances (QCMs). The deposition proceeded until the total thickness from both QCMs reached 1 µm.

Structure and morphological characterization: The morphologies of the samples were examined by a field-emission scanning electron microscope (SEM, FEI Inspect F). The X-ray diffraction (XRD) was characterized by a PANalytical X'Pert PRO MRD X-ray diffractometer with fixed incidence angle of 1.5°. The XRD patterns were recorded with Cu K α radiation ($\lambda = 1.5405980$ Å) in the 20 range from 30°-80° at step size of 0.02°. Pole figures were measured using an open Eulerian cradle and poly-capillary lens with $\Delta \theta = 5^{\circ} \Delta \psi = 5^{\circ}$.

Optical characterization: A variable angle spectroscopic ellipsometer (M-2000, J. A. Woollam, Inc.) was used in transmission mode to measure the first three rows of the Mueller matrix describing the sample with the $m_{11}(\lambda)$ element normalized to 1. The unpolarized transmission was measured by UV-visible spectrophotometer (JASCO V-570) and used to calculate both the unpolarized absorbance and the un-normalized $m_{11}(\lambda)$ Mueller matrix element. The unnormalized $m_{11}(\lambda)$ and $m_{14}(\lambda)$ elements were used to determine the selective transmission of the films. The Mueller matrix was measured at several azimuthal orientations, and the $m_{14}(\lambda)$ element was found to be independent of azimuthal orientation. Additionally, the ellipsometry measurements were carried out with both the Ag coating facing the incident light and facing opposite the incident light, and no change in the measured $m_{14}(\lambda)$ element was observed. These observations indicate that there are no significant linear artifacts in the $m_{14}(\lambda)$ spectra. Thus, the $m_{14}(\lambda)$ spectra describe only circular polarization effects. The generalized ellipsometry measurements in Section 2.2.7 were made in transmission mode at normal incidence, and a single measurement was used for each film.

2.2.2. Composite Ti/Ag helix (STF2)

As described above, different composite Ti/Ag helical thin films have been fabricated using co-deposition and DSG. One film morphology, that of STF2, is characterized by one turn helical nanostructures, and will be examined in detail in this section due to the importance of the helical shape in regards to chirality. Figure 2.2.1a and 2.2.1b show representative top and crosssection SEM micrographs of the DSG-fabricated Ti/Ag composite helices, STF2. The surfaces of the substrates are populated with randomly distributed helical metallic nanostructures that are variously sized. The nanostructure density is found to be $\sigma = 37 \ \mu m^{-2}$, and the individual helices are found to have an average height of $h = 110 \pm 30$ nm, a radius of curvature of $R = 75 \pm 20$ nm, a pitch of $p = 100 \pm 5$ nm, and an arm radius of $r = 30 \pm 10$ nm (see Figure 2.2.2 for parameter definitions). The large distributions in the morphological parameters result from the small incomplete helices and bifurcations and coalescence of helical arms. This film morphology is consistent with a nanostructure growth mechanism determined by both surface diffusion and atomic shadowing. Thus, while surface diffusion effects remain, the addition of a small quantity of Ti vapor flux (5 %/vol.) enables the generation of helical nanostructures via the shadowing effect at room temperature, where, under identical conditions, a pure Ag vapor flux does not (see Section 2.2.4 for pure Ag experiment).



Figure 2.2.1. (a) Top view and (b) cross-section SEM images of the Ti/Ag composite helical films. (c) X-ray diffraction pattern of the Ti/Ag films. The diffraction peaks are labeled and correspond with fcc Ag. (d) Ag (111) pole figure of the film, showing a (111) fiber texture. The asymmetry of the texture is the result of the helical structure of the film.

X-ray diffraction (XRD) measurements of STF2 were performed in order to confirm the material phase of the Ti/Ag helices. The obtained diffraction peaks (**Figure 2.2.1c**) are consistent with the diffraction pattern of oriented polycrystalline fcc Ag (JPCDS No. 00-004-0783). The XRD measurements do not reveal any contribution from Ti, although the overlap of the Ti (002) peak by the Ag (111) peak could obscure its contribution. As shown in the pole figures in **Figure 2.2.1d**, STF2 was found to grow with a (111) fiber texture. The intensity pattern of the (111) pole has a distinctive chiral shape that is consistent with the left-handed helical structure of the Ti/Ag material. These results agree with the typical growth mode of Ag thin films, which,



Figure 2.2.2. Schematic depicting the chiral nanostructure morphological parameters: height (h), diameter (d), radius of curvature (r), and pitch (p).

like most fcc metals, exhibits a preferred [111] growth direction.[95] Thus, although the addition of Ti does significantly change the morphological growth of Ag, it does not appreciably change the crystalline structure. Indeed, the XRD results for pure Ag films are very similar to **Figure 2.2.1c** (see Section 2.2.4).

The mechanisms by which Ti affects nanostructure growth at room temperature are not straightforward and could be the result of several factors. Ti is traditionally used as an adhesion layer or seed layer for other metals on metal oxide substrates.[96] The improved adhesion and nucleation from Ti are generally attributed to improved wetting, where the deposited metal can easily wet the metallic Ti surface and Ti can wet the metal oxide surface due its affinity for oxygen binding.[97] For the composite Ti/Ag structures, this buffer effect might play a role in increasing the initial nucleation rate and reducing the critical nucleation radius, but as growth proceeds the substrate/material interface becomes less important and Ti must act to reduce kinetic processes such that the atomic shadowing effect becomes dominant. Reduced mobility of Ag due to the presence of a Ti adhesion layer has been observed before and has been found to

depend strongly on the size, shape, distribution and oxidation state of the Ti atoms and clusters.[98] Alternatively, the effect of Ti on Ag during DSG growth can be understood by impurities-induced changes to the structure zone model of thin film growth.[99] Impurities that are not soluble in the lattice (*e.g.*, excess Ti atoms and Ti atoms that have reacted with residual gases) are segregated to grain boundaries and growth surfaces, increasing nucleation and reducing grain size, coalescence, and grain boundary migration.[100] That is, an increase in impurity concentration has the same effect on film growth as does a reduction in the homologous temperature, $T_h = T_s/T_m$, where T_s and T_m are the substrate and material melting temperature, respectively. T_h is a critical factor in determining the structure zone model of DSG film morphology.[70] In particular, $T_h < 0.24$ favors the production of rods that can be sculpted into helical shapes. Similar to the Ti/Ag composite films, an effective reduction in T_h and promotion of rod formation due to Ti-doping has been observed in Mg films fabricated using OAD.[101]

The optical properties of STF2 were further investigated through both unpolarized transmission spectroscopy and Mueller matrix transmission ellipsometry. As shown in **Figure 2.2.3a**, the unpolarized transmission spectrum has a broad valley over wavelengths $\lambda \approx 400$ – 1400 nm and reaches a minimum at $\lambda \approx 540$ nm. This broadband loss in transmission is attributed to the excitation of localized surface plasmon resonances of the Ti/Ag nanostructures of STF2, including contributions from both variously-sized helical structures and Ti/Ag islands of different shapes and sizes that ceased growing due to the competitive nature of DSG.[102-104] The difference in transmission between left and right circular polarized light (LCP and RCP, respectively) is determined from the m_{14} Mueller matrix element that is measured using transmission ellipsometry (**Figure 2.2.3b**). Similar to the plasmonic resonances, the optical activity is broadband and extends beyond the measurement range of the instrument. For $\lambda < 650$



Figure 2.2.3. (a) Unpolarized UV-Vis-NIR transmission spectrum of the helical Ti/Ag composite film. (b) The circular polarized differential transmission spectrum (black curve, left ordinate axis) and the anisotropy factor, g, plotted as a function of wavelength (red curve, right ordinate axis).

nm, the films transmit LCP light more efficiently than RCP, while for $\lambda > 650$ nm, the films transmit RCP light more efficiently. The circular polarization selectivity is greater at longer wavelengths, with the difference in transmission exceeding 10% for $\lambda \approx 1000$ nm. In order to directly compare the optical activity of STF2 with other DSG plasmonic helices and structures, we calculated the anisotropy factor, $g = \Delta A/A$, for the films, where ΔA is the difference in extinction between LCP and RCP light and *A* is the unpolarized extinction.[71] As shown in **Figure 2.2.3b**, the magnitude of *g* is quite large, with |g| > 0.3 for $\lambda \approx 460 - 560$ and 800 - 1000 nm and g = -0.39 for $\lambda \approx 500 - 520$ nm. These *g*-factors are significantly larger than those of the metal nanoparticle-coated dielectric DSG helices, which have anisotropy factors of $g \approx 0.2$.[71] Additionally, these g-factors exceed those of DSG-fabricated chiral Au nanoshells coated on ZnO pillars.[77]

2.2.3. Composite Ti/Ag helix: FDTD simulations

Finite-difference-time-domain (FDTD) simulations were performed in order to better understand the origin of the optical activity in the composite Ti/Ag helices of STF2. The simulated structure consists of left-handed metallic helices, which, as an approximation of the DSG film, are placed in a rectangular array with lattice spacing *a*. It is assumed that Ti (5%/vol.) has a negligible effect on the measured optical properties of the helices and a modified Debye-Drude model approximation of pure Ag is used for the calculation.[105] **Figure 2.2.4a** shows the simulated circular polarized transmission spectra of an array of helices with *a* = 300 nm; *R* = 65 nm, *r* = 25 nm, *h* = 100 nm, and *p* = 100 nm. The single pitch metallic helix has several resonances over wavelengths $\lambda = 400 - 2000$ nm in the different spectra. These different resonances correspond



Figure 2.2.4. (a) Circular polarized transmittance of an Ag helix (N = 1) calculated by FDTD. Note that $T(RCP \rightarrow LCP)$ (red curve) is completely overlapped by $T(LCP \rightarrow RCP)$ (green curve) and is not visible in the plot. The labels b - e correspond with the different plasmonic modes illustrated in figures (b) - (e). Here the arrows represent the direction of current flow at a particular instant in time. (f) Comparison of the g-factor obtained in experiment and calculated using FDTD by averaging different helices.

with the excitation of different plasmonic modes within the helices.[104] These modes are similar to standing waves and are illustrated in **Figures 2.2.4b** – **4e**, which show a snapshot of the direction of current flow within a helix at the different excitation wavelengths. The lowest energy mode at $\lambda \approx 1360$ nm corresponds with the fundamental mode having zero nodes, and, as the excitation energy increases, the number of nodes increases in integer steps. Importantly, while both RCP and LCP are able to excite each of these modes, a specific handedness of circular polarization produces a stronger coupling at each resonance, leading to a circular polarization selectivity that is a function of wavelength. Thus, the simulated helices transmit RCP more efficiently for $\lambda > 600$ nm and transmit LCP more efficiently for $\lambda < 600$ nm. These observations are consistent with previous studies of plasmonic metal helices.[102, 106]

It is important to note that the resonance wavelengths of the array exceeds the bounds given by traditional antenna theory for metal helices, *i.e.*, $\lambda \in 2\pi R\{3/4, 4/3\}$, because the structures do not conform to the traditional assumptions of R >> r and N > 3, where N is the number of pitches.[80] Therefore, the resonance wavelengths of the helical array may depend significantly on other morphological parameters in addition to R, such as p, r, and h.[106] Due to the statistical distribution of morphological parameters in shadowing growth as revealed by **Figure 2.2.1**, the Ti/Ag helices exhibit a broad optical response as seen in **Figure 2.2.3**. All of these parameters should contribute to the broadening of the experimental transmission loss, but it is expected that the primary means of broadening arises from incomplete helices, which is intrinsic to DSG growth due to the ongoing competition from atomic shadowing growth. In other words, the fastest growing Ti/Ag helices will persist in accumulating material throughout DSG growth, while the slower growing ones eventually fall into the vapor shadow and cease growing, leading to a film with a distribution in h and, equivalently, a distribution in N.

Therefore, in order to effectively model our experimental results, we fix the parameters of the helices, a = 300 nm; R = 65 nm, r = 25 nm, and p = 100 nm, and then vary the pitch number, N = 0.5 - 1.5. The film's response can then be approximated as the average response of all these helices. The resulting curve is plotted in **Figure 2.2.4f** alongside the experimental result, and the agreement is quite good. These FDTD simulations confirm that the results are consistent with previous reports of plasmonically active helices, and they also indicate that the experimental optical properties of the composite Ti/Ag helical films can be described by an average response of pure Ag helices with a distribution in *N*.

2.2.4 Pure Ag experiment

In order to demonstrate the importance of the effect of Ti on the morphological growth of Ag during DSG, we fabricated pure Ag DSG films using identical parameters as used for the composite Ti/Ag helix, STF2, except that we increased the deposition rate of Ag to maintain a total deposition rate of 0.2 nm/s. **Figures 2.2.5a and 2.2.5b** show the top-view and cross-section SEM images of the as-deposited Ag DSG films. Clearly, the morphologies of the individual pure Ag nanostructure are very different from STF2 (**Figures 2.2.1a and 2.2.1b**). Most Ag nanostructures have a symmetric, equiaxed grain morphology, consistent with growth affected by high surface diffusion. A few nanostructures do appear to have a slight twist or kink along their length when viewed in the cross-section image. **Figure 2.2.5c** shows the XRD pattern of the pure Ag DSG films, and the peaks are consistent with those of oriented polycrystalline fcc Ag (JPCDS No. 00-004-0783). The diffraction pattern is similar to the pattern obtained for the STF2 films (**Figure 2.2.1c**), except that the peaks are much sharper for the pure film. This indicates smaller crystalline domains and/or more non-uniform strain within the crystalline

lattice for the composite structure, both which is expected for composite/doped materials. In measuring the Mueller matrix ellipsometry of the pure Ag DSG films, we found the m_{14} element was non-zero over the measured wavelengths, indicating circular polarization anisotropy (note, $T_{\rm LCP} - T_{\rm RCP} = -2 m_{14}$). However, the magnitude of the selective circular polarized transmission is significantly smaller than that for STF2 (**Figure 2.2.1d**). This circular polarization anisotropy in the pure Ag DSG films might arise from kinked or slightly twisted nanostructures, similar to those seen in **Figure 2.2.5b**.



Figure 2.2.5. (a) Top-view and (b) cross-section SEM images of the pure Ag DSG films. (c) XRD diffraction pattern of the pure Ag film. The diffraction peaks are labeled, as are the extra peaks associated with Cu K β radiation. (d) $m_{14}(\lambda)$ spectra for the pure Ag and Ti/Ag composite DSG films.

2.2.5 Composite Ti/Ag vertical posts, helices, and quasi-helices

As described in Section 2.2.1, six different nanostructured composite Ti/Ag films, STF1, STF2, STF3, STF4, STF5, and STF6, have been fabricated, and each has a different morphology. Representative SEM images of these films are shown in **Figures 2.2.6a** – **1f**. It can be seen that the nanostructure morphologies of STF1 (**Figure 2.2.6a**) resemble conical, vertical posts, which are characteristic of DSG using a relatively fast azimuthal rotation rate and with a fast adatom



Figure 2.2.6. (a) - (f) Top-view and cross-section SEM images of STF1, STF2, STF3, STF4, STF5, and STF6, respectively. The coordinate system inset in each image depicts the approximate axes of the generalized ellipsometry measurements. The direction of light propagation, or the z-axis, points into the page.

