High Resolution Electron Energy Loss Spectroscopy of Plasmonic Nanostructures

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I am submitting herewith a dissertation written by Grace Pakeltis entitled "High Resolution Electron Energy Loss Spectroscopy of Plasmonic Nanostructures." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Materials Science and Engineering.

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High Resolution Electron Energy Loss Spectroscopy of Plasmonic Nanostructures

A Dissertation Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Grace E. Pakeltis

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Abstract

This dissertation discusses developing fabrication techniques to study the plasmonic phenomena of nanostructures utilizing high spatial and energy resolution of monochromated aberration-corrected scanning transmission electron. While standard lithography has been widely used to create planar nanostructures, investigation into 3-dimensional nanostructures is lacking. A robust synthesis approach utilizing focused electron beam induced deposition, atomic layer deposition, and thin film sputter deposition to fabricate complex 3D plasmonic architectures is described and characterization of single nanoresonators is presented. Additionally, this dissertation discusses the use of high-resolution electron energy loss spectroscopy to investigate the hybridization of gold nanorod oligomers. Experiment and simulation resolve magnetic and electric dipole resonances in the cyclic assemblies. Finally, the hybridization of split ring resonators is discussed. Both planar and 3D SRR arrangements are investigated to reveal the coupling dynamics in the systems.
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Figure 4.3 (a) Experimental EELS spectra taken at the SRR outer tip for planar rotational study. The progression from a splitting into the bonding and antibonding modes to a single mode (45°) reveal the transition from electric dipole-dipole coupling to magnetic dipole-dipole coupling. (b) Anticrossing-like plot of the experimental normal modes illustrating a consistent peak splitting as a function of rotation angle. (c-g) HAADF images of SRR with colored dot indicating where spectra were acquired. Corresponding spectrum images reveal the bonding (h-l) and antibonding (m-q) modes in the system. Scale bar = 300 nm.

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Chapter 1

Background
1.1 3D Focused Electron Beam Induced Deposition (FEBID):

The desire for customizable fabrication of complex objects has led to great advancements in 3d printing technologies. Although there is currently a widely accessible, commercial platform for macroscopic 3d manufacturing, there have been significantly fewer advancements in micro- and nano-manufacturing. Advancements in micro- and nano-scale 3d-manufacturing are motivated by areal density constraints and thus the need to extend device elements into the third dimension. Furthermore, design flexibility, enhanced functionality and new phenomena may emerge if nanoscale synthesis can extend into the third dimension. Movement towards direct-write 3d nanoprinting introduces significant flexibility for device fabrication and have the potential to revolutionize many fields including high density memories, (N)MEMS, magnetics, and photonics/plasmonics. Focused electron beam induced deposition (FEBID) is currently one of the only technologies which offers the ability to fabricate complex 2d and 3d structures with \(\sim 10\) nm resolution.

1.1.1 Basic Principles of FEBID:

Focused electron beam induced deposition utilizes the nanoscale resolution of a focused electron beam in a scanning electron microscope (SEM) as a nanoscale direct-writing technology. Common to many FIB/SEM (focused ion beam), is a gas transport system which includes a capillary tube that continuously flows a stream of gas molecules to a substrate (Figure 1.1). The stable local precursor coverage at the surface is vital for reliable growth. A fraction of the flowing molecules physisorb on the surface where they diffuse and can desorb from the substrate. The focused electron beam uses in short controllable electron pulses (dwell time) to dissociate the precursor molecules that have adsorbed on the surface. This dissociation leads to the volatile fragments which desorb from the beam impact area while the nonvolatile fragments condense on the substrate. During the next beam pulse, the position of the beam on the substrate is slightly displaced so that the new material grows on top and slightly shifted relative to the initial deposit.

The principles of FEBID give the process significant advantages over other 3D nanoprinting technologies. Complex 3D structures can be fabricated on virtually any substrate material with any surface morphology due to the adsorption of the precursor on the substrate. Additionally, because of the use of an electron beam, more complex architectures can be realized due to the ability to control movement with sub-nanometer precision. Finally, the use of electrons over ions, as are used in focused ion beam induced deposition (FIBID), avoids ion implantation and reduces substrate heating that is commonly found in FIBID.
Figure 1.1 The illustration above shows the basic principle of the FEBID process. Left) A gas injection nozzle continuously flows precursor gas molecules which desorb and absorb on the substrate surface. Middle) A short beam pulse dissociates the gas leaving a deposit on the surface. Right) Short beam pulses are slightly displaced in order to build the deposit. Figure borrowed from source\(^5\)
1.1.2 Growth Parameters:
The FEBID process is highly complex with a variety of interdependent parameters which continuously change during fabrication (Figure 1.2). Understanding and optimizing these parameters lead to higher reliability and fidelity in the 3D deposits. These processes, as illustrated in Figure 1.2, have been broken into three categories: beam parameters, gas parameters, and patterning parameters. There has been vast research into the development of various FEBID precursors for various applications (discussed in later section) and for each precursor it is necessary to find the appropriate working regime. Currently, extensive research has been done on the MeCpPt(IV)Me₃ precursor.6,9-11

1.1.2.1 Gas Parameters
In the FEBID process, there is a working regime which is a ratio between the available precursor molecules, the electron energies, patterning procedures, and gas parameters. Gas injection system (GIS) alignment and relation to the patterning direction play a significant role in the quality of the deposit. Simulations have shown that the precursor surface coverage and degree of depletion at the deposit has a large effect on the deposit.12,13 The GIS should be aligned close to the substrate surface (~100 μm) and the radial distance relative to the structure (~150 μm). In addition to GIS alignment, the temperature and type of precursor used will also influence the growth of 3D structures. For ideal growing rates, prior to growth, the precursor should be heated as lower temperatures will lead to lower growth rates.7

1.1.2.2 Beam Parameters
Beam conditions also play a critical role in the quality of FEBID deposits. This includes the primary electron energy and current as well as the beam focus and convergence angle. When growing 3D structures, low beam currents (<100pA) should be used as low beam currents have comparably high precursor surface coverage which allows for greater control over the growth. This leads to the elimination of morphological issues such as side branching and co-deposition.7,14 Additionally, lower beam currents minimize the influence of scan direction in relation to gas flux. The primary beam energy must also be chosen to control growth quality. As illustrated in Figure 1.3, an energy range of 5-30keV can be used for 3D FEBID, however, higher energy beams minimize co-deposition and allow for higher lateral resolution.7 As the primary beam energy increases, the size and shape of the interaction volume will change, ultimately changing the cross-section of the nanowire deposit from circular to ellipsoidal.5 Additionally, small deviations in the beam focus and beam astigmatism will lead to a blur in the beam significantly modifying the deposit. This will lead to deviations in the diameter in the pillar as well as in the segment angle which increase as the blur is increased. Recently, beam heating was determined to be the source for growth rate reduction...
Figure 1.2 Illustration outlining the various parameters that impact 3D FEBID structures. The parameters are separated into three categories: gas parameters, beam parameters, and patterning parameters. Figure borrowed from source^7
Figure 1.3 Tilted SEM images show calibration structures grown as various primary electron energies and beam currents. Co-deposition and co-branching is observed and indicated by the yellow and red circles respectively. Figure borrowed from source\(^7\)
particularly as structure height and segment length increases, creating additional difficulty in creating more complex structures. This work revealed that temperature increases due to energy dissipation within the segments which increases precursor desorption. The beam impact region is also reduced and growth rate suffers as a result.