	Height, h	Diameter, d	Radius of	Pitch, p	Pitch
	(nm)	(nm)	(nm)	(nm)	Number, N
STF1	160 ± 60	80 ± 60			
STF2	110 ± 30	70 ± 30	90 ± 20	100 ± 5	1.1 ± 0.3
STF3	240 ± 20	100 ± 70	260 ± 30	560 ± 50	0.43 ± 0.05
STF4	200 ± 50	80 ± 30	540 ± 20	900 ± 200	0.22 ± 0.07
STF5	200 ± 20	80 ± 30	1120 ± 90	1900 ± 200	0.11 ± 0.02
STF6	220 ± 20	60 ± 30	2000 ± 200	4200 ± 400	0.052 ± 0.007

Table 2.2.1. Morphological parameters of the individual chiral nanostructures

mobility.[70] These nanostructures are comparatively achiral and have very little shape anisotropy along the substrate plane. In comparison, the nanostructure morphologies of STF2 resemble helices as discussed above, while the morphologies of STF3, STF4, STF5, and STF6 resemble slanted, curved posts or quasi-helices. Thus, STF2 through STF6 are described by chiral nanostructures with increasing and aligned shape anisotropy within the substrate plane. These nanostructures are consistent with DSG growth having a decreasing azimuthal rotation rate. The average morphological parameters, height (h), diameter (d), radius of curvature (r), pitch (p), and pitch number (N = h/p) are defined in Figure 2.2.2, and the results for the different films are listed in Table 2.2.1. In general, these plasmonic films have highly aligned nanostructures and varying degrees of chiral and linear anisotropies arising from their These mixed anisotropies will result in a nontrivial polarization-dependent morphologies. optical response. The optical response of STF1 - STF6 will be discussed in greater detail in Section 2.2.7, after the development of an ellipsometric method for the extraction of the different optical parameters of aligned chiral films.

2.2.6 Experimental parameter retrieval of aligned chiral films using ellipsometry

Here, and very often in the literature, the materials under investigation use highly aligned chiral nanostructures. Unfortunately, the use of aligned chiral structures becomes problematic for polarization-dependent optical measurements, such as circular dichroism (CD) spectroscopy, because linear anisotropy resulting from structural alignment can introduce artifacts in circular polarization measurements.[107] These artifacts complicate experimental analysis and can obscure measurement of the true chiral plasmonic properties. The most popular method to account for these linear artifacts, known as the "front and back" method, [40] involves making CD measurements through both the front and back of the sample and then taking the average. However, this method may be difficult to implement for some experimental situations (e.g., in situ, time-resolved or real time measurements), and worse, it may not give accurate results.[108] The inaccuracy associated with the front and back method may not only arise from experimental considerations such as small sample size and non-uniformity, but also because anisotropies may not be additive for strong signals; therefore, averaging will not cancel out the linear effects. Thus, a simple method for reliably extracting and analyzing the circular polarization parameters of aligned or anisotropic chiral plasmonic structures is needed.

Spectroscopic ellipsometry measures the change in polarization state of light, as a function of wavelength, upon transmission or reflection from a sample.[109] Note that some references in the literature make the distinction between measurements made in reflection or transmission, calling the former ellipsometry and the latter polarimetry; this distinction is not considered here. Commercial ellipsometry instruments are available, and the technique has long been used for thin film analyses.[110] Among different ellipsometry measurement strategies, the generalized ellipsometry technique expands upon conventional ellipsometry to include

Effect	Symbol	Definition ^a			
Mean refractive index	ñ	$2\pi[(n_{\rm x}+n_{\rm y})l/\lambda_0]$			
Mean absorbance	Ã	$\ln 10(A_x + A_y)/2$			
(x - y) linear birefringence	LB	$2\pi[(n_{\rm x}-n_{\rm y})l/\lambda_0]$			
(x - y) linear dichroism	LD	$\ln 10(A_x - A_y)/2$			
45° linear birefringence	LB'	$2\pi[(n_{45}-n_{135})l/\lambda_0]$			
45° linear dichroism	LD'	$\ln 10(A_{45} - A_{135})/2$			
Circular birefringence	CB	$2\pi[(nn_+)l/\lambda_0]$			
Circular dichroism	CD	$\ln 10(A_{-} - A_{+})/2$			

Table 2.2.2. Retardances and absorbances: notation and definitions

^awhere *n* is the conventionally defined refractive index; *A* is the standard absorbance in the base *e*; *l* is the path length through the sample; λ_0 is the vacuum wavelength of light; and the subscripts refer to the polarization direction of light as *x*, *y*, 45° to the *x*-axis, 135° to the *x*-axis, right circular (+), or left circular (-).

measurement of the normalized off-diagonal Jones matrix elements of an optical system.[111] Thus, generalized ellipsometry is ideal for the characterization and analysis of homogenous, anisotropic samples. As described in **Appendix A**, a complete Jones matrix is a comprehensive description of a non-depolarizing optical system.[112] Notably, when an optical system or sample contains a combination of linear and circular anisotropy, the individual Jones matrix elements are a product of these different retardances and absorbances, whose individual magnitudes can be obtained through matrix decomposition or inversion in certain cases.[113-115] Recently, Arteaga and Canillas described an analytical method for such an inversion that permits the direct extraction of (x - y) linear birefringence and dichroism (*LB* and *LD*), 45° birefringence and dichroism (*LB'* and *LD'*), and circular birefringence and dichroism (*CB* and *CD*) from a single Mueller-Jones matrix, experimentally measured using a custom twomodulator generalized ellipsometer (these various retardance parameters are defined in **Table 2.2.2.**[115] This analytical method can easily be extended to encompass the inversion of generalized ellipsometry spectra obtained through ellipsometers with a single compensator, thus providing a readily available method for extracting and analyzing the circular polarization properties of aligned or anisotropic chiral plasmonic structures.[116]

In particular, by using a spectroscopic ellipsometer in transmission mode, one can obtain the normalized Jones matrix, J:

$$\mathbf{J} = t_{xx} \begin{bmatrix} 1 & t_{xy}/t_{xx} \\ t_{yx}/t_{xx} & t_{yy}/t_{xx} \end{bmatrix} = t_{xx} \begin{bmatrix} 1 & \tan \psi_{xy} e^{i\Delta_{xy}} \\ \tan \psi_{yx} e^{i\Delta_{yx}} & \tan \psi_{yy} e^{i\Delta_{yy}} \end{bmatrix},$$
(2.2.1)

where t_{xx} , t_{yy} , t_{xy} , and t_{yx} are the complex transmission coefficients for orthogonal directions, x and y, and ψ_{ij} and Δ_{ij} are the conventional generalized ellipsometric parameters, $\psi_{ij} = \tan^{-1} |t_{ij} / t_{xx}|$ and $\Delta_{ij} = \arg |t_{ij} / t_{xx}|$ for i, j = x, y, which describe the amplitude ratios and phase differences, respectively, for *x*- and *y*-polarization upon transmission through a sample.

Note that there are different conventions associated with normalization, range of Δ , and signs that will need to be considered when using experimentally obtained data. There are two main ellipsometry conventions that need to be taken into account when extracting the anisotropic optical properties of samples using generalized ellipsometry. The first arises from the different sign conventions from optics or physics. The optics community typically uses N = n - ik for the refractive index, while the physics community uses N = n + ik. These correspond with ellipsometric parameters as $\rho = \tan \psi e^{i\Delta}$ or $\rho = \tan \psi e^{-i\Delta}$, respectively. See Appendix 2 of Ref. [109] for further details. The second convention concerns the normalized Jones matrix obtained through ellipsometry. The Jones matrix shown in Equation (2.2.1) is normalized by a single diagonal element, in this case t_{xx} . Some ellipsometry companies (*e.g.*, J.A. Woollam) use the convention where the off-diagonal element is normalized by the diagonal element within the same column (*i.e.*, t_{yx}/t_{xx} and t_{xy}/t_{yy}). Conversion between these different conventions only requires multiplication and division.

As mentioned above, a Jones matrix can be parameterized by the various polarization dependent birefringence and dichroism values:[107, 115]

$$\mathbf{J} = e^{-i\chi/2} \begin{bmatrix} \cos\frac{T}{2} - \frac{iL}{T}\sin\frac{T}{2} & \frac{(C-iL')}{T}\sin\frac{T}{2} \\ \frac{-(C+iL')}{T}\sin\frac{T}{2} & \cos\frac{T}{2} + \frac{iL}{T}\sin\frac{T}{2} \end{bmatrix},$$
(2.2.2)

where $\chi = 2(\tilde{n} - i\tilde{A})$, $T = (L^2 + L^{2} + C^2)^{1/2}$, L = LB - iLD, L' = LB' - iLD', C = CB - iCD, and \tilde{n} and \tilde{A} are the mean refractive index and mean absorbance, respectively (**Table 2.2.2**). Following the method of Arteaga and Canillas, we identify parameters in Equation (2.2.1) with the parameters in Equation (2.2.2):

$$\begin{bmatrix} \cos\frac{T}{2} - \frac{iL}{T}\sin\frac{T}{2} & \frac{(C-iL')}{T}\sin\frac{T}{2} \\ \frac{-(C+iL')}{T}\sin\frac{T}{2} & \cos\frac{T}{2} + \frac{iL}{T}\sin\frac{T}{2} \end{bmatrix} = K \begin{bmatrix} 1 & \tan\psi_{xy}e^{i\Delta_{xy}} \\ \tan\psi_{yx}e^{i\Delta_{yx}} & \tan\psi_{yy}e^{i\Delta_{yy}} \end{bmatrix},$$
(2.2.3)

where K is a complex constant. The following relationships are determined by solving the systems of equations created by combining the different matrix elements:

$$LB = \operatorname{Re}[i\Omega(1 - \tan\psi_{yy} e^{i\Delta_{yy}})], \qquad (2.2.4)$$

$$LB' = \operatorname{Re}[i\Omega(\tan\psi_{xy} e^{i\Delta_{xy}} + \tan\psi_{yx} e^{i\Delta_{yx}})], \qquad (2.2.5)$$

$$CB = \operatorname{Re}[\Omega(\tan\psi_{xy} e^{i\Delta_{xy}} - \tan\psi_{yx} e^{i\Delta_{yx}})], \qquad (2.2.6)$$

$$LD = -\mathrm{Im}[i\Omega(1 - \tan\psi_{yy} e^{i\Delta_{yy}})], \qquad (2.2.7)$$

$$LD' = -\mathrm{Im}[i\Omega(\tan\psi_{xy} e^{i\Delta_{xy}} + \tan\psi_{yx} e^{i\Delta_{yx}})], \qquad (2.2.8)$$

$$CD = -\mathrm{Im}[\Omega(\tan\psi_{xy} e^{i\Delta_{xy}} - \tan\psi_{yx} e^{i\Delta_{yx}})], \qquad (2.2.9)$$

$$\Theta = [\tan \psi_{yy} e^{i\Delta_{yy}} - (\tan \psi_{xy} e^{i\Delta_{xy}} \tan \psi_{yx} e^{i\Delta_{yx}})]^{-1/2}, \qquad (2.2.10)$$

where $\Omega = T \Theta / (2 \sin[T/2])$ and $T = 2 \cos^{-1}[\Theta(1 + \tan \psi_{yy} e^{i\Delta_{yy}})/2]$. Equations (2.2.4) –

(2.2.10) provide a direct relationship between the generalized ellipsometry parameters and the birefringent and dichroic properties defined in **Table 2.2.2**.

It is important to note that most aligned chiral films (*e.g.*, DSG films) will show a mixture of anisotropies, meaning that each film is generally defined by elliptical birefringence and dichroism, *i.e.*, the eigenpolarizations are neither linear nor circular. Therefore, it is convenient to define a generalized retardance vector, T = (L, L', -C), which has absolute magnitude $|T| = (LB^2 + LD^2 + LB^{2} + LD^{2} + CB^2 + CD^2)^{1/2}$ in order to quantify and assess the total anisotropy of the individual films. For circular polarization applications it is also useful to consider the magnitude of circular retardance normalized by the magnitude of total anisotropy, $C_T = |C| \times |T|^{-1}$, which quantifies the degree of circular polarization of the transmitted light.

From the discussion above it is clear that there are distinct advantages to using generalized ellipsometry for polarization-sensitive optical measurements, especially for the characterization of highly aligned chiral plasmonic nanostructured thin films. In particular, all of the retardances can be quantified using a single generalized ellipsometry measurement. This is a significant improvement over typical CD spectroscopy methods, which require at least two separate measurements and may not provide accurate results. Furthermore, because the total polarization anisotropy is measured through generalized ellipsometry, interesting and useful phenomena of chiral plasmonic nanostructures can be observed that might go unnoticed by solely measuring CD spectroscopy. For example, the polarization eigenstates of different films can be effectively measured.

2.2.7 Extracted optical parameters of STF1 – STF6

The generalized ellipsometry spectra of the Ti/Ag composite films were measured using a commercial ellipsometer in transmission mode at normal incidence, and then the polarization dependent retardances and absorbances were extracted from these measurements using Equations



Figure 2.2.7 Retardances and absorbances extracted from generalized ellipsometry measurements of the Ti/Ag chiral films: (a) – (c) Linear, 45°, and circular birefringence spectra, and (d) – (f) Linear, 45°, and circular dichroism spectra, respectively.

(2.2.4) – (2.2.10). These results are plotted in **Figure 2.2.7**. The measured linear birefringencedichroism pairs (*LB-LD* and *LB'-LD'*) are consistent with expectations given the nanostructure morphology and alignment with the experimental coordinate system (**Figure 2.2.6**). For example, the nanostructures of STF5 are primarily aligned with the *x*-axis, and therefore show the most significant *LB* and *LD* (**Figures 2.2.7a** and **2.2.7d**), with *LB* ~ 1.1 at wavelength λ ~ 600 nm and *LD* ~ 1.4 at λ ~ 1000 nm. On the other hand, the nanostructures of STF4 and STF6 are very much in congruence with the 45°-axis, and therefore have relatively small values for *LB* and *LD* but have large values for *LB'* and *LD'*, *LB'* > 1 at λ = 600 nm and *LD* > 1.2 at λ = 1000 nm (**Figures 2.2.7b** and **2.2.7e**). In comparison, the nanostructures of STF1, STF2, and STF3 have a higher degree of symmetry with respect to both the *x*- and 45°-axes and therefore have smaller values for *LB*, *LD*, *LB'*, and *LD'* than the more anisotropic films. As shown in **Figures 2.2.7c** and 2.2.7f, the films with helical or quasi-helical morphologies, STF2 through STF6, exhibit significant circular polarization effects, as expected, while the vertical posts of STF1 show very slight *CB* and *CD*. Due to its small radius of curvature and full helicity, STF2 shows a characteristic bisignate *CD* response over the measured wavelengths. STF3 through STF6 show broadband *CD* peaks that alternate between positive and negative, in agreement with the alternating handedness of their helicities. Interestingly, STF4 is a quarter-turn quasi-helical film and has stronger *CB* and *CD* than STF2 and STF3, which contain full-turn and half-turn helices, respectively. This result is surprising. However, a number of factors can contribute to the large obtained CB and CD magnitudes of STF4. Plasmonic optical activity can be enhanced not only by a highly chiral shape, but also through efficient mixing of different plasmonic modes.[33] Additionally, recent studies have demonstrated that noble metals shaped into arcs or incomplete helices can exhibit substantial plasmonic optical activity.[75, 117]

It is important to note that like most aligned chiral films, all of the chiral Ti/Ag films show a mixture of anisotropies, meaning that each film is generally defined by elliptical birefringence and dichroism, *i.e.*, the eigenpolarizations are neither linear nor circular. Therefore, it is useful to analyze the generalized retardance vector, T = (L, L', -C), which has absolute magnitude $|T| = (LB^2 + LD^2 + LB^{2} + LD^{2} + CB^2 + CD^2)^{1/2}$ in order to quantify and assess the total anisotropy of the individual films. As shown in Figure 2.2.8a, |T| generally increases for STF1 through STF6, as the nanostructure morphology changes from vertical postlike to helical to quasi-helical, *i.e.*, as the nanostructures exhibit increasing shape anisotropy along the substrate plane. For circular polarization applications it is also useful to consider the magnitude of circular retardance normalized by the magnitude of total anisotropy, $C_T = |C| \times |T|^{-1}$,



Figure 2.2.8. (a) The magnitude of the generalized retardances, |T|, of the Ti/Ag chiral films, and (b) the normalized magnitude of the circular retardance, $C_T = |C| \times |T|^{-1}$. (c) Plot of C_T at $\lambda = 650$ nm versus pitch number, N.

which quantifies the degree of circular polarization of the transmitted light. The results for the different chiral Ti/Ag films are shown in **Figure 2.2.8b**. Remarkably, STF2 has $C_T \sim 1$ for wavelengths 550 nm $\leq \lambda \leq 650$ nm, indicating that the anisotropy is purely circular in that region. Though STF2 does not exhibit the greatest values of *CB* or *CD* of the films examined in this report, it does have among the highest reported values of optical chirality,^[72] and it will transmit circular polarized light without polarization conversion over 550 nm $\leq \lambda \leq 650$ nm, making it ideal for device applications. By comparing the morphological parameters from Table 2.2.1 with **Figure 2.2.8b**, it is clear that C_T increases with pitch number, *N*, of the quasi-helical Ti/Ag films. In fact, C_T is approximately equal to the pitch number for $N \leq 1$ and $\lambda \geq 650$ nm, as shown in **Figure 2.2.8c**, which plots C_T at $\lambda = 650$ nm versus *N* for the quasi-helical films. These results illustrate the possibility of designing chiral plasmonic structures with specific elliptical polarization eigenstates over a large region of wavelengths.

2.2.8 Composite Ti/Ag helical structures: conclusions

In conclusion, we leverage the concept of composite materials in order to overcome the challenges to the fabrication of plasmonic helices that are optically active in the visible wavelength region. That is, by combining Ag with a small quantity of Ti in vapor form, a new material with reduced adatom surface diffusion compared to pure Ag is created, allowing it to be sculptured into helices using a straightforward DSG process, yet the final film still retains the exceptional optical properties of Ag. This is because the small quantity of Ti greatly alters the morphological growth of Ag, but does not significantly affect the crystalline structure. The achieved films exhibit large circular birefringence and dichroism in addition to large linear anisotropy, and some of these films rank among the most optically chiral films to date. Furthermore, the results demonstrate that the polarization eigenstates can be effectively tuned from purely circular to approximately linear by changing the pitch number, *N*, of the plasmonic helices for $N \leq 1$.

While in this case the benefits of a Ti/Ag composite has been demonstrated for the physical vapor deposition of chiral plasmonic films, surface diffusion and nucleation of Ag are critical factors in most nanofabrication methods,[118] and atomic diffusion is also important in such material phenomena as electromigration and the Kirkendall effect.[119-121] Therefore, the demonstration of a material with the exceptional properties of Ag but with reduced surface diffusion and increased nucleation could benefit other fabrication methods and find other applications beyond optics.

2.3 Composite Ag/MgF₂ Helices

Optical loss in plasmonic metamaterials is a challenge that must be overcome before some practical devices can be realized.[122] A simple way to reduce the losses associated with plasmonic materials is just to use less plasmonic materials by creating composite nanostructures where a portion of the noble metal has been replaced by a transparent dielectric. In spite of using less plasmonic material, optimized composite structures can exhibit significant optical activity.[71] An additional benefit of using noble metal/dielectric composite materials for DSG fabrication is that one can also take advantage of the slow adatom diffusivity of dielectrics to generate nanohelices. For example, by simultaneously evaporating MgF₂ and Ag, where MgF₂ is the major constituent of the vapor atoms, it is possible to create a transparent, helical MgF₂ host environment using DSG, but still retain the plasmonic effects due to the presence of Ag.[123] The well-behaved growth properties of MgF₂ are not significantly affected by the presence of a small amount of Ag. Similarly, as Ag is incorporated into the growing MgF₂ helix, it segregates into isolated Ag nanoparticles both within and on the surface of the MgF₂ helix, and these isolated nanoparticles still retain the characteristic optical properties of Ag.

In order to demonstrate the feasibility of such metal/dielectric helices through DSG and co-deposition, composite helical films were fabricated using the same system and similar method described in Section 2.2, except in this case, the composite structure consisted of a dielectric, MgF₂ (99.9 %, Kurt J. Lesker), and a noble metal, Ag (99.995 %, Kurt J. Lesker). **Figure 2.3.1a** shows a representative transmission electron microscopy (TEM) image of a 1:10 (volume ratio) Ag/MgF₂ helix. Here, the lighter colored helical backbone of the nanostructure corresponds with MgF₂, while the dark, somewhat spherical nanoparticles decorating the surface and interior of the nanostructure correspond with Ag. The contrast difference between the two
materials is due to their different electron scattering cross-sections, the result of different atomic masses. This structure is similar to noble metal coated dielectric helices described in Ref. [71], except that here the Ag nanoparticles are part of the helical structure and not a surface coating.

The physical principles governing the chiral optical properties of the Ag/MgF₂ composites should be the same as those of other helical assemblies of separated achiral nanoparticles,[48-50, 71] but are different than those for noble metal nanoparticles with a true chiral shape, *e.g.*, a continuous helix.[33] The chiral optical properties for helical assemblies arise from Coulomb interactions of the plasmonic nanoparticles placed in a chiral arrangement.[34] Thus, the spectral features of the chiral optical response will be a convoluted function of both the helical parameters and nanoparticle morphology. Specifically, the nanoparticles will have particular optical resonances determined by their size, shape, and separation, while the helical parameters that are determined by the dielectric support will also constrain the chiral optical response to particular wavelength ranges. These effects can clearly be seen in **Figure 2.3.1b** which shows the ΔT spectra for Ag/MgF₂ helices with the same compositions but different helical picth, *p*, and number of turns, *N*, and in **Figure 2.3.1c** which



Figure 2.3.1. (a) Representative TEM image of an Ag/MgF2 composite helix. (b) ΔT spectra for Ag/MgF2 helical films with the same composition but with different handedness, helical pitch p, and pitch number N. (c) ΔT spectra for Ag/MgF2 helical films with the same handedness, p, and N but different compositions.

shows the ΔT spectra for Ag/MgF₂ helices with the same *N* and *p* but different compositions. As expected, all spectra have an approximate bisignate shape that is characteristic of helically arranged nanoparticles, and different handed helices have opposite ΔT spectra.[49] Additionally, increasing the helical pitch height, *p*, tends to red-shift the bisignate spectral features for Ag/MgF₂ helices of the same composition (**Figure 2.3.1b**). Increasing the amount of Ag in the helical structures increases the size of the individual nanoparticles as well as decreases the distances between them. This is expected to cause corresponding red-shifts in the ΔT spectra as well as increase the strength of the Coulomb interaction between the nanoparticles, respectively,[34, 71] and these effects are observed in **Figure 2.3.1c**.

In order to better understand the chiral optical properties of the Ag/MgF₂ helices, we use an analytical point-dipole method developed by Fan and Govorov to calculate the circular dichroism response of helical chains of Ag nanoparticles embedded in a MgF₂ ambient.[34] The physical mechanism for chiral nanoparticle assemblies has some similarity with the optical chirality due to the Coulomb dipole-dipole interaction in a large chiral molecule (*e.g.*, α -helix or DNA).[25] However, there is an important difference between the plasmonic CD effect and the CD effect in biomolecules. The elementary building blocks of a complex biomolecule are interacting chromophores, which are generally described as single dipoles. On the other hand, in chiral complexes of nanoparticles, the elementary building blocks, individual spherical nanoparticles, have three plasmonic dipoles. In the dipole approximation, the electric dipole moment of a single nanoparticle *i* is given by

$$\boldsymbol{d}_{i} = \alpha_{i} \boldsymbol{E}_{tot,\omega,i} = \alpha_{i} \left(\boldsymbol{E}_{ext,\omega,i} + \boldsymbol{E}_{induced,\omega,i} \right), \tag{2.3.1}$$

where α_i is the polarizability of nanoparticle *i*, $E_{tot,\omega,i}$ is the total field acting on nanoparticle *i*, $E_{ext,\omega,i}$ is the incident electromagnetic field acting on nanoparticle *i*, and $E_{induced,\omega,i}$ is the field induced by all other nanoparticles with $j \neq i$. Using a point dipole approximation, the dipole moment can be written as

$$d_{i} = \alpha_{i} \left(E_{ext,\omega,i} + \sum_{j \neq i} \left[\frac{3(d_{j} \cdot n_{ji})n_{ji} - d_{j}}{\varepsilon_{0} r_{ij}^{3}} (1 - \kappa \sqrt{\varepsilon_{0}} r_{ij}) + \kappa^{2} \frac{-(d_{j} \cdot n_{ji})n_{ji} + d_{j}}{r_{ij}} \right] e^{i\kappa \sqrt{\varepsilon_{0}} r_{ij}} \right), \qquad (2.3.2)$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ is the position vector pointing from nanoparticle *i* to nanoparticle *j* and $\mathbf{n}_{ij} = (\mathbf{r}_j - \mathbf{r}_i)/|\mathbf{r}_{ij}|$ is the unit vector pointing from nanoparticle *i* to nanoparticle *j*. This set of 3*N* linear equations can be solved self-consistently for the individual dipole moments of *N* different nanoparticles. Then, the total absorption and extinction can be calculated using the following equations, respectively:

$$Q_{abs} = (1/2)\omega\varepsilon_0 \sum_i \operatorname{Im}\left(\frac{d_i^*}{\alpha_i^*} \cdot d_i\right)$$
(2.3.3)

$$Q_{ext} = (1/2)\omega\varepsilon_0 \sum_i \operatorname{Im} \left(\boldsymbol{E}^*_{ext,\omega,i} \cdot \boldsymbol{d}_i \right).$$
(2.3.4)

The optical chirality arises from the lack of mirror symmetry in the dipole coupling in chiral assemblies. Thus, Fan and Govorov consider their method the classical analog to the Rosenfeld equation.[26]



Figure 2.3.2. Plot of the Ag nanoparticle arrangement used in the point-dipole method calculations.

In order to create a simple model for the Ag/MgF₂ DSG helices, we assume 20 spherical Ag nanoparticles of radius r_{np} are equally spaced in a helical arrangement of radius r = 265 nm, pitch p = 800 nm, and pitch number N = 0.5 (**Figure 2.3.2**). Here we have used variations in r_{np} to account for the different volume ratios, where 1:10, 2:10, 3:10, and 4:10 have $r_{np} = 15.5$, 19.5, 22.3, and 24.6 nm, respectively. These values were calculated assuming the Ag nanoparticles are in embedded in MgF₂ helices with an arm diameter of 60 nm and a total length of 1100 nm. For the calculations, we also assume the ambient to have a refractive index of $n_0 = 1.38$ to match MgF₂, and the Palik values were used for the Ag nanoparticles.[124] Assuming a point dipole response from each individual Ag nanoparticle, the total electromagnetic field experienced by each nanoparticle is the external incident field plus the induced field from all other dipoles in the assembly. The problem of calculating the extinction of this entire assembly for different incident fields (*e.g.*, circular polarized light, LCP and RCP) can be solved self-consistently as described above. Using this analytical method we have calculated the circular dichroism, ε_{CD} , where $\varepsilon_{CD} = \varepsilon_{LCP} - \varepsilon_{RCP}$ and ε_{LCP} are the extinctions for LCP and RCP, respectively. The results of



Figure 2.3.3. (a) Plot of the theoretical CD spectra for the Ag nanoparticle arrangement depicted in Fig.2.4.2 for different Ag volume ratios. (b) Plot of the theoretical CD spectra normalized by the unpolarized extinction, ε , raised to the exponential value, ξ , given in the plot.

these calculations for the parameters given above are shown in **Figure 2.3.3a**. The calculated spectra differ slightly from the experimental spectra in that the films with greater Ag volume are theoretically predicted to have an increasingly higher CD response. Thus, for our experimental films, as the Ag volume ratio increases, polarization-insensitive extinction also increases leading to a less than ideal CD response. Here, we describe this effect empirically by multiplying ε_{CD} by $\varepsilon^{-\xi}$, where ε is the unpolarized extinction and ξ is an arbitrary exponential value. These results, which qualitatively agree with the experimental values (**Figure 2.3.1c**), are plotted in Figure **Figure 2.3.3b**.

In conclusion, Ag/MgF₂ helices have been fabricated by combining co-deposition and DSG, and the measured chiral optical properties were analyzed using the interacting point-dipole approach.⁴⁷ It was found that polarization-insensitive scattering increases with the increasing Ag volume ratio in these structures. Increasing the helical pitch height, *p*, was found to red-shift the bisignate spectral features for Ag/MgF₂ helices of the same composition, as did increasing the Ag composition in MgF₂ helices with the same parameters. These observations illustrate the importance of nanoparticle and helix geometries in designing metal/dielectric composite plasmonic helices with specific chiral optical responses. Finally, we note that while these non-optimized helical arrangements of Ag nanoparticles exhibit the smallest ΔT magnitudes of the structures presented in this dissertation, the obtained circular dichroism is much greater than that of naturally occurring materials. For example, ΔT for the 1:10 Ag/MgF₂ helix at $\lambda = 460$ nm (**Figure 2.3.1b**) corresponds with circular dichroism having an ellipticity value of 0.450°; biological molecules typically exhibit ellipticities around 0.010°.[125]

CHAPTER 3

THREE-DIMENSIONAL CHIRAL SHAPES FROM COLLOID TEMPLATES

3.1 Introduction

The production of helices on smooth substrates using DSG, as described in Chapter 2, demonstrates the ability to create chiral structures within a symmetric environment. However, the use of templates for DSG processes can not only provide a regular array of nucleation centers to create well-defined lattices of nanostructures, but templates also can provide distinctive shadowing profiles to generate unique arrays of chiral nanostructures. Self-assembled colloidal nanosphere monolayers (SACM) make particularly attractive templates because their fabrication is relatively simple and scalable, traits that complement the DSG technique. Furthermore, the hexagonal close packed (HCP) lattice of spheres offers distinctive and desirable shadowing properties. This chapter describes the use of SACMs in combination with DSG to fabricate chiral plasmonic structures. Most of the discussion will be focused on the so-called "chiral patchy particles," as this structure and its fabrication is the most illustrative.