1.1.3 Patterning Parameters

Advances in FEBID software has led to the ability to fabricate structures using a patterning software. The 3BID software gives the user full control over the patterning sequence. This includes modifying vertices and choosing an interlacing strategy for multi-branch patterning. The 3BID software creates an exposure file (also known as a stream file) which contains a list of XY coordinates and corresponding dwell times. Generally, 3D structures are fabricated using a patterning velocity, which is a ratio between the pulse duration or dwell time and the patterning pixel distance or point pitch (PoP). The 3D CAD program optimizes the patterning velocity by either modifying the PoP and keeping the dwell time constant or modifying the dwell time and keeping the PoP constant. As with the beam energy and current, there is a working regime where the PoP and dwell time will produce the most reliable and reproducible deposits, which is dependent on the precursor. Additionally, when fabricating more complex, multibranch geometries, an interlaced patterning sequence should be used. This technique reduces sample drift issues as well as inhomogeneous structure bending by minimizing heating effects.

1.1.4 Functional FEBID Structures:

Much work has been done to advance the state of FEBID materials. Currently, there is a vast number of FEBID materials with varying functionalities including electrically conducting, magnetic, or optically active materials. Table 1.1 shows the precursors that have been demonstrated previously. One drawback in 2d and 3d printing via FEBID is the deposited material often contains high residual carbon content (up to 90%) from the organometallic precursor, and thus the as-deposited functionality is often limited. Significant research has gone into various post-processing steps to purify deposits. Although several processes exist to purify 2D deposits, they often lead to asymmetric purification leading to structural deformities when used for 3D deposits. Thermal annealing has proven to work for cobalt pillars, however the as-deposited cobalt content is already high (~70 at.%). For Au pillars, post-deposition oxygen plasma procedure results in a 70 at.% deposit, however this process is not viable for complex 3D structures. Currently, two processes exist for purifying complex 3D structures: e-beam assisted purification in water vapor and laser assisted purification. These processes, however, still result in structural distortions/shrinkages that must be accounted for during the design stage.
Table 1.1 List of FEBID precursors that have been investigated for 3D deposits. Table borrowed from source with references therein

<table>
<thead>
<tr>
<th>Core Element</th>
<th>Precursor</th>
<th>Core Element</th>
<th>Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Me$_2$Au(tfac)</td>
<td>Mo</td>
<td>Mo(CO)$_6$</td>
</tr>
<tr>
<td></td>
<td>Me$_2$Au(acac)</td>
<td>Pt</td>
<td>CpPtMe$_3$</td>
</tr>
<tr>
<td>C</td>
<td>C$<em>{14}$H$</em>{10}$</td>
<td>Rh</td>
<td>[RhCl(PF$_3$)$_2$]$_2$</td>
</tr>
<tr>
<td>Co</td>
<td>Co$_2$(CO)$_8$</td>
<td>Si</td>
<td>TEOS</td>
</tr>
<tr>
<td>Cu</td>
<td>(hfac)Cu(VTMS)</td>
<td>W</td>
<td>W(CO)$_6$</td>
</tr>
<tr>
<td></td>
<td>Cu(hfac)$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(hfac)Cu(MHY)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(hfac)Cu(DMB)</td>
<td>Co-Fe</td>
<td>HCo$<em>3$Fe(CO)$</em>{12}$</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(CO)$_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe$_2$(CO)$_9$</td>
<td></td>
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</tr>
</tbody>
</table>
Some success has been found with magnetic precursors. Work has shown high metal content deposits (~80 atomic %) with strong magnetization have been achieved, which has led to the fabrication of complex 3d magnetic structures using the HCo$_3$Fe(CO)$_{12}$ precursor to explore new magnetic phenomena. Achieving deposits with high metal content, however, has proven to be more difficult in precursors with plasmonic signatures. Silver 3d structures grown from the AgO$_2$F$_3$Prop and AgO$_2$Me$_2$Bu precursors contain less than 75 at% Ag content, while AuC$_x$ grown from the Me$_2$Au(acac) precursor shows high carbon content (up to 95 atomic %) and only has a very weak plasmonic signal.

Recent work has demonstrated an additional path to functional 3D structures using FEBID. For instance, non-magnetic FEBID structures were used as a scaffold for a subsequent magnetic materials coating deposited via physical vapor deposition. A similar approach has been used to fabricate plasmonic nanoantennas by coating a FEBID silica core with Au. One particular application that has actively been pursued for 3D synthesis is chiral/helical structures for optical metamaterials (see recent review). To this end several groups have synthesized 3D helical nanostructures and demonstrated dichroism for circular polarization.

1.2 General Plasmonics:

The field of plasmonics exploits the unique property of metallic nanostructures manipulate light at the nanometer scale. The use of plasmonic properties dates back to when medieval craftsmen would use certain metals in stained glass to have certain colors in the glass. Fast forward to today, the efficiency in which plasmonic nanostructures couple light into intense optical near-fields has led to a variety of applications across multiple fields including, e.g., sensing, imaging, photovoltaics, and photocatalysis.

1.2.1 Background:

By definition, plasmons are the collective oscillations of free electrons in metal. When light interacts with a metal particle, electrons within the particle can resonate at a well-defined frequency defined as the plasmon frequency. As illustrated in Figure 1.4, there are three types of plasmons that can occur: volume/bulk, surface, and localized. The bulk plasmon generally occurs at higher energy and are the longitudinal electron oscillations in the bulk material which are unable to couple to transversal electro-magnetic fields because the plasmon and photon energy dispersion curves do not cross. Bulk plasmons are electrostatic and longitudinal and thusly they couple efficiently to moving charges allowing for excitation via electron beam versus photoexcitation. The behavior of the volume plasmon can be described using the Drude model. Using this model, the complex dielectric function of an ideal metal is:
where $\gamma$ is the damping constant and $\omega_p$ is the frequency of the volume plasmon which is expressed as:  

$$\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0 m}}$$  

where $n$ is the free electron density of the material, $e$ is the charge of the electron, $m$ is the electron mass, and $\varepsilon_0$ is the permittivity of free space.

Alternatively, surface plasmons (SP) are electron oscillations that occur at a metal and dielectric medium interface. A surface plasmon polariton (SPP) propagates along the interface when an electromagnetic field couples to the oscillation of the electron cloud of the metal where the frequency of the incident light is equal to the frequency of the surface plasmon resonance (SPR). Surface plasmon modes can be excited through a variety of configurations with common ones being Grating, Otto, and Kretschmann. The properties of SPRs are impacted by a variety of parameters including material constants (dielectric constant), film thickness, and film characteristics (adsorbed particles, grain boundaries).