3.2 Chiral Patchy Particles

DSG can be combined with SACMs to produce "patchy particles," which are particles with precisely designed regions or "patches" that have specific properties.[126-129] Recently, it has been proposed that chiral patchy films obtained by DSG and SACMs may exhibit circular

dichroism (CD).[130] However, similar to films produced through nanosphere lithography,[131] the properties of the obtained patchy films will depend on the nature and quality of the self-assembled micro-/nanosphere monolayers, which are typically polycrystalline with randomly-oriented domains that range in size from $10 - 100 \ \mu m^2$. The mechanism by which optical chirality can arise from a symmetric coating of such randomly-oriented, self-assembled colloidal templates is not obvious, and it remains an open question whether or not meaningful chiroptical effects can be achieved using this straightforward fabrication method. In this section, we investigate both the optical and geometric chirality of such chiral patchy Ag films. It is found that the racemic symmetry of the polycrystalline colloidal template is broken by the substrate rotation direction, producing films with strong optical chirality and even stronger local chiralities.

3.2.1 Chiral patchy particles: experimental details of fabrication and morphological characterization

<u>Self-assembled colloid monolayer (SACM) preparation</u>: Colloid monolayers are formed using an air/water interface technique using polystyrene (PS) bead solutions (Polyscience, 2.6 wt%) containing beads of different diameters, d = 200, 350, 500, 750, and 2000 nm. First, the PS bead solutions are washed using ultra-pure (18 M Ω) water by centrifugation and then diluted with ultra-pure water to concentrations ranging between 0.6 to 0.24 wt%. After ultra-sonication for 30 minutes, the solution is further diluted by adding a 2:1 ratio of bead solution and ethanol. Next, a cleaned petri dish, tilted at a 3° angle from a flat surface, is filled with a shallow layer of ultrapure water. In order to control the flow of the prepared PS solutions into the petri dish, a syringe (Monoject) with a 90° bent needle is attached to a syringe pump (KD Scientific). The tip of the needle is positioned close, but not touching the water surface, and PS solution droplets are

dispensed onto the water's surface at rates ranging between 0.008 to 0.015 mL/min. The dispersion of the beads on the water surface forms well-ordered monolayers over time. After the monolayer is completely formed, the water level is slowly raised, and a Teflon ring is placed on the surface of the water to confine the monolayer. Ultra-pure water is simultaneously pumped in by the syringe pump and removed using a multi-staltic water pump (Buchler Instruments) to remove any residual sunken beads. Then, pre-cleaned Si and glass substrates are carefully placed underneath the monolayer by sliding them to the area below the Teflon ring using tweezers. Lastly, the syringe pump slowly removes all water allowing the confined monolayer to deposit on the surface of the underlying substrates.

DSG deposition: The patchy films were fabricated using a unique, custom-designed vacuum deposition system (Pascal Technology). Ag pellets were used as source materials (Plasma Materials, 99.99%). The monolayer substrates were loaded onto the DSG substrate holder, which was positioned such that the substrate normal formed an 86° angle with respect to the vapor incident direction. The chamber was evacuated to 1×10^{-6} Torr, and was maintained at a pressure of $< 5 \times 10^{-6}$ Torr throughout the deposition. The Ag evaporation rate (0.05 nm/s) and thickness were monitored by a quartz crystal microbalance (QCM). Material was deposited in 30 nm increments at each azimuthal rotation angle until the final desired QCM thickness of 120 nm at each angle was achieved. The clockwise (CW) and counter-clockwise (CCW) films were rotated azimuthally in -120° and 120° increments, respectively. For the CW/CCW film fabrication, we deposited 30 nm at each angle, $\phi = 0^{\circ}$, -120°, and -240°, then we deposited another 30 nm at each angle, $\phi = 0^{\circ}$, 120°, and 240°, and so forth until a total QCM reading of 120 nm was deposited at each azimuthal angle.

<u>Morphological Characterization</u>: Scanning electron microscope (SEM) images were collected using a field emission scanning electron microscope (FEI Inspect F). Atomic force microscopy (AFM) imaging was performed using a Bruker Nanoscope V atomic force microscope in tapping mode using a scan area of 2 μ m² and a scan rate of 0.200 Hz. For the AFM data shown in **Figures 3.2.tkc and 3.2.tkd**, a portion of the original plane fit AFM height data was selected such that it only contained the height information for one patchy particle. Then, a hemisphere corresponding to a 500 nm bead was subtracted from this data to give the thickness of the coating at each point. The original AFM images for the CW and CCW films are shown in **Figures 3.2.1a and 3.2.1b**, respectively.



Figure 3.2.1. Original AFM images for the (a) CW and (b) CCW films. Boxes are drawn around the patchy particles shown in Figures 3.2.6c and 3.2.6d.

3.2.2 Chiral patchy particles: fabrication and morphology

The fabrication process for the chiral patchy Ag films begins by self-assembling colloidal monolayers of 500 nm polystyrene nanospheres onto glass or Si substrates, which act as hexagonal close-packed (HCP) two-dimensional polycrystalline templates. These templates are then loaded into a vacuum deposition system such that the surface normal and the vapor incident direction form an oblique polar angle, $\theta = 86^{\circ}$, in order to increase the geometric shadowing effect between neighboring spheres. Ag is then deposited incrementally at azimuthal angles, $\varphi = 0^{\circ}$, 120°, and 240°, *i.e.*, rotating counter-clockwise (CCW) until the desired thickness at each φ is achieved (see Section 3.2.1). Two additional patchy films with identical parameters are also fabricated: one using clockwise substrate rotations instead (CW) and one where material is built up at each azimuthal angle using alternating rotation directions (CW/CCW). Scanning electron microscopy reveals that the CW, CCW, and CW/CCW films are composed of polycrystalline



Figure 3.2.2. (a) - (d) SEM images showing the various morphologies of the coatings for a CCW Ag patchy particle film. The different shapes are from different colloidal domains on the same film.

domains (area, $3 - 50 \ \mu\text{m}^2$) of patchy particles. **Figure 3.2.2** presents some representative SEM micrographs of various patch morphologies observed in a CCW film, demonstrating that some, but not all, of the structures are chiral. Statistical analyses of the SEM micrographs of both CW and CCW films reveal that they are racemic; 23% of patchy particles show left-handed morphologies and 24% show right-handed ones, where the handedness here is defined by the curling direction of the arms. As will be discussed in greater detail below, such a racemic mixture is expected for a symmetric coating of a polycrystalline SACM template with randomly oriented domains.



Figure 3.2.3. Illustration of the HCP lattice of a colloidal domain, showing the definitions of the polar and azimuthal angles, θ and φ .

In order to understand the origin of the optical chirality of these racemic mixtures of patchy particles, it is important to understand the origin of the morphologies of the coatings. A diagram of the HCP arrangement of a SACM domain is shown in **Figures 3.2.3**, and the orientation with respect to the vapor incident direction is described by the polar and azimuthal angles, θ and φ . As θ approaches 90°, the shadowing effect between neighboring spheres becomes significant, creating regions on the spheres that are shadowed from the vapor flux. Due

to the 6-fold rotational symmetry of the HCP lattice, the shape of this shadowed region is a periodic function of φ . For rotations about the substrate normal described by $\varphi = \varphi_0 + 60^\circ n$, where *n* is an integer and φ_0 is the original orientation of the domain with respect to the vapor incident plane, the shape of the patch coated at φ will be the same as the patch coated at φ_0 . For rotations described by $\varphi = 60^\circ n - \varphi_0$, the shape of the patch coated at φ will be the mirror image of the patch coated at φ_0 due to reflection symmetry planes occurring along $\varphi = 30^\circ n$. A patchy film deposition described by coatings at $\varphi = 0^\circ$, 120°, and 240° should have 3-fold rotational symmetry, but the structural chirality will be determined by the different φ_0 values of each domain, with $0^\circ < \varphi_0 < 30^\circ$ resulting in right-handed enantiomers and $30^\circ < \varphi_0 < 60^\circ$ resulting in left-handed ones.

3.2.3 Chiral patchy particles: morphology simulation

A simple simulation is used to estimate the thickness distribution of the patchy structures. As illustrated in **Figure 3.2.4a**, an array of close-packed beads with diameter D = 500 nm is in x-y plane. A uniform vapor flux approaches the array of beads in direction \hat{l} (θ_0 , φ_0). In order to calculate the thickness distribution on bead *O*, the nearest 36 beads are taken into account, which potentially affect the deposition on bead *O*. As shown in **Figures 3.2.4.b and 3.7.4c**, the surface of bead *O* is split into small surface elements. Each element is denoted as the coordinate of its center (θ , φ), where $\theta = i \cdot \Delta \theta$, $\varphi = j \cdot \Delta \varphi$, $\Delta \theta = \Delta \varphi = 0.5^{\circ}$, $i = 0, 1, \dots 360, j = 0, 1, \dots 720$.

The simulation is based on three assumptions:

- 1. Only the shadowing effect and material accumulation are considered. Other physical processes, such as surface diffusion, are neglected.
- The deposition at different surface elements happens simultaneously as long as they are directly exposed to vapor.



Figure 3.2.4. (a) Sketch of vapor deposition on an array of beads, (b) the surface of bead O split into numbers of surface elements, (c) a surface element on bead O.

3. The as-deposited film is non-porous and is uniform within each surface element.

In the simulation of the patchy structure, there are three simulation steps. A 120° azimuthal rotation of \hat{l} happens at the end of each step. In each simulation step, the thickness at each surface element $h(\theta, \varphi)$ is updated,

$$h_{i+1}(\theta, \varphi) = h_i(\theta, \varphi) + \Delta h. \tag{3.2.1}$$

In order to calculate the change of thickness Δh , we need to first determine whether point (θ, φ) is directly exposed to the vapor flux. If point (θ, φ) is in the shadow of other structures, then $\Delta h = 0$. For the uniform condition, the shadowed area does not take into account previously deposited material, *i.e.*, the surface profile of the template remains constant. For the CW and CCW simulations, previously deposited material on neighboring beads will contribute to the shadow because the surface profile is updated at each step. These different conditions are achieved by considering the following effects. If (θ, φ) can receive vapor, then Δh can be expressed as,

$$\Delta h = \Delta m / (\rho S(\theta, \varphi), \qquad (3.2.2)$$

where Δm is the mass of material deposited on surface element (θ, φ) within time $\Delta t, \rho$ is the density of the material, and $S(\theta, \varphi)$ is the area of surface element (θ, φ) . The vapor flux Φ is defined as,

$$\Phi = \Delta m / (\Delta t S_N) = \text{const.}, \qquad (3.2.3)$$

where S_N is the projection of $S(\theta, \varphi)$ onto the plane perpendicular to the vapor flux \hat{l} . With β defined as the angle between \hat{l} and the surface normal vector \hat{n} , S_N can be expressed as,

$$S_N = S(\theta, \varphi) \cos \beta. \tag{3.2.4}$$

By combining Equations 3.7.2 - 3.7.4, we obtain the final expression of Δh ,

$$\Delta h = (\Phi / \rho) \,\Delta t \cos \beta. \tag{3.2.5}$$

In each step, we set $(\Phi / \varrho) \Delta t$ as 15 nm.

Figures 3.2.5a shows simulated morphologies of the coatings for various φ_0 orientations when material is uniformly deposited at $\theta = 86^\circ$ and $\varphi = 0^\circ$, 120°, and 240°. The orientation of the monolayer domain with respect to vapor incidence is the primary factor in determining the morphology of the coating. Therefore, a SACM substrate with randomly oriented monolayer domains should ideally function as a template to produce a racemic mixture of chiral patchy particles. However, this idealized simulation does not take into account the dynamic effect of material accumulation on the surface of the beads during the deposition. The shape of the coating is determined by the shadowing effect of the surface profile of the template, which will change as material is deposited. This change in the shadowing profile is unique to the specific deposition process parameters, such as rotation direction, material thickness, θ , φ , etc. This could result in different enantiomers for the CW and CCW substrate rotations. **Figures 3.2.5b** and **3.2.5c** shows the simulated morphologies of coatings for both deposition directions, CW and CCW, respectively, for various φ_0 orientations when the shadowing effect of previously



Figure 3.2.5. Simulated patch morphologies showing the dependence of the handedness and structure on the original orientation of the domain with respect to the vapor incident direction, φ_0 for the (a) symmetric, (b) CW, and (c) CCW deposition conditions with $\theta = 86^\circ$.

deposited material is taken into account. In contrast to the uniform simulation, these simulations demonstrate that different structures can result from different rotation directions during fabrication. In particular, the lengths and thicknesses of individual arms are different for the CW and CCW conditions, and the orderings of these arms by decreasing thickness and increasing length follow the rotation direction and, therefore, are not related by a cyclic permutation. In other words, the material distribution within the chiral patches is enantiomorphic, where the different handedness is determined by the substrate rotation direction. While the simulated coatings shown in the uniform condition depicted in **Figure 3.2.5a** do approximate the obtained morphologies of the patchy films (**Figure 3.2.2**), close inspection of the fabricated patchy films *via* SEM and atomic force microscopy (AFM) reveals that there are some morphological differences between similar patches of the same handedness for the CW and CCW films, *i.e.*, a

chiral patch corresponding with a particular φ_0 will be different for the two different rotation directions. These differences are illustrated in **Figures 3.2.6a** – **3.2.6d**. Specifically, the lengths of the arms increase in ~20 nm increments while the thickness of the arms decreases in ~20 nm increments in the direction of rotation. These results are in qualitative agreement with the CW and CCW simulations, *i.e.*, the ordering of the different arms by decreasing thickness and increasing length follows the rotation direction (**Figures 3.2.5b and 3.2.5c**). It is not obvious how the chiral distributions of different thicknesses and arm lengths will contribute to the geometric and optical chirality in the quasi-three dimensional patchy coatings, and these effects will be analyzed in more detail below.



Figure 3.2.6. SEM images highlighting the morphological differences of coatings with similar φ_0 values but with the different rotation conditions, (a) CW and (b) CCW. AFM height data with the hemisphere of the bead subtracted out in order to show the Ag thickness distribution for similar patch morphologies for the different rotation conditions, (c) CW and (d) CCW. Note that the SEM and AFM images are from different domains.

3.2.4 Geometrical chirality

Throughout the discussion above and this dissertation in general, chirality has only been quantitatively examined within the context of optical properties. However, chirality is a property that is directly related to an object's geometry, and any chirality detected in optical measurements arises from some asymmetry of the probed structure. From a theoretical and design standpoint, it would be useful to have a mathematical description or measure of chirality as it relates to an object's shape or structure. Traditionally, an object is said to be chiral if it cannot be brought into congruence with its mirror image, as mentioned above. Unfortunately, by defining chirality as a negative concept (*i.e.*, lacking reflective symmetry), chirality is a property with only two possible quantities; chiral (true) and achiral (false). In order to understand structural chirality as quantifiable property, we can employ a continuous chirality measure to analyze the geometric chirality of a structure.[132] These measures treat chirality as a continuous property that can be quantified, allowing the degree of chirality for different structures to be compared.[133] In particular, we will employ a specific two-dimensional chirality measure, the angular bisection method developed by Potts et al.,[134] to quantify and compare the chirality of the different chiral patchy structures produced through CW or CCW depositions. m_1



Figure 3.2.7 The labeling convention for the triangle used in the chiral index calculation. Ref.[134]

An understanding of this method begins by noting that the most basic chiral object in two dimensions is defined by a set of three points. They propose that if they can construct a measure of chirality for a three-point set (in other words a triangle), then the theory can be extended to any structure with any degree of complexity by simply summing this measure over all the contributions arising from every possible subset of three points. In order to formulate their measure of chirality in 2D, a set of conditions that define the required behavior of the chirality index is outlined:

The basic chiral element is the triangle. The chirality index (*K*) of any set of *N* points (N > 3) can be derived, therefore, by summing the chirality indices of all possible permutations of triangles (**Figure 3.2.7**). This then leads to the first condition.