A localized surface plasmon is a localized, non-propagating excitation of the free electrons in a metallic nanostructure by an electromagnetic field. This occurs when a surface plasmon is confined to a nanoparticle whose size is comparable to the wavelength of light. The electrostatic approximation can be used for nanoparticles smaller than the wavelength of light allowing LSPRs to be treated as a mass-spring harmonic oscillator where the electron cloud in the nanoparticle oscillates parallel to the direction of the applied electric field. This approximation is accurate for particles $<100$ nm that are illuminated with visible to near IR light. Similar to SPPs, LSPs can only be excited with light with frequency in resonance with the oscillation of the free electrons. The polarizability of a nanoparticle is used to describe the displacement of the electron cloud in response to an electric field:

$$\alpha = 4\pi a^2 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}$$

where $a$ is the radius of the nanoparticle, $\varepsilon$ is the complex dielectric function of the nanoparticle, and $\varepsilon_m$ is the dielectric function of the medium. The polarizability can be used to calculate the scattering, absorption, and extinction cross sections of a nanoparticle.
Figure 1.4 Illustration of the types of plasmons: a) bulk plasmons and propagating surface plasmon polaritons (PSPPs) and b) localized surface plasmons (LSPs). c) Schematic of LSPs modeled by a mass on a spring. Figure borrowed from source\textsuperscript{33}
\[
\sigma_{\text{scat}} = \frac{k^4}{6\pi} |\alpha|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right|^2
\]

\[
\sigma_{\text{abs}} = k \text{Im}[\alpha] = 4\pi k a^3 \text{Im} \left[ \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m} \right]
\]

\[
\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}} = \frac{9}{c} \frac{\omega}{\varepsilon_m} a^3 \left| \frac{\varepsilon_2}{\varepsilon_1 + 2\varepsilon_m \varepsilon_2} \right|^2
\]

where \( k = \frac{2\pi}{\lambda} \), \( a \) is the radius of the nanoparticle, \( \varepsilon \) is the dielectric function of the nanoparticle \((\varepsilon = \varepsilon_1 + i\varepsilon_2)\), and \( \varepsilon_m \) is the dielectric function of the medium. The extinction spectra can be enhance when the Fröhlich condition is met, if \( \text{Im}(\varepsilon) \) is small near the resonance frequency and therefore the denominator of Eq. 1.3 is minimized to:

\[
Re(\varepsilon) = -2\varepsilon_m
\]

Eqs. 1.4-1.6 confirm the plasmonic properties dependence on dielectric function while also showing a dependence on surrounding dielectric medium, particle shape, size, and composition (discussed later). The real \( \text{Re}[\varepsilon] \) and complex \( \text{Im}[\varepsilon] \) parts of the dielectric function of a plasmonic system describe the resonance frequency and losses in a plasmonic system respectively. Losses occur due to radiative damping, electron gas confinement, structural imperfections, heating, and most commonly intraband transitions. Figure 1.5 shows \( \text{Re}[\varepsilon] \) and \( \text{Im}[\varepsilon] \) for a variety of materials. It is observed for Ag and Au, two common plasmonic systems, that Au has higher losses than Ag in the visible range leading to reduced plasmon intensity in that region. Both the real and complex parts of the dielectric function contribute to the overall plasmonic performance of the material and can be used to estimate the quality factor \( Q \). Quality factors are a ratio of the enhanced local-field to the incident field. They are greatly dependent on the shape of the particle leading to various expressions for calculating quality factors existing and can be determined for LSPRs, SPPs, transformation optics, and super lenses. In the case of LSPR quality factors, two common geometries exist: sphere (Eq. 1.8) and spheroid (Eq. 1.9)

\[
Q_{\text{LSPR}}(\omega) = -\frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)}
\]

\[
Q_{\text{LSPR}}(\omega) = \frac{\varepsilon_1(\omega)^2}{\varepsilon_2(\omega)}
\]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real and complex parts of the dielectric function, respectively. Materials with large negative \( \varepsilon_1 \) and small \( \varepsilon_2 \) have greater quality factors and thus stronger near field enhancements. This is illustrated in Figure 1.5 which plots the quality factor for various materials. Additionally this illustrates why Ag and Au are common plasmonic systems and have been studied extensively.
Figure 1.5 a) Real and b) imaginary parts of the permittivity and c) the calculated localized surface plasmon resonances quality factors for Ag, Au, Na, K, and Al. Figure modified from source. 

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1.2.2 Plasmonic Characterization:

There are many ways to characterize the LSPR of plasmonic nanostructures (Figure 1.6). Many optical characterization techniques exist including transmission and reflectance UV-vis spectroscopy, dark field spectroscopy, surface-enhanced Raman spectroscopy (SERS). The most common technique is transmission UV-vis spectroscopy as it is the most straightforward. This technique is used to measure the extinction spectra and thus can be used to extract the absorption and scattering spectra. Light is passed through the sample, often containing multiple nanoparticles, and the wavelength dependence of the sample is recorded. For nontransparent samples, a modified experimental setup is needed for reflective geometry. In this setup, light is directed to the sample and the reflectance from the surface is recorded. Dark-field spectroscopy is used for samples with a smaller sample area or for single nanoparticles/nanostructures. This technique measures the scattered light at a lower angle than the incoming white lights. Like DFS, SERS is used for smaller sample measurements. The sample is excited by a laser and the Raman scattered light is passed through a spectrometer onto a detector.

Alternative to optical techniques, electron energy loss spectroscopy (EELS) is often used to characterize the LSPR of individual nanoparticles/nanostructures. Using a scanning transmission electron microscope (STEM), EELS measures the energy distribution of electrons that have interacted with a sample (Figure 1.7). The electrons pass through a sample and inelastically scatter revealing properties of the sample. EELS can be used for elemental analysis as well as the identification of plasmons. Samples can be probed in various positions to acquire individual spectra for the volume plasmon or LSPR. By placing the electron beam through the structure, the volume plasmon is excited while moving to the aloof position will excite the SPP and LSPRs. EELS can also be used to map the LSPRs of a structure. A spectrum image can be taken which shows the samples response at a given energy. One challenge with characterizing nanostructures via EELS is that when the resonance peaks shift into the infrared region, they are not accessible. Advances in high energy resolution aberration corrected, monochromated EELS, however, has made near infrared modes accessible.