Postulate 3.2.1. If K_{ijk} is defined as the chirality index of a triangular set of points represented by the vectors $(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$, then

$$K = \frac{1}{6} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} K_{ijk}.$$
 (3.2.6)

Lemma 3.2.2. The chirality index of any triangle, K_{ijk} , must be proportional to the mass at each vertex,

$$K_{ijk} = m_i \, m_j \, m_k \, \Lambda_{ijk} \tag{3.2.7}$$

where m_i , m_j , and m_k are the masses at each of the three vertices defined by $(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$ and Λ_{ijk} is another chiral function that depends only on the spatial positions of the points i, j, and k. Λ_{ijk} is a massless chirality measure, called the specific chirality index. In this case, mass represents the total number of point masses at a given point or in a given area and is therefore equivalent to the integral of the two-dimensional density distribution function, $\rho(\mathbf{r})$, over that area.

Postulate 3.2.3. The chirality index should be continuous and single-valued.

Lemma 3.2.4. The chirality index cannot be dimensionless, but must decrease in magnitude as the size of the structure decreases. This can be achieved if the chirality index contains a term that is dependent on the actual area of each triangle. A scaling function that varies linearly with area is the most elementary choice.

Postulate 3.2.5. If the chirality index scales linearly with the area of the triangle, Δ_{ijk} , two triangles that are similar (*i.e.* their corresponding angles are identical) should have chiral indices that are proportional. Consequently, it should be possible to define a dimensionless chirality index, Γ_{ijk} , that is a function of the ratios of the sides of the triangle or its three angles, but is independent of its area, Δ_{ijk} . Combining equation (3.2.2), Lemma 3.2.4 and Postulate 3.2.5, the following is obtained

$$K_{ijk} = m_i m_j m_k \Lambda_{ijk} = m_i m_j m_k \Gamma_{ijk} \Delta_{ijk}$$
(3.2.8)

Postulate 3.2.6. Γ_{ijk} must always be finite in order to ensure that the chirality index, *K*, of a finite system is always finite.

Postulate 3.2.7. The chirality index must be inverted under any reflection operation (*i.e.* If $x \Rightarrow -x$, then $K \Rightarrow -K$). As the area of the triangle will remain unchanged by such an operation, then it is also true that $\Gamma_{ijk} \Rightarrow -\Gamma_{ijk}$ for the same reflection operation. Thus, *K* and Γ_{ijk} are both zero for any isosceles or equilateral triangle.

Lemma 3.2.8. The chirality index of any set of three co-linear points must be zero. This is satisfied if Γ_{ijk} is finite for a co-linear set ($\Delta_{ijk} = 0$).

Lemma 3.2.9. If any two points of a triangle are coincident in space, then the chirality index must be zero. This implies that $K_{ijk} \rightarrow 0$ as $|\mathbf{r}_{ij}| \rightarrow 0$, where $|\mathbf{r}_{ij}|$ is the length of any side of the triangle.

Using this set of conditions, Potts *et al.* construct several different continuous chirality measures. Of these different measures, they find one particular method, the angular bisection method to be the most suitable.

The angular bisection method is essentially a method of comparing the asymmetry in the distribution of the area of the original triangle defined by three arbitrary points, (r_i , r_j , r_k), and its enantiomer (Figure 3.2.8). This is done by superimposing the two triangles and measuring the amount of common area that they share. In particular, the specific chirality index, Λ_{ijk} , is defined as the area of those parts of the enantiomeric triangle that are not superimposed on any part of the original triangle. A "handedness" (right or left, positive or negative) is determined by the difference in areas of the original triangle across the mirror plane, and it is arbitrarily chosen such that the area to the right-hand side of the mirror plane has a positive sense (the area to the left thus being negative). Additionally, a consistent mirror plane, with respect to individual sides or vertices, must be chosen to prevent any ambiguity in the handedness and because the Λ_{ijk} calculation must be repeated for each side or vertex so that the resulting total represents the



Figure 3.2.8. (a) The original triangle (white) with its vertices and sides labeled and its enantiomer (shaded). (b) The angular bisection method. Ref.[134]

chirality of the whole triangle and not the arbitrary value from only one viewpoint. For the angular bisection method, the mirror plane that bisects the angle at any vertex of the triangle is used (**Figure 3.2.8b**). The difference in areas subtended by the triangle across this line as a fraction of the total area of the triangle can be calculated

$$\Gamma_1 = \frac{\Delta_{\rm R} - \Delta_{\rm L}}{\Delta_{\rm R} + \Delta_{\rm L}} = \frac{a_2 - a_3}{a_2 + a_3},\tag{3.2.9}$$

where Δ_L is the area to the left of the mirror plane and Δ_R is the area to the right as viewed from the vertex, a_2 and a_3 are the lengths of sides 2 and 3. The process needs to be repeated for all three vertices in order to arrive at an expression that properly reflects the chirality of the triangle as a whole, rather than just the property of a single vertex. The dimensionless chirality index is then given by

$$\Gamma_{ijk} = \frac{a_1 - a_2}{a_1 + a_2} + \frac{a_2 - a_3}{a_2 + a_3} + \frac{a_3 - a_1}{a_3 + a_1}.$$
(3.2.10)

Analysis of Equation 3.2.10 will show that it satisfies Postulates and Lemmas 3.2.1 – 3.2.9, as described above. Finally, by defining a triangle by three vectors, $(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$, the chirality model can be extended to any ensemble of *N* points as follows:

$$K = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} m_i m_j m_k \frac{|r_{ij}| - |r_{ik}|}{|r_{ij}| + |r_{ik}|} \Delta_{ijk}, \qquad (3.2.11)$$

where $r_{ij} = r_j - r_i$ and $r_{ik} = r_k - r_i$. Thus, by using Equation 3.2.11, a chirality index is calculated for any arbitrary structure. This chirality index, *K*, gives a quantifiable measure of structural chirality that can allow comparison between different asymmetric structures. It is important to note that the relationship between structural chirality, *K*, and optical chirality (*CB* or *CD*) is not straightforward, though some correlation between the two phenomena should be expected, especially if the structural chirality is on the order of the wavelength of interest.

3.2.5 Chiral patchy particles: geometrical chirality calculation

In order to understand the effects of the material distribution enantiomorphism on the structural chirality of the chiral patchy particles, we can use the angular bisection method to calculate the chirality index, K, for the simulated structures for different deposition conditions (**Figures 3.2.5a** - **3.2.5c**): when there is no rotational dependence, uniform; and when rotational effects are considered, CW and CCW. To begin, we first use the simulations described in Section 3.2.3 to generate thickness data for the different morphologies (**Figure 3.2.9a**). These data are transformed into a Cartesian array, where each data point contains the *x*-component, *y*-component, and thickness value of the simulated morphology (**Figure 3.2.9b**). Then the total number of data points, N, is reduced from ~260000 to 325 to reduce the calculation time, which will scale as N^3 (**Figure 3.2.9c**). These data points are then inserted into Equation 3.2.11 where the x- and y-components define the *r* value and the thickness value is used for *m*.

The results from the calculations are summarized in **Table 3.2.1**. For the uniform structures, *K* is negative for $0^{\circ} < \varphi_0 < 30^{\circ}$ and positive for $30^{\circ} < \varphi_0 < 60^{\circ}$, and averaging *K* over $0^{\circ} < \varphi_0 < 60^{\circ}$, K_{avg} , results in zero. Note that the sign of *K* determines the handedness of the structure, and an achiral structure will have K = 0. Thus, a large, random ensemble of uniform



Figure 3.2.9. (a) Simulated morphology for a uniform coating at $\varphi_0 = 5^\circ$. (b) Plot of the Cartesian array of thickness data points. (c) Plot of the reduced Cartesian array used for the chirality index calculation.

structures is an achiral racemic mixture. The CW and CCW structures follow the same general trend for *K* over $0^{\circ} < \varphi_0 < 60^{\circ}$, with *K* initially negative and increasing to positive values as φ_0 approaches 60°. However, *K* is not symmetric about $\varphi_0 = 30^{\circ}$, and averaging *K* over $0^{\circ} < \varphi_0 < 60^{\circ}$ does not result in zero in either case, with $K_{avg} = -40$ and $K_{avg} = 40$ for the CW and CCW structures, respectively. This means that ensembles of CW structures and ensembles of CCW structures are chiral mixtures of opposite geometric handedness. The effect of the geometric chirality on the optical chirality will be examined in Section 3.2.7

Table 3.2.1. Chirality index, K, for different simulated patch morphologies

$arphi_0$	Symmetric	CW	CCW
5°	-630	-480	-440
15°	-170	-200	-30
30°	0	10	-10
45°	170	30	200
55°	630	440	480
Kavg	0	-40	40

3.2.6 Chiral patchy particles: experimental details of optical measurements

<u>Bulk Optical Characterization</u>: A variable angle spectroscopic ellipsometer (M-2000, J. A. Woollam, Inc.) was used in transmission mode (beam spot diameter, 2 mm) to measure the first three rows of the Mueller matrix describing the sample with the $m_{11}(\lambda)$ element normalized to 1. The unpolarized transmission was measured by UV-visible spectrophotometer (JASCO V-570) and used to measure the un-normalized $m_{11}(\lambda)$ Mueller matrix element. The un-normalized $m_{11}(\lambda)$ and $m_{14}(\lambda)$ elements were used to determine the selective transmittance of each sample,

which is then converted to differential absorbance and ellipticity to quantify the circular dichroism. The Mueller matrix was measured at several azimuthal orientations, and the $m_{14}(\lambda)$ element was found to be independent of azimuthal orientation. This is an important consideration for oriented films, as discussed in Section 2.2.6. Additionally, the ellipsometry measurements were carried out with both the Ag coating facing the incident light and facing opposite the incident light, and no change in the measured $m_{14}(\lambda)$ element was observed.

<u>*Microscopic Optical Characterization*</u>: The circular polarized color micrographs shown in **Figures 3.2.10c** and **3.2.10d** were obtained by placing a rotatable Glan Thompson linear polarizer (Thorlabs, Inc.) and an achromatic quarter-wave plate (Thorlabs, Inc., 450-800 nm) over the illumination light source of a microscope (Enwave Optronics, Inc., Microsense, Leica). The different circular polarizations, left or right (LCP and RCP), were chosen by rotating the Glan Thompson polarizer to the appropriate azimuth with respect to the fast axis of the quarterwave plate. The images were collected by the light passing through sample and into a $40 \times$ objective, and captured using the microscope's software (RamanReader – M).

For the more detailed quantitative analysis, the same Glan Thompson polarizer and quarter-wave plate were placed over the light source of a Mitutoyo Ultraplan FS110 microscope. Additionally, a bandpass filter (Edmund Optics, Inc., RT-830) was placed after the quarter wave plate to select wavelengths greater than 700 nm. The filtered, circular polarized light illuminated the samples from below, and the images of the samples' surfaces were captured using a camera (Vision Research, Phantom V9.1) through a 10× objective mounted above the sample stage. The images of the different samples (bare polystyrene monolayer, CW, CCW, and CW/CCW) illuminated using RCP and LCP light were analyzed using CellProfiler image analysis software in order to calculate the average intensity of the images. The transmitted intensity for the

different polarizations for the CW, CCW, and CW/CCW films were calculated by normalizing their measured average intensities to the measured average intensity of the bare polystyrene monolayer under the same polarization condition. The transmittances for LCP and RCP for each sample were then used to calculate the circular dichroism (CD) of each sample. In order to measure the CD of individual domains, the images were cropped such that they only contained the domain of interest, and then the cropped images were analyzed as described above.

3.2.7 Chiral patchy particles: optical properties

Figure 3.2.10a shows the unpolarized transmission spectra of the three different films. The spectra all appear very similar, especially for the CW and CCW films, with transmission dips occurring at nearly the same wavelengths, $\lambda \approx 450$, 520, 600, and 750 nm. Thus, for unpolarized light the different patchy films appear effectively identical. **Figures 3.2.10b** shows the measured CD spectra of the CW, CCW, and CW/CCW films, and in spite of their quasi-racemic nature, the patchy films show distinct CD spectra that vary significantly over the incident wavelengths, which cover the entire visible wavelength region and into the near-infrared region. All films show both positive and negative features, but the substrate rotation direction during fabrication determines the magnitude and handedness of the optical activity at a specific wavelength. While the CW/CCW film generally shows a weak response, the CW and CCW films exhibit considerable CD of opposite handedness, with magnitudes reaching as large as 2.2°. In fact, the CD strengths of the CW and CCW films are comparable to some chiral metamaterials, such as twisted photonic crosses and planar gammadions, [42, 135] and is significantly stronger than many recent self-assembled and solution-based structures, such as gold nanoparticle helices



Figure 3.2.10. (a) Transmission spectra and (b) Circular dichroism spectra for the CW, CCW, and CW/CCW patchy particle films. 40× optical micrographs of a CW film showing individual monolayer domains and where the illuminating light is either (c) left circular polarized, LCP, or (d) right circular polarized, RCP. Certain domains are labeled with "R", "B", or "N" in order to highlight the apparent color change with different circular polarizations.

assembled using DNA or peptide scaffolding and chiral core-shell nanoparticles consisting of gold nanorods coated with a chiral silica shell.[49, 84, 136]

In order to visualize how the different domains of the polycrystalline monolayer template contribute to the bulk CD response, the films were examined using a microscope and circular polarized light. **Figures 3.2.10c** shows a representative color micrograph of a CW film under $40 \times$ magnification and illuminated using right circular polarized light (RCP), while **Figures 3.2.10d** shows a micrograph of the same region of the film illuminated using left circular polarized light (LCP). In these micrographs one can see that different colloidal domains have different responses under RCP and LCP illumination. Domains similar to the one labeled N in Figures 3.2.10c and 3.2.10d do not perceptibly change colors under the different circular polarizations and could correspond with an achiral morphology such as Figures 3.2.2a. Other domains, similar to those labeled R and B, change color with the different circular polarizations, demonstrating that these domains have a chiral response and could correspond with highly chiral morphologies such as those depicted in Figures 3.2.2b and 3.2.2d. The R and B domains in the figures have a symmetric response, but that is not necessarily true for all chiral domains. Quantitative analysis of microscopic images demonstrates that the CD averaged over many different domains agrees with bulk CD measurements. The CD for wavelengths 700 - 800 nm for the CW, CCW, and CW/CCW films are found to be 0.89°, -1.9°, and 0.07°, respectively. However, the CD of individual domains in the CW film are found to have CD as large as 9.6° over wavelengths 700 -800 nm, which is an order of magnitude larger. Thus, the microscopic analysis reveals that the significant circular dichroism of the film is actually the result of an incomplete cancellation of the even stronger local optical chiralities of individual domains. Furthermore, the optical measurements in general confirm that the chirality index, K, calculations for the simulated structures capture the essence of the optical measurements. The CW/CCW film is approximated by the uniform condition, and the local chiralities of the domains (*i.e.*, both K and CD) effectively cancel each other out. The local chiralities of the CW and CCW films do not cancel each other out, resulting in chiral ensembles and optically active films.

3.2.5 Chiral patchy particles: conclusions

In conclusion, by combining SACMs with DSG, we have fabricated films composed of chiral patchy particles, where right- and left-handed enantiomers exist in equal proportion. However, the shadowing effect coupled with the rotation direction during fabrication breaks the racemic symmetry and results in a chiral distribution of material that enhances the overall geometric chirality of one set of enantiomers relative to the other. This additional level of geometric chirality adds another controllable parameter in the fabrication of optically active films, allowing the response to be optimized for specific applications. For example, a non-active racemic mixture of strongly chiral nanostructures is desirable for certain applications where large dissymmetry factors are essential, [137, 138] and by alternating the deposition directions, such a film can be achieved using this method. For applications requiring significant optical activity, the substrate orientation and rotation direction can be tuned to match the template structure to increase the response. Furthermore, chiral patchy coatings are not limited to plasmonic materials, and it is possible to design chiral patchy films with adjustable chirality in other properties, e.g., magnetic, hydrophobic, catalytic, etc. The ease of fabrication and scalability of the method combined with significant and tunable chirality makes DSG chiral patchy films promising candidates for many applications.

3.3 Stretched Chiral Patchy Particles

As described above, SACMs can be used to fabricate chiral patchy particles, where an additional structural chirality results from the substrate rotation direction. This is a natural consequence of the shadowing effect due to the presence of previously deposited material. Intentionally depositing different thicknesses of material at each azimuthal angle can artificially enhance this

intrinsic effect and increase the structural chirality of the films. Structures fabricated in this way are referred to as stretched chiral patchy particles because the difference in thickness appears to stretch the morphology of the traditional chiral patchy structures.

The stretched chiral patchy films are prepared similar to the chiral patchy films, except that material is deposited in different incremental amounts at each azimuthal angle. For example, for the 180-120-60 film, material is deposited in 45 nm, 30 nm, and 15 nm increments at 0°, 120°, and 240°, respectively, through four cycles. Figures 3.3.1a – 3.3.1c show SEM images of such Ag stretched chiral patchy particles on d = 350 nm polystyrene spheres where different thicknesses of Ag have been deposited at three different azimuthal angles, $\varphi = 0^{\circ}$, 120°, and 240° (Deposition 1, 2, and 3, respectively), following a CCW rotation. Here, the labeling convention for the different films is that the deposition thickness in nanometers for each azimuthal angle is listed in order, e.g., 140-120-100 corresponds with a CCW stretched patchy film where the thickness for Depositions 1 - 3 were 140 nm, 120 nm, and 100 nm, respectively. The stretching effect on the morphology is more pronounced for the 180-120-60 patches as seen in Figure **3.3.1a**. In Figures **3.3.1b** and **3.3.1c**, the 140-120-100 patches appear virtually identical to the 160-120-80 patches. However, the chiral optical responses for the different stretched chiral patchy films are significantly different, as shown in the ΔT spectra (Figures 3.3.1d). The main features of the ΔT spectra generally blue-shift with increasing disparity in the azimuthal thicknesses. Interestingly, the maximum magnitude for ΔT is observed for the 160-120-80 film and not for the 180-120-60 film, indicating that the thickness distribution effect on chirality does not monotonically increase with increasing disparity. These considerations are not just relevant to chiral patchy particles, as such chiral azimuthal thickness distributions can be employed in other fabrication techniques to achieve plasmonic optical activity.[75]



Figure 3.3.1. SEM images of stretched chiral patchy films on 350 nm-diameter SACM substrates where the thickness for Depositions 1, 2, and 3, respectively are (a) 180, 120, 60 nm; (b) 160, 120, 80 nm; and (c) 140, 120, 100 nm. (d) Circular polarization ∆T spectra for the stretched chiral patchy films shown in the SEM images.

3.4 Oligomers

In the stretched chiral patchy particle case, the structural and optical chirality of chiral patchy particles are enhanced by intentionally increasing the thickness disparity between azimuthal angles of the patch structure. Although different thicknesses of Ag are deposited, all of the patches are approximately located in the same plane (though curved), which means that the structure itself is not truly 3D, rather quasi-3D. If the individual patchy layers can be pulled out of the plane to different heights, a true 3D structure can be formed. A simple and chiral way to obtain such an arrangement is to deposit a thin dielectric spacer layer after each Ag deposition



Figure 3.4.1. (a) Schematic of the fabrication process for the CW oligomer structure. (b) Unpolarized UV-visible absorbance spectra and the (c) circular polarization ΔT spectra for CW and CCW oligomer films on 500 nm-diameter SACM substrates.

(steps 3, 5, and 7) to achieve a helical arrangement of patches, as illustrated in **Figure 3.4.1a**. Specifically, 15 nm of MgF₂ is deposited at vapor incident angle $\theta = 0^{\circ}$. Then, the substrate is repositioned such that the vapor incident angle is $\theta = 86^{\circ}$, and 80 nm of Ag is deposited. Next, the substrate is rotated azimuthally by $\varphi = 90^{\circ}$, and the MgF₂ and Ag depositions are again repeated using $\theta = 0^{\circ}$ and $\theta = 86^{\circ}$, respectively. The substrate is then rotated azimuthally by another $\varphi = 90^{\circ}$, and the MgF₂ and Ag depositions are repeated once more. A final MgF₂ deposition at $\theta = 0^{\circ}$ finishes the process.

By stacking the patches helically, the rotation direction, CW or CCW, between patch depositions will more robustly define right- and left-handed enantiomers. These structures are

referred to as oligomers since the individual patches are designed to be close but not touching, and are similar topologically to 3D oligomer structures fabricated using EBL.[40, 139] **Figure 3.4.1b** shows the unpolarized transmission spectra for CW and CCW oligomers films fabricated using the exact process shown **Figure 3.4.1a**, *i.e.*, three 80 nm Ag patches at $\varphi = 0^\circ$, 90°, and 180°, respectively, separated by 15 nm MgF₂ layers. Similar to the results for the planar chiral patchy films, unpolarized light interacts with the CW and CCW oligomer films identically. However, the chiral enantiomorphism of the oligomers is obvious in the ΔT spectra (**Figure 3.4.1c**), where it can be seen that CW and CCW oligomers exhibit significant yet opposite chiral optical properties.

3.5 Patchy Staircase

The motivation behind the patchy staircase structure is similar to that behind the oligomer structure. That is, the patchy particle concept is quasi-3D, and additional optical chirality might be achieved by fully extending patchy coatings to three dimensions. For the staircase structure, the idea is to deposit a dielectric scaffold (*e.g.*, SiO₂) onto SACMs, taking advantage of their symmetric shadowing profile to create unique structures. A uniform layer of a noble metal (*e.g.*, Ag) is deposited such that it just covers the dielectric scaffold. In this way, the dielectric scaffold pulls the plasmonic layer out of the substrate plane, creating a 3D structure.

This patchy staircase concept has been investigated using the stretched chiral patchy particle motif. **Figure 3.5.1** shows a simple simulation of the patch morphology on a bead where the original orientation of the monolayer domain is described by $\theta = 86^{\circ}$ and $\varphi_0 = 5^{\circ}$. Three depositions of different thicknesses are performed at the same polar angle but at different azimuthal angles: 90 nm at φ_0 , 60 nm at $\varphi_0 + 120^{\circ}$, and 30 nm at $\varphi_0 + 240^{\circ}$. Although it is not



Figure 3.5.1. Simple simulation of the patch morphology on a bead where the original orientation of the monolayer domain is described by $\theta = 86^{\circ}$ and $\varphi_0 = 5^{\circ}$. Three depositions of different thicknesses are performed at the same polar angle but at different azimuthal angles: 90 nm at φ_0 , 60 nm at $\varphi_0 + 120^{\circ}$, and 30 nm at $\varphi_0 + 240^{\circ}$

required, such azimuthal rotational steps (*i.e.*, 60° or 120°) match the rotational symmetry of the HCP lattice of the SACMs. To complete the process, a uniform Ag layer is deposited, following the same azimuthal step increments. This process is used to create six different chiral patchy staircase structures with 60 nm of Ag on different SiO₂ scaffolds using 200 nm SACM substrates. Following the naming convention of the stretched chiral patchy particles (Section 3.3), the dielectric scaffolds are: 30-20-10, 60-40-20, 90-60-30, 40-20-10, 90-30-10, and 160-40-10. These different heights were chosen to examine the effect of both uniform and non-uniform step heights.

The CD spectra of the different samples were extracted from transmission generalized ellipsometry measurements using the method outlined in Section 2.2.6 These spectra, presented in **Figure 3.5.2**, show the characteristic bisignate signal resulting from a dipolar resonance. For the set of films with uniform incremental steps, 30-20-10, 60-40-20, 90-60-30 (Deposition 1, 2, 3, respectively), it appears that there is an optimal incremental spacing of the "steps" to maximize the CD response in the visible region. In this case, 20 nm steps are the best. There is also an optimal spacing for the set of films with non-uniform incremental steps, 40-20-10, 90-30-10, and 160-40-10 (Deposition 4, 5, 6, respectively). In this case, the spacing increase of $3 \times is$

optimal. Finally, it is interesting to note that the CD spectra for the uniform and non-uniform sets of films are approximately opposite. Since the patchy staircase structures have a true chiral shape, the origin of their optical activity most likely arises from plasmonic mode mixing.[33]



Figure 3.5.2. CD spectra for the (a) 30-20-10, 60-40-20, 90-60-30 patchy staircases, Deposition 1, 2, 3, respectively and for the (b) 40-20-10, 90-30-10, and 160-40-10 patchy staircases, Deposition 4, 5, 6, respectively

3.6 Spectral Tuning Through Galvanic Replacement Reaction

For all of the structures described above, the fabrication of chiral structures is achieved through the "dry process" of physical vapor deposition. However, the introduction of "wet chemistry" into the fabrication procedure will allow for additional modification and optimization of the different chiral structures. In particular, the galvanic replacement reaction (GRR) is an interesting chemical process that is a facile and efficient way to replace Ag with a thin, conformal layer of Au. While the GRR for Au replacing Ag is the best known, GRRs are a broad class of reactions, and the mechanism behind these spontaneous reactions is a difference in redox potentials.[140] The specific GRR for Au replacing Au happens according to the following equation:[141]

$$3Ag(s) + HAuCl_4 \rightarrow Au(s) + 3AgCl(s) + HCl(aq)$$
 (3.6.1)

The standard reduction potential is 0.22 V for the AgCl/Ag pair and 0.99 V for AuCl₄-/Au versus the standard hydrogen electrode, which drives the oxidation of the template material (Ag) by the metal (Au) salt precursor. This single-step spontaneous electroless deposition process is a well-known method and has been comprehensively studied.[142] It has been established that GRR proceeds through two different processes (**Figure 3.6.1**):[143] (1) the Ag template is dissolved as Au atoms deposit epitaxially on the surface of the template to form a seamless, hollow nanostructure with an outer boundary composed of Au/Ag alloy; (2) a dealloying process that selectively removes Ag atoms from the alloyed walls leads to the formation of pores in the walls.



Figure 3.6.1. Schematic of the GRR process. The major steps include the following: (A) initiation of replacement reaction at a specific spot with relatively high surface energy; (B) continuation of the replacement reaction between Ag and HAuCl₄ and the formation of a partially hollow nanostructure; (C) formation of nanoboxes with a uniform, smooth, homogeneous wall composed of Au-Ag alloy; (D) initiation of dealloying and morphological reconstruction of the Au-Ag nanobox; (E, F) continuation of dealloying, together with the formation of pores in the wall; and (G) fragmentation of the porous Au nanobox. The cross-sectional views correspond to the plane along dashed lines. Ref.[143]

Thus, the GRR offers a route to modify Ag nanostructures to variously create bimetallic Ag/Au structures, porous Ag/Au bimetallic structures, and porous pure Ag nanostructures, where the different type of structure achieved depends on the reaction parameters (time, concentrations, etc.). This offers a potential method to tune the plasmonic properties of nanostructure, which is a function of material and morphology. Furthermore, such bimetallic structures can exhibit unique properties not found in single material nanostructures, including enhanced activity of plasmonic resonances.[144]

From the discussion above, it is clear that chiral plasmonic nanostructures could benefit from the application of the Au/Ag GRR, yet no such study has been performed. Therefore, we have applied the Au/Ag GRR (reaction equation 3.6.1) to the chiral patchy particle structure, and monitored the optical response as a function of time using in-situ transmission ellipsometry. Specifically, GRR was performed by first completely immersing each of the as-deposited chiral patchy films into a separate Eppendorf tubes containing 1 mL of 0.1 mM chloroaurate acid solution (HAuCl_{4.3}H₂O, 99.999%, Sigma-Aldrich). The Ag patchy particle substrates were immersed in solution for a pre-determined times, corresponding with a total immersion time of t= 1 s, 30 s, 1 min, 2 min, 3 min, 4 min, 5 min, 7 min, 10 min, 15 min, and 20 min. After removing from the test tubes at a specified time period, each sample was rinsed thoroughly by DI water, followed by N₂ drying, measured by ellipsometry, and then either re-immersed for further treatments and measurements or set aside for morphological characterization.

The CD spectra for a chiral patchy particle film for different GRR times at various increments over 20 minutes are shown in **Figure 3.6.2**. The chiral patchy particle film is a single domain structure, and therefore, the CD response is initially very strong, showing many resonances and convoluted bisignate features. As the GRR time, *t*, proceeds, these features


Figure 3.6.2. The CD spectra for a chiral patchy particle film for different GRR times at various increments over 20 minutes. Peaks 1 and 2 represent the lowest and highest energy peaks in the measured region.

decrease in intensity and red-shift, and after t = 10 minutes, a significant reduction in intensity is observed. No significant changes are observed in the spectra over the t = 15 - 20 minute period. Notably, the negative peak that is initially around $\lambda = 700$ nm, Peak 1, red-shifts by more than 250 nm during the GRR process, and after only 4 minutes reaction time, it has already shifted to near $\lambda = 900$ nm (**Figure 3.6.3a**). Furthermore, the intensity of this peak does not significantly



Figure 3.6.3. (a) Peak location and (b) CD intensity of Peaks 1 and 2 as function of time

change over the range t = 0.5 - 4 minutes (Figure 3.6.3b), and over this same period, the peak shifts from $\lambda \sim 700 - 900$ nm. On the other hand, Peak 2 does not significantly change its spectral location over the GRR, hovering around $\lambda = 520$ nm, yet its intensity follows the same pattern as Peak 1 and does not significantly change over the range t = 0.5 - 4 minutes (Figure 3.6.3). Thus, the GRR method offers a potential method to dynamically tune the CD response over a wide range in the visible and near-infrared region.