1.2.3 Plasmonic Materials:

As previously discussed, the dielectric function of a material determines the plasmonic response of a material. Traditionally, monoatomic metals are used for plasmonic applications, but increased research interest has been found in alloyed metals as well as doped semiconductors. By choosing specific materials or manipulating them, the plasmonic properties can be tuned.
Figure 1.6 Schematic of the experimental setup for optical characterization techniques: a) transmission and b) reflectance geometries, c) dark-field scattering, and d) surface-enhanced Raman scattering. Figure borrowed from\textsuperscript{43}
Figure 1.7 a) Schematic of EEL spectrum acquisition in a STEM alongside b) a schematic of a monochromater. c) Improvements in monochromation has led to a decreased FWHM of the zero-loss peak for EELS characterization improving the resolution and allowing for infrared modes and phonon modes to be resolved. Figures modified from sources.46
Common monoatomic plasmonic metals include Ag, Au, Al, Cu, Mg, Ni, Pt, and Pd. Figure 1.8 shows common metals with their transmission spectra. Ag and Au are most commonly used, however, due to their low loss in the visible and near IR range leading to their higher transmission. Although Ag has lower loss than Au, Ag films oxidize and therefore degrade fairly quickly while Au films are chemically stable. Cu is also considered a promising plasmonic material, with losses in the visible and NIR range, but like Ag oxidation occurs fairly quickly and will degrade the film. Aluminum has recently gained interest for its plasmonic properties in the UV range. Al will also oxidize, however, it self-passivates with a ~3nm native oxide layer. One of the challenges of noble metal (Ag, Au, Cu, and Al) is their low melting points. Alternative metals such as Mg, Ni, Pt, and Pd are alternative plasmonic materials that can withstand higher temperatures. Generally, these metals have a red-shifted LSPR.

Alloying metals has proven to be a viable option to obtain better plasmonic properties than are found in a single element. This method can be used to tune the dielectric function while improving the stability of the material. Noble metal alloys have been widely studied for improving the plasmonic response. One study explored the dielectric function of Au-Ag, Au-Cu, and Ag-Cu binary alloys and showed that the quality factor for SPPs of the Ag$_{0.5}$Au$_{0.5}$, Au$_{0.1}$Cu$_{0.9}$, and Ag$_{0.9}$Cu$_{0.1}$ had higher Q-factors than the single elements in certain optical regions (Figure 1.9). Additionally, an extensive study of the Au-Al system revealed that the dielectric function can be tuned in the mixed phase region of Al-AuAl$_2$.

Alternative materials such as transition metal nitrides and doped semiconductors are also potential materials for plasmonic properties. The carrier concentration of the transition metal nitrides is tunable by the stoichiometry of the components. Viable metal transition metals include TiN, ZrN, HfN, and NbN with TiN and ZrN being most promising. Although these materials have worse near-field enhancement compared to Au, they have higher thermal stability making them promising for thermoplasmonic applications. In order to achieve low-loss plasmonic properties, semiconductors must have a large bandgap and be heavily doped. Conductive oxides such as indium-tin-oxide (ITO), aluminum-zinc-oxide (AZO), and gallium-zinc-oxide (GZO) are promising low-loss plasmonic materials in the near infrared. For all the conductive oxides, the optical properties are dependent on the growth/deposition processes and conditions. In the case of ITO, modifying the In$_2$O$_3$ concentration as well as annealing the film will affect the conductivity and reduce losses in the NIR range.
Figure 1.8 Top) Melting point of common monoatomic plasmonic metals with corresponding (bottom) transmittance spectra of the bare metal and 4nm Al₂O₃ coating. Figure borrowed from source 47.
Figure 1.9 Measured real and imaginary parts of the dielectric function for metallic thin-film alloy systems: a) Au-Al, b) annealed Au-Al, c) Ag-Au, d) Au-Cu, and e) Cu-Ag. Figure modified from sources\textsuperscript{49, 50}
1.3 Electromagnetic Metamaterials:
Since their theoretical proposal by Veselago\textsuperscript{53} and experimental verification by John Pendry,\textsuperscript{54} metamaterials have been of great interest in the field of photonics due to their ability to realize intriguing new properties. Utilizing nanostructures as artificial atoms allows for the realization of electromagnetic phenomena that is unachievable in natural materials. Metamaterials have advanced from the microwave region to terahertz and optical frequency to realize artificial magnetism, negative refractive index, and superlenses.\textsuperscript{55}

1.3.1 Background:
The properties of bulk materials are determined by the chemical elements present and the bonds in the material. Commonly, modifying material properties comes from altering the chemical constituents with processes like alloying or doping.\textsuperscript{55} Metamaterials offer an additional route to investigating improved material properties by designing structures to exhibit desired properties. The properties of metamaterials are dependent on the geometry (shape, size) of the nanostructures rather than the intrinsic property of the materials.\textsuperscript{56, 57} Nanostructures act as artificial atoms that when arranged deliberately can exhibit properties that are not available in naturally occurring or chemically modified materials. Of particular interest, is a material that exhibits both negative permeability and negative permittivity.\textsuperscript{53, 56}

In describing the electromagnetic property of a material, two fundamental parameters exist: electric permittivity ($\varepsilon$) and magnetic permeability ($\mu$).\textsuperscript{55} The electromagnetic properties of a material can be described using a modified Drude-Lorentz model:\textsuperscript{54, 55, 58, 59}

\begin{align*}
\varepsilon_r(\omega) & = 1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 + i\gamma\omega} \\
\mu_r(\omega) & = 1 - \frac{\omega_p^2}{\omega^2 - \omega_0^2 + i\gamma\omega}
\end{align*}

where $\omega_p$ is the plasma frequency, $\omega_0$ is the resonant frequency, and $\gamma$ is the damping constant. Additionally, the e and m subscripts denote the electric and magnetic responses. Given these two properties, materials can be described using a "material parameter space."\textsuperscript{55} Although no natural materials appear in quadrant III, early theoretical work proposed that materials where there is both negative permittivity and negative permeability could introduce new phenomena.\textsuperscript{53}

Metamaterials utilize arrays of nanostructures that are smaller than the wavelength of incident light to act as artificial atoms. The array of nanostructures interact with the electromagnetic waves as a homogeneous medium analogous to the behavior of atoms in a crystalline lattice respond.\textsuperscript{55} By designing arrays of nanostructures, complete flexibility and tunability is available to investigate new material properties. It is common for metamaterial
nanostructure design to be made with noble metals. This is due to the negative permittivity that they exhibit below the plasma frequency. As discussed in Section 1.2, noble metals also exhibit a strong resonant interaction with light which is necessary for strong metamaterial performance.\textsuperscript{60}

1.3.2 Split Ring Resonator:

One of the fundamental building blocks of metamaterials is the split-ring resonator (SRR). Original work by Hardy and Whitehead as well as Pendry displayed that the magnetic permeability of a metallic structure could be tuned based on the geometric properties.\textsuperscript{54} On resonance, incident light can couple to the SRR leading to negative permeability. SRRs have can have a variety of geometric factors which affect the overall performance of the structure. The original SRR design consisted of two concentric split rings with opening on opposite directions as illustrated alongside other common arrangements in Figure 1.10. SRRs have been extensively studied due to their relative ease of fabrication through standard lithography techniques at low frequency.\textsuperscript{61}

The SRR uses basic magnetostatics which states that a magnetic dipole moment is induced perpendicular to a circulating ring current of a coil. When combined with a capacitor as illustrated in Figure 1.11, an increased current, and therefore increased magnetic dipole moment, are realized. These structures are considered LC circuits because they consist of a plate capacitor with capacitance $C$ and a magnetic coil with inductance $L$. The capacitance and inductance of a SRR can be calculated:

\begin{equation}
C = \varepsilon_0 \varepsilon_C \frac{wt}{d} \tag{1.12}
\end{equation}

\begin{equation}
L = \mu_0 \frac{l^2}{t} \tag{1.13}
\end{equation}

where $w$ is the width of the metal, $d$ is the gap of the capacitor (SRR), $t$ is the metal thickness, $l$ is the width of the coil (SRR), and $\varepsilon_C$ is the permittivity of the capacitor. These can ultimately be used to estimate the resonant frequency and wavelength:

\begin{equation}
\omega_{LC} = \sqrt{\frac{1}{LC}} \propto \frac{1}{\text{size}} \tag{1.14}
\end{equation}

\begin{equation}
\lambda_{LC} = \frac{2\pi c_0}{\omega_{LC}} = 2\pi l \sqrt{\varepsilon_C} \sqrt{\frac{W}{d}} \tag{1.15}
\end{equation}

where $L$ and $C$ are the geometric inductance and capacitance of the structure respectively, $\omega_{LC}$ is the resonant frequency and $\lambda_{LC}$ is the resonance wavelength. When the LC resonance frequency is much smaller than the metal plasma frequency, the resonance wavelength is proportional to the size. This size dependence leads to tunability with fabrication and lead to the observation of a negative permeability in optical frequencies.
Figure 1.10 Illustration of various SRR designs: a) original circular structure, b) squared structure, c) single ring structure, and d) multiple ringed structure. Figure borrowed from source. 
Figure 1.11 a) Illustration of a conventional LC circuit which is analogous to b) the schematic of an SRR with dimension labels. c) SEM image of a common SRR design fabricated using electron beam lithography. Figure borrowed from source\textsuperscript{62}
As seen in Eq. 1.12 and 1.13, the resonance frequency and wavelength of an SRR is highly
tunable through geometric design as well as permittivity of the structure. Experimental and
simulated EEL spectra and mapping of various Au SRRs has been studied and revealed the
dependence of the m=1-4 modes on the SRR size. In this work a systematic red-shift in each mode
occurs as the SRR increased in size. EEL spectra and spectrum images were also used to investigate
the behavior of eight eigenmodes in Ag SRRs. Studies have also shown that the size of the gap in a
SRR will greatly influence the strength of the field. By decreasing the gap size, orders of magnitude
enhancement of the electric field can be realized.

1.3.3 Coupled Metamaterials:
The coupling interactions between the “atoms” or nanostructures in a metamaterial array
play a vital role in the overall response of the arrangement. Through a greater understanding of the
coupling fundamentals, greater design and optimization can be done to tune desired optical
responses from the structures.

1.3.3.1 Coupled Nanowires:
Pairs of “cut-wires” can act as a magnetic “atom” in a simplified nanostructure design. These
wires effectively behave like a SRR with the bottom arm removed. This results in an increased
capacitance with an increase in the magnetic resonance frequency. It is well known that a single
nanowire an electric dipole is excited by incident light. When two nanowires are separate by a
finite distance, plasmon hybridization occurs leading to two electric dipoles: one that is
symmetrically aligned and one asymmetrically aligned. The symmetrically aligned mode
corresponds to the electric dipole while the antisymmetric mode is considered the “magnetic
mode”. At the simplest level, the coupling of two wires can induce a magnetic dipole from the
antisymmetric mode as illustrated in Figure 1.12. Illustration of the transverse coupling between
two coupled metallic nanowires. Figure borrowed from source.

1.3.3.2 Coupled SRRs:
Extensive research has been done optically on SRRs that are positioned in various arrangements in
the same plane. It has been observed that by rotating one SRR with respect to the other with
change the coupling mechanisms. For example, when SRRs are positioned in a side-by-side
arrangement with 0° rotation and they are excited, the electric dipoles will longitudinally couple
while the magnetic dipoles will couple transversely (Figure 1.13). By simply rotating the SRR to
90°, the electric dipoles are perpendicular to each other and the coupling between the magnetic
dipoles lead to spectral splitting (Figure 1.13). In addition to rotational dependence, the coupling
strength is highly dependent on the distance between the centers of two SRRs. As the coupling
Figure 1.12 Illustration of the transverse coupling between two coupled metallic nanowires. Figure borrowed from source\textsuperscript{66}
Figure 1.13 Laterally coupled SRRs with rotation of a) 0° and b) 90°. The increased resonance splitting is seen when the gap is eliminated in a 90° rotated arrangement. Figure modified from source66
distance decreases, the coupling strength and the resonance splitting is increased. This coupling strength can be increased further by vertically stacking the SRRs.\textsuperscript{55, 66}

Utilizing EELS, the hybridization behavior of coupled SRR systems have been investigated. Coupled Au SRRs were arranged to be 0\textdegree, 90\textdegree, and 180\textdegree and characterized via EEL spectra and spectrum images to reveal the hybridization schemes of the fundamental modes. Experimental data alongside numerical calculations were able to resolve the energy splitting of the modes and derive the electric and magnetic moments.\textsuperscript{83} One study has also shown that as SRR arrays increase in size (ie 2-4 SRRs to over 100 SRRs) the distinct bright and dark modes form a quasi-continuum of modes.\textsuperscript{84}

1.3.3.3 Coupled Nanoparticles:

While SRRs have proven to be an effective structure for metamaterial design, lithography and material limits make it challenging to push their response to higher frequency. To solve this problem, cut split ring resonators and series of nanoparticles have demonstrated the ability to achieve high frequency. Metal nanoparticles arranged in rings have been shown to have a magnetic dipole response in the near-infrared and visible regime.\textsuperscript{67, 68} As illustrated in Figure 1.14, when arranged in rings the particles act as a series of \textit{LC} circuits.\textsuperscript{69} Unlike the SRR, however, the series of plasmonic nanoparticles are only weakly related to the ring size. Instead, these meta-molecule arrays depend on the response of the individual nanoparticles. This has led to studies showing that as nanoparticles are simply moved closer to one another (decreasing the gap size) the magnetic dipole resonance shifts.\textsuperscript{70, 71}
Figure 1.14 (a) Schematic of a ring of plasmonic nanoparticles with red arrows illustrating the circulating electric dipole moments inducing a magnetic moment. (b) An illustration showing the progression from a single SRR to a series of plasmonic nanoparticles. (c) A corresponding schematic of the circuit description of a single SRR to that of the ring of plasmonic oligomers. Figure borrowed from reference$^{23}$
Chapter 2