In order to better understand the morphology changes in the Ag chiral patchy particles during the GRR, SEM images were taken at various stages during the reaction process. **Figure 3.6.4** shows the micrographs for t = 0, 1.5, 20 minutes. There appears to be a slight increase in the porosity and surface roughness of the structures after t = 1.5 minutes. After t = 20 minutes, the patchy coating is significantly rougher and more porous, and some of the patches have been pulled off of the polystyrene beads. Additionally, new crystal structures appear on the surface of the film. Interestingly, these crystals interact strongly with the electron beam of the microscope, and change from well-defined cubic and rectangular structures to globular, amorphous structures after a few seconds of electron beam irradiation (**Figure 3.6.5**).



Figure 3.6.4. SEM micrographs of the Ag chiral patchy structure after GRR reaction times of (a) - (c) t = 0, 1.5, 20 minutes, respectively.



Figure 3.6.5. SEM micrographs showing the morphological changes induced by the electron beam irradiation. The arrows indicate the time flow.

Energy-dispersive X-ray spectroscopy (EDX) measurements were performed in order to confirm the composition of the patchy particles during the GRR process. Interestingly, the EDX spectra were virtually identical over the t = 0.5 - 20 minute time period, showing only the presence of Ag and Cl within the large background of C and Si (from the SACM substrates). Thus, X-ray diffraction (XRD) measurements were also used to determine the crystalline composition of the patchy particles. As expected, the chiral patchy particles show a polycrystalline Ag diffraction pattern at t = 0 (**Figure 3.6.6a**). However, after t = 20 minutes, new peaks emerge that correspond with the diffraction pattern of AgCl. Thus, it is highly likely that the new crystals seen in the SEM images at t = 20 minutes (**Figure 3.6.4**) are AgCl that are produced during the reaction, as described in Equation 3.6.1. The known reversible photochromic decomposition of AgCl could be related to the morphological changes seen in



Figure 3.6.6. XRD diffraction pattern for the Ag chiral patchy particles after GRR reaction times of (a) t = 0 and (b) t = 20 minutes. (c) *XRD* peak attributions

(Figure 3.6.4). It is important to note that the XRD measurements are not able to detect the presence of Au in this case since the diffraction peaks of Au are completely overlapped by the peaks of Ag. It does appear that the GRR reaction occurs as described in Equation 3.6.1 given the presence of AgCl in significant enough amounts to be detected by XRD. That is, Ag from the chiral patchy coatings is being consumed and creating AgCl. However, it does not appear that the Au epitaxially replaces Ag within the patches during the GRR process, especially since EDX does not provide direct evidence for the presence of Au on the surface of the films. At this point it is not clear where the Au does deposit, if it does not deposit epitaxially, and further analyses are necessary. It is suspected that the surface roughness of the deposited Ag and the presence of the polystyrene nanospheres might play a role in the abnormal behavior of the Au atoms in this structure.[145, 146]

In conclusion, chiral patchy particle films were modified by the Au/Ag galvanic replacement reaction. The reaction induced morphological changes in the Ag patchy coatings by increasing the surface roughness, creating additional pores, and depositing AgCl on the surfaces. While Au or Au/Ag alloy was not detected in meaningful quantities, the GRR significantly modified the CD spectra of the chiral patchy films in a very short time period. In general, the CD intensity decreased and the spectral features red-shifted. Notably though, a negative peak shifted from $\lambda \sim 700 - 900$ nm over the reaction times t = 0 - 4 minutes, without a change in magnitude. Thus, as desired, the GRR method does dynamically modify the CD response of the chiral patchy particles over a wide range of wavelengths in the visible and near-infrared region. These results demonstrate that the combination of DSG for chiral structure fabrication, coupled with wet chemical methods, such as GRR, offers significant freedom and potential in the design of chiral plasmonic structures for specific applications.

CHAPTER 4

CHIRAL SENSORS

4.1 Introduction

Chirality is an intrinsic property of living matter, and the homochirality of biomolecules is one of science's greatest unanswered questions. That is, biomolecules are generally chiral, and for some unknown reason, most naturally occurring biomolecules have the same handedness. For example, amino acids are almost always left-handed, while sugars are almost always righthanded. Even without its implications regarding the origin of life, the homochirality of life is an extremely important consideration because it means that different handed molecules can have vastly different effects on the human body. Perhaps the most famous and tragic example of this is the case of thalidomide. One enantiomer of thalidomide is effective in the treatment of morning sickness, while the other causes severe birth defects. Unfortunately, the drug was administered in racemic mixtures (equal quantities of both enantiomers) to pregnant women, and over ten thousand infants worldwide were born without limbs or with shortened limbs. Therefore, there is a clear advantage to biomolecule detection methods that can detect not only the chemical composition, but also the chirality of a molecule.

Interestingly, chiral plasmonic materials have very recently demonstrated a number of unique properties that could serve as the basis for such chiral sensing platforms.[23, 147-149] For example, Hendry *et al.* have shown that the chiral optical plasmonic resonances of a chiral



Figure 4.1.1. Changes induced in the chiral plasmonic resonances of the PCM are readily detected using CD spectroscopy. (a) CD spectra collected from LH/RH PCMs immersed in distilled water. The three modes that show the largest sensitivity to changes in the local refractive index of the surrounding medium have been labeled I, II and III. Shown to the right of each spectrum is an electron micrograph of the PCM displaying the gammadion structure and periodicity. (b) Influence of the adsorbed proteins haemoglobin, β-lactoglobulin and thermally denatured β-lactoglobulin on the CD spectra of the PCMs. Red spectra were collected in Tris buffer before protein adsorption (solid line, LH PCM; dashed line, RH PCM), and black spectra were collected after protein adsorption. Magnitudes and directions of DlRH/LH values of mode II for β-lactoglobulin adsorption have been highlighted. Ref. [23]

metamaterial composed of gold gammadions are not only sensitive to ambient refractive index changes induced by adsorbed biomolecules as in traditional localized surface plasmonic resonance (LSPR) sensing, but are also sensitive to the chiral molecular structure of these molecules. In this case, adsorbed molecules altered the circular dichroism (CD) spectra of metamaterials composed of identical, yet different handed gammadions, where the change in magnitude and spectral location of the CD response depended on *both* the handedness of the material *and* the specific supramolecular structure of the biomolecule (Figure 4.1.1).[23] This



Figure 4.1.2. Schematics for PCR assembly of Au NRs. (a) PCR replication procedure in which a DNA strand can be amplified using primer, template DNA, taq plus polymerase and four different DNA bases. (b) PCR-based gold NRs ETE assembly. (c) PCR-based gold NRs SBS assembly with inter-NR gap d; in the bottom part of the panel the DNA chains were removed for clarity. Ref. [148]

sensitivity to the structural chirality of the surrounding medium is an entirely new phenomenon and is attributed to coupling between the adsorbed molecules and the superchiral local electromagnetic fields generated by the chiral noble metal meta-atoms.[150] Even without such exotic effects, chiral plasmonic sensing can achieve remarkable sensitivity by target-induced changes in the chirality of metal nanoparticle assemblies, *i.e.*, the molecule of interest alters the structural chirality of metal nanoparticle assemblies, which then can be measured by CD spectroscopy (**Figure 4.1.2**). For example, DNA has been detected with attomolar sensitivity by using DNA-bridged gold nanorod helical assemblies, [148] and target-induced chiral dimerization of gold nanoparticles has demonstrated the ultrasensitive detection of both an environmental toxin, microcystin-LR, and a cancer biomarker, prostate-specific antigen.[149] These chiral plasmonic approaches offer significant improvements in the level of detection over other available methods, and such excellent results are attributed to the strong plasmonic signals and signal amplification due to the bisignate nature of CD bands.

Though the concept of chiral plasmonic sensing is new, the basic premise is similar to traditional LSPR sensors,[151] except that in the chiral case the signal is provided by two different entities, the spectral location of the LSPR peak and the polarization state of the measured light. The additional information provided by the polarization increases sensitivity, improves signal-to-noise ratios and accuracy, creates redundancy in the measurement, and allows for novel implementation schemes without significantly increasing the complexity of measurement, as the polarization state can be assessed using linear polarizers. Given their potential for simple measurement and high sensitivity, chiral metamaterial sensors could negate the need for advanced laboratory equipment and personnel for analysis, and instead the optical response could be measured by the naked eye or smartphone.[152] Such straightforward interpretation would take biomolecule detection out of the laboratory and into the field and retail/household environments.

From the discussion above, it is clear that chiral plasmonics have significant potential for sensor applications. Unfortunately, chiral metamaterials and chiral nanoparticle assemblies that are active in the visible wavelength region must have nanoscale chiral structural features (1-100 nm), and this makes their fabrication very challenging, generally requiring expensive and time-consuming processes. Consequently, systematic studies of optical sensing using chiral plasmonic materials are severely lacking. Furthermore, not only do these fabrication challenges serve as impediments to the applied research of chiral plasmonics, but they also impose a severe obstacle to their transition out of the laboratory and into the real world. Sensing applications are

inherently substrate intensive and industrially minded, and, consequently, a simple and scalable method of producing chiral metamaterials is necessary in order to investigate their promise as ultrasensitive optical sensors. As described in Chapters 2 and 3, DSG is a simple and straightforward method to obtain chiral materials with properties that are comparable with the best performing devices produced using other elaborate methods. Thus, the DSG method of fabricating chiral plasmonic structures is ideally suited to investigate chiral plasmonic sensing applications. This chapter describes an initial experiment in using DSG chiral nanostructures for biosensing of chiral molecules.

4.2 Stretched SiO₂ Patchy Particles + Ag Thin Film

A new DSG chiral nanostructure, stretched SiO₂ patchy particle + Ag thin film, was chosen and designed for the biosensing experiment. The structure is very similar to the patchy staircase (Section 3.5). A SiO₂ stretched chiral patchy structure (90-60-30, in this case) is used as a dielectric scaffold for a subsequent Ag layer, which, different from the patchy staircase, is deposited as a thin film (*i.e.*, vapor incident angle, $\theta = 0^{\circ}$) in order to coat the entire top surface of the SACM with a uniform layer of Ag. Five different Ag thicknesses were used ($t_{Ag} = 0, 5, 10, 20, \text{ and } 50 \text{ nm}$), and three different SACM diameters were used (d = 200, 350, and 500 nm), creating 15 different films to be tested. SEM micrographs of some these different films are shown in **Figure 4.2.1**. As can be seen in the films with $t_{Ag} = 10 \text{ nm}$, the SiO₂ patch has a more defined morphology for the larger diameter SACM substrates (d = 350 and 500 nm) due to the less severe curvature and the improved monolayer quality. As the thickness increases, the Ag layer transitions from smaller, more isolated islands for $t_{Ag} = 10 \text{ nm}$ to a mostly continuous thin film for $t_{Ag} = 50 \text{ nm}$. This array of different structures was chosen such that the plasmonic



Figure 4.2.1. SEM micrographs of the 90-60-30 $SiO_2 + 10$ nm Ag structure on (a) – (c) D = 200, 350, and 500 nm SACM substrates, respectively. (d) 90-60-30 $SiO_2 + 20$ nm Ag structure on d = 200 nm SACM substrates (e) 90-60-30 $SiO_2 + 50$ nm Ag layers on d = 200 nm SACM substrates. The scale bars are 0.5 µm, unless otherwise noted.

properties of the films could be optimized for use as both chiral sensors and SERS substrates. This requires that there be strong plasmonic absorption near the excitation wavelength of the Raman laser ($\lambda = 785$ nm), a significant number of hotspots, and considerable optical activity.

The plasmonic absorbance can be characterized by UV-visible-NIR transmittance measurements, and the spectra for the different films are shown in **Figure 4.2.2**. The d = 200 nm films do not show a Bragg mode peak from the SACM substrates, and an obvious plasmonic dip is observed for all Ag thicknesses. This transmittance loss generally broadens and red-shifts with increasing t_{Ag} . For the d = 350 and 500 nm films, the Bragg resonances from the SACM substrates are convoluted with LSPR resonances of the Ag layer, but similar to the d = 200 nm films, there are obvious broadband transmittance losses which intensify, broaden, and red-shift



Figure 4.2.2. Transmittance spectra for the 90-60-30 SiO₂ + Ag structures on (a) – (c) $D = 200, 350, and 500 \text{ nm SACM substrates, respectively. The Ag layer thickness varies from <math>t_{Ag} = 0 - 50 \text{ nm}.$

with increasing t_{Ag} . In general, all films with $t_{Ag} > 20$ nm exhibit plasmonic absorbance at $\lambda =$ 785 nm. The optical activity of the films can be characterized by transmission ellipsometry, where CD is proportional to the m_{14} Mueller matrix element. The m_{14} spectra of the different films are shown in **Figure 4.2.3**. In general, these spectra follow the same trends established in the transmittance spectra. Films on d = 350 and 500 nm SACM substrates show more complicated spectra due to chirality induced in the Bragg modes. The addition of an Ag layer creates new spectral features at the longer wavelengths, and these generally intensify, broaden, and red-shift with increasing t_{Ag} . Corresponding with the increase in plasmonic absorbance, all films with $t_{Ag} > 20$ nm exhibit significant plasmonic optical activity.

In order to test their SERS activity, the "standard" SERS measurements were performed on these different substrates. Specifically, 2 μ L of 10⁻⁵ of trans-1,2-bis (4-pyridyl) ethene (BPE, Aldrich, 99.9+%) solution in methanol (MeOH) was dropped onto the surface of the films and allowed to dry. Then the films were loaded onto the Raman microscope stage, where the SERS spectra were collected using the λ = 785 nm laser at 30 mW of power and 10 second integration time. The resulting spectra are averaged over 10 measurements. Representative SERS spectra are shown in **Figure 4.2.4**. Previous studies have shown that the BPE molecule exhibits



Figure 4.2.3. m_{14} spectra for the 90-60-30 SiO₂ + Ag structure on (a) – (c) $D = 200, 350, and 500 \text{ nm SACM substrates, respectively. The Ag layer thickness varies from <math>t_{Ag} = 0 - 50 \text{ nm}.$ Note that the $t_{Ag} = 50 \text{ nm}$ film has the ordinate axis to the right.

characteristic SERS peaks at $\Delta v = 1200 \text{ cm}^{-1}$, 1604 cm⁻¹, and 1634 cm⁻¹, which are attributed to the C=C stretching mode, aromatic ring stretching mode and in-plane ring mode, respectively.[153] The obtained SERS spectra show many more peaks due to the background signal, but peaks at $\Delta v \approx 1604 \text{ cm}^{-1}$ and 1640 cm⁻¹ are distinguishable. In general, it was found that the $t_{Ag} = 20 \text{ nm}$ film always exhibited much larger SERS activity than the other thicknesses, while the diameter of the SACM had little effect on the SERS activity, with the 350 nm SACM usually having slightly higher activity than the 500 nm and more than the 200 nm. These results are consistent with the trends seen in the optical properties and morphologies. Films of different SACM diameters with $t_{Ag} \ge 20 \text{ nm}$ all exhibited strong absorbance at $\lambda = 785 \text{ nm}$, and therefore,



Figure 4.2.4. (a) BPE SERS spectra from 90-60-30 SiO₂ + 20 nm Ag structures with different SACM diameters. (b) BPE SERS spectra from 90-60-30 SiO₂ + Ag structures on d = 350 nm with different t_{Ag} .

should couple fairly equally with the excitation laser. However, the morphology of the Ag films with $t_{Ag} = 20$ nm most likely produces many more hotspots due to the small junctions between the closely packed Ag islands (**Figure 4.2.1d**). Thus, the SiO₂ stretched patchy particle film with an Ag layer thickness $t_{Ag} = 20$ nm is the best candidate for the SERS and chiral sensing experiment due to the large SERS and optical activity.