Focused Electron Beam Induced Deposition Synthesis of 3D Photonic and Magnetic Nanoresonators
A version of this chapter was originally published by Grace Pakeltis, Zhongwei Hu, Austin G. Nixon, C. Praise Anyanwu, Claire A. West, Juan Carlos Idrobo, Harald Plank, David J. Masiello, Jason D. Fowlkes, and Philip D. Rack: G. Pakeltis, Z. Hu, A. Nixon, E. Mutunga, C. Anyanwu, C. West, J C Idrobo, H. Plank, D. Masiello, J. D. Fowlkes, P. D. Rack, Focused Electron Beam Induced Deposition Synthesis of 3D Photonic and Magnetic Nanostructures. ACS Appl. Nano Mater. 2019, 8075-8082. Grace Pakeltis conducted the sample fabrication, TEM characterization, analysis, and wrote the manuscript. Zhonwei Hu, Austin G. Nixon, C. Praise Anyanwu, and Claire A. West performed the eDDA/DDA simulations. The manuscript was written through contributions of all authors. The manuscript has been modified to include supplemental material here.

2.1 Background:

The efficiency in which plasmonic nanostructures couple light into intense optical near-fields has led to a variety of applications across multiple fields including, e.g., sensing, imaging, photovoltaics and photocatalysis. New breakthroughs and better understanding of the underlying theory have led to an increased demand for advanced design, synthesis, and device integration strategies for plasmonic nanomaterials. Three-dimensional (3d) plasmonic nanostructures have the potential to significantly advance applications and enable new classes of optical metamaterials. For practical application of 3d plasmonic structures, there is a need for flexible design in the shape and size of the nanostructure, accurate positioning of single and nanostructure arrays, and detailed characterization of the resultant optical and magnetic properties. By utilizing direct-write or 3d printing approaches, new architectures can be rapidly explored and thus the discovery process can be significantly accelerated. To this end, advances in focused electron beam induced deposition (FEBID) have recently extended this traditionally two-dimensional direct-write synthesis technique to high-fidelity 3d nanoprinting with structures approaching 10 nm resolution; for a demonstration of some of the complex structures that can be grown and for a recent review see and references therein.

FEBID uses a focused electron beam to dissociate a physisorbed precursor gas molecule into volatile fragments and a condensed solid. Appropriate electron scanning regimes allow for 3d growth and high-fidelity electron beam control, enabling the generation of complex 3d architectures that standard lithography cannot achieve. Conveniently, computer aided design (CAD) tools have been created, which convert a 3d scaffold into an electron beam scanning stream file, that can be executed to generate the desired object. One drawback in 2d and 3d printing via FEBID is the deposited material often contains high residual carbon content (up to 90%) from the organometallic precursor, and thus the as-deposited functionality can be limited. High metal
content deposits (~80 atomic %) with strong magnetization have been achieved, which has led to the fabrication of complex 3d magnetic structures using the HCo$_3$Fe(CO)$_{12}$ precursor to explore new magnetic phenomena. Achieving deposits with high metal content, however, has proven to be more difficult in precursors with plasmonic signatures. Silver 3d structures grown from the AgO$_2$F$_2$Prop and AgO$_2$Me$_2$Bu precursors contain less than 75 at% Ag content, while Au$_x$ grown from the Me$_2$Au(acac) precursor shows high carbon content (up to 95 atomic %) and only has a very weak plasmonic signal. Though purified 3d structures have demonstrated good plasmonic responses, care must be taken during the purification process as asymmetric purification can lead to structural deformations in the intended geometry.

Recent work has demonstrated an additional path to 3d structures; for instance, non-magnetic FEBID structures were used as a scaffold for a subsequent magnetic materials coating deposited via physical vapor deposition. A similar approach has been used to fabricate plasmonic nanoantennas by coating a FEBID silica core with Au. One particular application that has actively been pursued for 3d synthesis is chiral/helical structures for optical metamaterials (see recent review). To this end several groups have synthesized 3d helical nanostructures and demonstrated dichroism for circular polarization.

This contribution builds on some of our previous work where we have correlated the beam speed (for instance dwell time at constant pitch here) to the resultant segment angle and determined the effect that beam heating has on the angle. We also leverage the 3d CAD program that was previously developed and distributed for general 3d FEBID. While we have previously explored purified gold structures grown via FEBID of Me$_2$Au(acac) and characterized them via EELS, here we use the hybrid process overview below to synthesize nanoresonator structures for photonic and magnetic meta-atoms. As mentioned above, previous groups have Au-coated FEBID silica structures, but recent work suggests that more complex geometries exhibit charging and thermal effects which affects the fidelity of the structures; thus the ALD step used here could be a more ubiquitous and robust approach for functional 3d architectures.

Here we demonstrate a hybrid synthesis approach and explore the photonic and magnetic properties of various split ring and ring nanoresonator structures. Figure 2.1 a) illustrates a simulated tilted diamond structure that is created using a stream file generated by the 3BID CAD program; see Figure 2.10 a) for a full plasmonic structure grown from the same stream file. Note that this structure is grown using intermittent mode, where multiple wires are exposed simultaneously. The standard (CH$_3$)$_3$Pt(CPCH$_3$) precursor is used for 3d FEBID growth of the 3d scaffolds. Critical to the CAD program is the so-called growth calibration curve, which is simply a
plot of the experimental segment angle versus the electron beam dwell time for a fixed electron beam energy, current, and pixel pitch (Figure 2.1 b). Figure 2.1 c) illustrates an example segment angle grown on a holey SiNx membrane, which is used so we could characterize the 3d plasmonic structures via high resolution electron-energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM). SiO2 is subsequently conformally deposited via atomic layer deposition (ALD) which, as illustrated recently,9 enhances the mechanical robustness of the scaffolds and also insulates the PtCx (x≈5) deposits (Figure 2.1 d). Finally, the scaffolds were functionalized via sputter deposition of a plasmonically active gold layer (Figure 2.1 e). The resultant cross-section is also illustrated in Figure 2.1 e). Various rod-like structures, split ring nano-resonators (SRNR), ring resonators (RR), prolated ring resonators, and nano-diamonds were synthesized and their plasmonic properties were analyzed via EELS. Complementary EELS simulations82,83 were performed to rationalize the experimental spectral details and determine the resultant electric and magnetic fields that are generated. While the focus here is the characterization of individual meta-atoms, the ability to control the tilt angle of these nanoresonators out of the substrate plane should enable new coupling regimes that are not achievable in two dimensions. Furthermore, the tilt axis of the nanoresonators dictates the coupling of external magnetic and electric fields, thus angular anisotropy or isotropic nanoresonator metamaterials can be realized.

2.2 Methods:
2.2.1 FEBID Parameters:
3d FEBID structures were grown in a FEI NOVA 600 dual-beam microscope equipped with multiple gas injection systems (GIS). The MeCpPt(IV)Me3 precursor gas was injected using an FEI GIS where the precursor temperature was set to 45°C and allowed to equilibrate for ~30 min. The gas needle was positioned ~100 μm from the surface of the sample and ~37.5 μm from the area of the structure growth. All structures were grown perpendicular to the gas flow vector84 to further optimize the growth conditions. Prior to opening the gas valve, the chamber was pumped to a base pressure of ~2x10^{-6} Torr and prior to FEBID growth, the gas valve was opened and the chamber pressure allowed to equilibrate for 60 seconds to establish chamber growth pressure of ~8x10^{-6} Torr.

The PtCx scaffolds were grown on 200 nm thick SiNx holey (1000 nm hole diameter) TEM membranes (Ted Pella; Prod. No.: 21581-10). To mitigate the charging, a base layer of ~20 nm Au was sputter deposited on the SiNx surface, which resulted in stable and consistent growth. Prior to scaffold growth, calibration structures were also grown to determine the vertical growth rate (VGR).
Figure 2.1 a) 3D simulation of FEBID growth for a tilted diamond scaffold (total growth time \(~10.4\) s). b) Calibration curve of PtCx segment angle as a function of dwell time (inset are SEM images of some of the various PtCx segments). c)-e) Schematic and SEM images illustrating the hybrid synthesis process for the functional 3d plasmonic structures: c) the FEBID 3d scaffold is initially deposited and subsequently d) conformally coated with SiO2. Finally, e) a top layer of Au is deposited on the scaffold making an isolated plasmonic rod. A schematic of the cross-section of a fully fabricated plasmonic rod is also demonstrated in e).
and dwell time necessary to achieve various segment angles. A beam condition of 5 keV and 25 pA was used to deposit the rod, prolated ring resonator, and diamond architectures while 30 keV and 21 pA was used to deposit the split ring resonators. The inset of Figure 2.1 d) shows an example calibration curve which shows the measured segment angle as a function of dwell time; the fit calibration curve was used to grow the scaffolds grown at 5 keV and 25 pA.

2.2.2 SiO₂ Atomic Layer Deposition and Au Sputter Deposition:

Figure 2.1 shows a schematic and scanning electron microscope (SEM) images of a) the FEBID scaffolds which were subsequently coated with b) SiO₂ and c) Au. The 20 nm conformal SiO₂ layer was deposited via ALD to enhance the structural integrity of the scaffolds; however, it also isolates the Au layer from the PtCx scaffold to minimize possible plasmon damping. It has been shown that FEBID structures begin to lose their structural integrity at temperatures above ~120°C, therefore the SiO₂ was deposited at 110°C to minimize structural changes. After ALD, the resulting structures densify slightly and thus decrease in length as well as experience a slight change in the segment angle (see Table 2.1 for detailed measurements); thus compensations are made to accommodate the ALD process while designing the CAD.

Due to its well-known plasmonic properties as well as its stability in atmosphere, ~20 nm Au was subsequently deposited on the scaffolds via dc magnetron sputtering (7 W, 3 mTorr). Figure 2.1 e)-f) illustrate the sample was placed inside a metal ring on the outer track of the magnet assembly during deposition to reduce the off-axis sputtering on the scaffolds.

2.2.3 Architectures:

A variety of individual and dimer structures were synthesized and characterized via high-resolution low-loss EELS to investigate the plasmonic properties based on size, shape, and angle. For all the structures, an initial pillar was grown at one edge of a membrane hole to allow the shape of interest to be suspended over the hole to enhance the sensitivity of the EELS measurements.

2.2.3.1 Rods:

As illustrated in Figure 2.2 a)-b), rods were grown off an initial 400 nm pillar at angles of 15°, 30°, 45°, 60°, and 70° relative to the pillar normal (see 1a)). A set of single rods were grown with total lengths and projected lengths ranging from 100-500 nm with 100 nm increments at 30°, 45°, and 60° (+/-8°) (Figure 2.2 c-d). In addition to single rods, rod dimers were also grown at varying, prescribed gap lengths of 60 and 100 nm (Figure 2.2 e-f). The gap lengths were designed to account for the slight contraction of the FEBID structures during growth and additional length realized from the SiO₂ and Au film.
Table 2.1 Measurements were taken after each stage of fabrication to calculate the change due to each fabrication step.

<table>
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<tr>
<th>Angle (°)</th>
<th>Measured Angle FEBID (nm)</th>
<th>Measured Length FEBID (nm)</th>
<th>Measured Angle ALD (nm)</th>
<th>Measured Length ALD (nm)</th>
<th>Change in Angle after ALD (°)</th>
<th>Change in Length after ALD (nm)</th>
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<td>15.05°</td>
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</tr>
<tr>
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</tr>
<tr>
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<tr>
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<td>81.97</td>
<td>470.93</td>
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<td>-7.78</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>Measured Angle Au (°)</th>
<th>Measured Length Au (nm)</th>
<th>Total Change in Angle (°)</th>
<th>Total Change in Length (nm)</th>
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</thead>
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<tr>
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<td>3.60°</td>
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<td>16.26</td>
</tr>
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</table>
Figure 2.2 a-b) A top (a) and 45° view of a series of fully fabricated 500nm single rods were grown at 15°, 30°, 45°, 60°, and 70°. c-d) A top and 45° view of a series of fully fabricated single rods increasing in length from 100-500nm at 100nm increments both in actual rod length as well as in projected length. These series were grown at 30°, 45°, and 60°. e-f) A top and 45° view of a series of fully fabricated rod dimers with prescribed gaps of 60 and 100nm at 30°, 45°, and 60°. g-h) A top (a) and 45° view of a series of fully fabricated ring resonator dimers with prescribed gaps of 60 and 100nm at 30°, 45°, and 60°.
2.2.3.2 Ring Resonators:
To investigate the effect of asymmetries in the plasmonic signature of ring resonators, prolated torii and diamonds were also grown off the apex of 400 nm pillars at angles of 30°, 45°, and 60° (Figure 2.2 g-h). To grow the lassos, an interlaced scanning strategy was used to grow the patterns. The lassos consisted of 20 individual segments (x2 interlaces) to make the 500 nm long shape. Unlike the rods, the lassos grew at angles about 15° larger than prescribed. Lasso dimers were also grown with gap lengths similar to the rods. An interlacing strategy was also used for the squares however only 2 segments (x2 interlaces) were necessary.

2.2.3.3 Split Ring Resonators:
To demonstrate the functionality of a 3d nanostructure, various split ring resonators (SRNR) were grown. The SRNRs were also grown off the apex of a 400 nm pillar at an angle of 15° and 45° (+/-8°). A variety of SRNR geometries were investigated including: a series of azimuthal angles ranging from 135°-360°, at increments of 45°; two tilt angles (15° and 45°); and two diameters (300 and 500 nm). To grow the SRNRs, an interlaced scanning strategy was used to grow the patterns where each half arc was grown in parallel by rastering the electron beam back and forth to each growth front. The SRNRs consisted of 3-12 individual segments (x2 interlaces), depending on the azimuthal angle, to make the 300 nm and 500 nm diameter shapes. SRNR geometries for each of the angles and diameters.