4.3 Tryptophan Sensing

The analysis of the different structures above was done in order to determine an optimal structure that could be used for both SERS measurements and chiral sensing. The benefit of combining both techniques is that SERS can be used to identify a particular type of molecule due to characteristic molecular vibrations specific to its chemical makeup. That is, each molecule has a unique SERS spectrum that can serve as a fingerprint. However, biomolecules are generally chiral, and the different handed enantiomers have the same chemical composition and bonding, which means that SERS measurements cannot distinguish between them because they will have

identical spectra. As discussed above, knowledge of molecular chirality can be extremely important because different handed molecules can have vastly different effects on the human body. Thus, there is a clear advantage to a sensor that can detect not only the chemical composition of an adsorbed molecule through SERS, but also can be used to detect the chirality of the molecule.

The molecule chosen for this initial study is tryptophan (Trp), which is an essential amino acid in the human diet. Trp has two different enantiomers L-Trp and D-Trp, and only the L-Trp enantiomer is used in the body. Notably, Trp is also one of the molecules that demonstrated coupling with the superchiral field of a chiral metamaterial, as demonstrated by Hendry et al. in the first report of superchiral sensing.[23] For the chiral sensing experiment, two different enantiomeric film structures were used, a 90-60-30 stretched SiO₂ patchy particle with a 20 nm Ag thin film layer and a 90-30-60 stretched SiO₂ patchy particle with a 20 nm Ag thin film layer, both on 350 nm SACM substrates. Freshly deposited films were placed in cuvettes, allowed to soak in deionized (DI) water for 30 minutes, and then the films were dried in a stream of N₂, while remaining in the cuvette. Transmission ellipsometry measurements were then performed through a pinhole mask that allowed for nine different sites on the film to be measured individually. Throughout the whole process the films remain in the cuvettes, affixed to the sides with double-sided tape. After ellipsometry measurement, the films were incubated in the dark at room temperature in a 1 mg/mL aqueous solution of either L-Trp or D-trp for an hour. After incubation, the films were again dried in a stream of N₂, taking care not to disturb the placement of the film inside of the cuvette. Transmission ellipsometry measurements were again performed through a pinhole mask, which allowed for the same nine sites to be measured again.

The obtained spectra were then processed to compare changes before and after Trp incubation. The CD spectra were extracted from the generalized ellipsometry spectra according to the process outlined in Section 2.2.6. Generally, a change in peak positions and intensities is apparent in the CD spectra after Trp incubation, similar to what is seen in the work by Hendry *et al.* We use Fourier analysis to quantify these changes. In particular, the FFT of the CD spectra are taken, where the phase is unwrapped. The magnitude of the FFT phase before incubation is subtracted from magnitude of the FFT phase after Trp incubation ($\Delta \varphi = |\varphi_{Trp}| - |\varphi_{bare}|$). **Figure 4.3.1** shows the $\Delta \varphi$ spectra for D- and L-Trp for the 90-60-30 and the 90-30-60 films, along with



Figure 4.3.1. Δφ spectra for D- and L-Trp for the (a) 90-60-30 and the (b) 90-30-60 films. The chiral biomolecules induce a shift in the spectra where the magnitude and direction of that shift depends on the handedness of both the biomolecule. (c) and (d) Raw CD signals for the 90-30-60 film before and after incubation with L-Trp and D-Trp, respectively.

the raw CD signals for the 90-30-60 films. Similar to what is seen by Hendry *et al.*, the chiral biomolecules induce a shift in the CD spectra where the magnitude and direction of that shift depends on the handedness of both the biomolecule (*i.e.*, D- or L-) and the plasmonic structure



Figure 4.3.2. (a) – (f) SERS spectra and peak attributions for D- and L-Trp on both the 90-60-30 and 90-30-60 films over wavenumber regions 300 – 500 cm⁻¹, 500 – 720 cm⁻¹, 720 – 900 cm⁻¹, 900 – 1100 cm⁻¹, 1100 – 1400 cm⁻¹, 1450 – 1650 cm⁻¹, respectively. The symbols for vibrations and rings: v, stretching; β, bending (further categorized into α, scissoring; γ, rocking; ω, wagging; δ, twisting); θ, ring breathing; def., deformation; s, symmetric; as, asymmetric; R, benzene ring; r, pyrrole ring. Attributions and symbols from Ref. [154]

(*i.e.*, 90-60-30 or 90-30-60). Specifically, the D- enantiomer induces a negative $\Delta \varphi$ in the 90-60-30 structures, but induces a positive $\Delta \varphi$ in the 90-30-60 structures. On the other hand, the Lenantiomer induces a positive $\Delta \varphi$ in the 90-60-30 structures, but induces a negative $\Delta \varphi$ in the 90-30-60 structures. These responses are opposite of each other. It is also interesting to note that the D-Trp molecule induces a larger magnitude shift in general. The amount of experimental uncertainty in this initial study is not insignificant, as seen in the error bars. However, these results are promising, and for one structure, 90-60-30, the differences in values for $\Delta \varphi$ for the different handed molecules are statistically significant, having *p*-values less than 0.05.

Finally, after ellipsometry measurements, the films are loaded onto the Raman microscope for SERS measurements. The incident laser light is unpolarized and has a wavelength of $\lambda = 785$ nm laser. Forty different measurements are taken at 30 mW of power using a 10 second integration time, and then these are averaged together. As shown in **Figure 4.3.2**, the SERS spectra contain many different intense peaks, and many match the wavelengths of known Trp peaks.[154] However, the SERS spectra in general also match the background



Figure 4.3.3. SERS spectra for D- and L-Trp and for the background using a 90-30-60 film.

spectrum (**Figure 4.3.3**), and therefore, they cannot be used to identify Trp. Thus, further investigations are necessary to reduce these contamination peaks enough so that the apparent weak Raman scattering of Trp molecules can be observed.

4.4 Conclusion

This chapter investigated DSG-fabricated chiral plasmonic thin films for chiral sensing applications. The SiO₂ stretched patchy particle + Ag thin film structure was optimized for both SERS and CD sensing. Importantly, the SiO₂ stretched patchy particle + Ag thin films showed sensitivity to the chiral structure of adsorbed molecules. Different handed molecules induced opposite changes in the CD response. While work remains to be done to improve the signal to noise ratio in the CD measurements and to remove background/contamination peaks in the SERS measurements, these initial results are very promising, and demonstrate the feasibility of using DSG to fabricate chiral plasmonic thin films for real world applications.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

Although simple to implement, DSG is a powerful tool that promises to further our understanding of the relationship between structural chirality and optical chirality, as well as underlie the construction of devices for real world applications. Accordingly, this dissertation demonstrates several new DSG strategies for the production chiral plasmonic films, including continuous plasmonic helices composed of metal composites, metal/dielectric composite helices, and various chiral coatings based on nanosphere monolayers. This list of structures is certainly not exhaustive, and it is clear from this sampling that DSG techniques offer significant freedom in the choice of materials, composition, morphology, and templates, giving access to a huge parameter space to create 3D chiral structures with specific properties, even when feature sizes must be small enough to exhibit visible optical activity. Notably, the dynamic azimuthal motion of the substrate with respect to the vapor source is the critical feature in the generation of chirality from a symmetric environment for all cases outlined above. For example, substrate rotation is crucial for breaking the racemic symmetry of polycrystalline arrays of SACMs to form chiral patchy films with optical activity. The ability to use these readily available templates, or none at all, is a distinct advantage of DSG. However, high quality templates will also produce high quality structures and films, and the use of scalable high quality templates, such as those fabricated using roll-to-roll or nanoimprint techniques,[155-157] in combination

with DSG needs further investigation. Additional improvements can also be made in the quality of the obtained films by using advanced deposition techniques, such as ion beam-assisted deposition or Phi-Sweep method.[158, 159] Though, in refining DSG methods for the production of chiral plasmonic structures, careful consideration must be given to preserving the simplicity and scalability of the method.

Some experimental and theoretical methods and models have been adapted in this dissertation in order to better study chiral DSG structures. In particular, an anisotropic parameter retrieval method has been applied for experimental analysis, and geometric chirality, FDTD, and the point-dipole approximation have been applied for theoretical analyses. While the simplicity of the DSG method is beneficial in many respects, the non-idealities of the obtained structures makes theoretical analysis more challenging. That being said, computer simulations of the morphologies of DSG structures using techniques such as Monte Carlo and molecular dynamics are well established. The combination of these methods with well-known computational electromagnetic techniques (FDTD, DDA, FEM, etc.) to simulate chiral DSG structures has not received much attention, yet such a study would be beneficial and interesting.

Finally, DSG does have the distinction of being a simple and scalable method, but this advantage is inconsequential if real world applications of the fabricated films are non-existent. Thus, the application of chiral DSG films needs further investigation. The chiral sensing properties of DSG films have been introduced in this dissertation. The initial results presented here are promising, but much more work needs to be done to improve experimental uncertainty. Other applications of chiral plasmonic films, such as perfect lenses, cloaking devices, or non-linear materials could also prove exciting.

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APPENDIX A

JONES AND MUELLER DESCRIPTIONS OF LIGHT PROPAGATION

A uniform plane wave is a particular solution of Maxwell's equations in a homogeneous region of the space.[160] The polarization state of such a plane wave traveling along the z axis can be described by superimposing two electric fields whose directions are parallel to the x and y directions since Maxwell's equations impose that the electric field should be transverse to the direction of propagation. Thus, the total electric field of the electromagnetic wave traveling along the z axis with angular frequency, ω , and wavenumber, κ , is given by the vector sum of electric fields E_x and E_y :

$$\boldsymbol{E}(z,t) = \boldsymbol{E}_{\boldsymbol{x}}(z,t) + \boldsymbol{E}_{\boldsymbol{y}}(z,t) = (\boldsymbol{E}_{x0} \exp[i\delta_{x}] \mathbf{x} + \boldsymbol{E}_{y0} \exp[i\delta_{y}] \mathbf{y}) \exp[i(\omega t - \kappa z)]$$
(A.1)

where E_{x0} and E_{y0} are the real amplitudes, δ_x and δ_y are the initial phases, and **x** and **y** are unit vectors in the *x* and *y* directions, respectively. Note that this dissertation will follow the convention that, when considering polarization, only the electric field vector is described since the magnetic field is perpendicular and proportional to the electric field, as described by Maxwell's equations. Eq. A.1 can be written in column vector form, known as a Jones vector:

$$\boldsymbol{E}(z,t) = \exp[i(wt - \kappa z)] \begin{bmatrix} E_x \\ E_y \end{bmatrix},$$
(A.2)

where $E_x = E_{x0} \exp[i\delta_x]$ and $E_y = E_{y0} \exp[i\delta_y]$. In most optical measurements and analyses, only relative changes in amplitude and phase are taken into account, the intensity is normalized, and

conventionally, the exponential term is neglected.[109] Thus, linearly polarized waves in the x and y directions are generally described by the following Jones vectors, respectively:

$$\boldsymbol{E}_{\boldsymbol{x}} = \begin{bmatrix} 1\\ 0 \end{bmatrix},\tag{A.3}$$

$$\boldsymbol{E}_{\boldsymbol{y}} = \begin{bmatrix} \boldsymbol{0} \\ \boldsymbol{1} \end{bmatrix}. \tag{A.4}$$

While linearly polarized light oriented at 45° from the x direction, can be expressed as:

$$\boldsymbol{E}_{+45^{\circ}} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1\\1 \end{bmatrix}.$$
(A.5)

Finally, the Jones vectors for right and left circular polarizations are given respectively by:

$$\boldsymbol{E}_{\mathbf{RCP}} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1\\ i \end{bmatrix},\tag{A.6}$$

$$\boldsymbol{E}_{\text{LCP}} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1\\ -i \end{bmatrix}. \tag{A.7}$$

As mentioned in Section 1.1, both linear and circular polarizations are equally valid bases for the description of the polarization state of an electromagnetic wave. The coordinate transformation from polar coordinates (circular) to Cartesian coordinates (linear) is given by

$$\mathbf{T} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1\\ -i & i \end{bmatrix}.$$
(A.8)

That is, a Jones vector of a polarization state given in the circular base can be converted to the linear basis by multiplying on the left by \mathbf{T} , and, similarly, the conversion from the linear basis to circular basis is achieved through multiplication by \mathbf{T}^{-1} .

The Jones matrix representation is a mathematical description of the variations in an initial polarization state after interacting with an optical system. Specifically, an optical system can be described by a series of 2×2 Jones matrices that act on an initial polarization state through matrix multiplication to give a Jones vector of the final polarization state. The Jones

representation provides a complete mathematical description of any optical system as long as the light is initially fully polarized and the system is non-depolarizing.

Since Jones vectors cannot account for unpolarized or partially polarized light, a different calculus must be used for depolarizing optical systems. In this case, Stokes parameters are used to create a Stokes vector. Using light intensity, *I*, the Stokes parameters are given by

$$S_0 = I_x + I_y \tag{A.9}$$

$$S_1 = I_x - I_y \tag{A.10}$$

$$S_2 = I_{+45^\circ} - I_{-45^\circ} \tag{A.11}$$

$$S_3 = I_{RCP} - I_{LCP.} \tag{A.12}$$

 S_0 describes the total light intensity, S_1 and S_2 are related to the light intensity of linear polarization, and S_3 is related to the intensity of circular polarization. These parameters can be arranged into a vector,

$$\boldsymbol{S} = \begin{bmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{bmatrix}, \tag{A.13}$$

and this Stokes vector can be used to describe any polarization state. For any vector S the following relation must hold:

$$S_0^2 \ge S_1^2 + S_2^2 + S_3^2. \tag{A.14}$$

Here, the equality holds only for fully polarized light, and for partially polarized light the inequality holds. For partially polarized light, the degree of polarization is given by

$$p = (S_1^2 + S_2^2 + S_3^2)^{1/2} / S_0.$$
(A.15)

Similar to the Jones matrix representation, the variation in an initial state of polarization given by a Stokes vector upon interaction with an optical system can be described mathematically by matrix multiplication. In this case, optical elements are described using 4×4 matrices known as Mueller matrices.

While the Mueller matrix representation can account for depolarization, which is not included in a Jones description, it does not carry any phase information, as the Jones description does, since the Stokes parameters are derived from intensity values. Additionally, it is important to note that any Jones vector or matrix has a corresponding Stokes vector and Mueller matrix. However, it is not necessarily true that any Stokes vector or Mueller matrix can be described in the Jones calculus.[161] A Mueller matrix that is derived from (and can be converted to) a Jones matrix is often referred to as a Mueller-Jones matrix.