2.2.3.4 EELS:
Low-loss EEL spectra were taken using a Nion aberration-corrected high energy resolution monochromated EELS-STEM (HERMES) operated at an accelerating voltage of 60 kV. The convergence and collection semiangles used for the spectrum acquisition were 20 and 15 mrad, respectively. The energy resolution (full width at half-maximum of the zero-loss peak) was approximately 35 meV for the rod spectra and 11 meV for the SRNR and closed prolated ring resonator and diamond geometries. The EEL spectra presented in Figure 2.4-Figure 2.11 were energy aligned and normalized to the zero-loss peak.

2.2.3.5 Simulations:
Optical and electron energy loss simulations were performed using DDA and e-DDA, respectively. DDA and e-DDA have been successfully used for many different nanostructures and is often more flexible than other numerical methods for irregular shapes. e-DDA and DDA are therefore well suited for the ring, diamond and prolated ring shapes studied in this work. Figure 2.3 shows the 3-dimensional displays of split ring nano-resonators and ring resonators used in the e-DDA and DDA simulations. Shows the 3-dimensional displays of all the nanostructures used in simulation. We note that the non-metal layers, substrates, and the pillar were omitted to simplify
Figure 2.3 Shows the 3-dimensional displays of split ring nano-resonators and ring resonators used in the e-DDA and DDA simulations.
simulations. For all optical simulations we have chosen the shape orientation and the polarization direction such that the magnetic field is normal to the ring of the 3d structure. For all EELS simulations, the shapes have been orientated accordingly based on the experimental counterparts and the primary electron beam energy was set to be 60 keV and the impact parameter was chosen as 9 nm. Tabulated dielectric constants for gold have also been used in order to obtain reasonable signals at the low energy range (< 600 meV). Unless specified, all electric field maps were generated in a plane parallel to the nanostructures with a distance of 30 nm.

2.3 Rod-like Structures

An initial series of vertical pillar-plus-segments (segment angle of 54° +/- 2°), similar to what is shown in Figure 2.1 c), were grown and characterized via EELS. The inset in Figure 2.4 shows a schematic of the structure relative to the electron beam. Experimental low loss EEL spectra reveal a clear shift in the plasmon peaks, from ~460 to ~280 meV, as the total pillar-plus-segment length increases from 580 to 1100 nm, respectively. These peaks are associated with the dipole mode \((m=1)\), however, they locate at lower energy than what are expected for rods with the segment length only; thus, the gold is likely also deposited onto the pillar, making the total pillar-plus-segment the characteristic rod dimension (see legend). The dipole of the 1100 nm rod is shifted into the zero-loss peak (ZLP) of the transmitted electron beam, which for our system the residual of the tail is observed at < 200 meV. The peak at ~420 meV for the 1100 nm rod is the \(m=2\) mode.

2.4 Split Ring Nanoresonators:

The hybrid growth approach to the 3d structures offers a route to investigate various plasmonic nanoresonator geometries. A common element in optical metamaterial architectures is the RR and split ring resonator (SRR). On resonance, individual RR or SRR couple to magnetic fields and generate an electric current which can enhance or oppose the applied field. Arrays of SRRs have been used in various metamaterial applications such as the experimental verification of a negative permeability and negative index of refraction. To extend the application of RR and SRRs towards higher frequency, planar arrays of plasmonic RR and SRR geometries have been explored. Here we demonstrate the growth and EELS characterization of various 3d RR and 3d SRNR geometries. Importantly, arrays of templated 3d nanostructures provide a route to investigate higher frequency SRNR metamaterials with increased design flexibility.

While much work has been devoted to optically modeling and characterizing plasmonic SRNR arrays, only a few studies have investigated SRNRs with EELS in a TEM. EELS characterization has the unique ability to resolve all the plasmonic modes of the material target.
Figure 2.4 Aloof EEL spectra of single rods with a tilt angle of 54°. A clear, red-shift in the first order modes is observed as the rod length increases; note the red peak at ~ 420 meV is the $m=2$ mode as the dipole peak is convoluted in the zero-loss peak < 200 meV.
with nanometer resolution. For instance, studies on Ag SRNRs identified the electric and magnetic modes by mapping the resultant peaks and identifying the lowest order mode. Additionally, EELS mapping of various Au SRNR modes has been studied and the energy dependence of the \( m = 1-4 \) modes were characterized as a function of the SRNR length; a systematic red-shift in each mode occurs as the SRNR size increases. Work has also shown that appropriately tilting the SRNR with the electron beam can reveal the gap mode of the SRNR. EEL spectra and mapping have also been used to investigate the plasmon hybridization of coupled split ring resonators with various arrangements. One challenge with characterizing SRNRs via EELS is that for practical effective lengths of > 500 nm, the resonance peak shifts into the infrared region. Advances in high energy resolution monochromated EELS, however, has made near infrared modes accessible.

Figure 2.5 a)-d) show scanning electron microscope (SEM) images of the ~500 nm diameter SRNRs grown at a tilt angle of ~15° (+/- 5°) and select azimuthal angles ranging from 135° to 360°. The associated experimental EEL spectra are shown in Figure 2.5 m) with an inset schematic illustrating the measurement geometry. Similar to the rods in Figure 2.5 m), these spectra show a clear shift in the plasmon peak energy from ~600 to 300 meV as the SRNR azimuthal angle increases from 135° to 315°. Corresponding simulated electric field maps of the 135° to 315° SRNRs and RR are shown in Figure 2.5 e)-h) to illustrate the profiles of the first order \( (m=1) \) or dipole modes. The red-shift in the dipole mode results from an increase in the effective arc length of the SRNRs. Simulated magnetic field maps of the 135° to 315° SRNRs and RR, shown in Figure 2.5 i)-l), illustrate the progression of the induced magnetic field for the SRNRs at the electric dipole energy. As expected, a clear change in the resonance is observed for the closed (360°) RR electric and magnetic field at the electric dipole energy. The simulated EEL spectra, shown in Figure 2.5 n), are in good agreement with the experimental spectra and also clearly show the spectral red-shift with increasing azimuthal angle. Experimental and simulated EEL spectra for the complete azimuthal angle study are shown in Figure 2.6 illustrating the same red-shift as explained prior. The higher energy peak observed in each experimental and simulated spectrum corresponds to the \( m=2 \) or quadrupole SRNR mode (see Figure 2.7 for quadrupole electric field maps). Table 2.2 lists the specific geometric properties of the 3d SRNRs. Figure 2.5 p) displays the dependence of the electric and magnetic near-fields produced by plane wave excitation field on the SRNR azimuthal angle (maps shown in Figure 2.8). The plane wave is oriented such that the magnetic polarization is normal to the plane of the SRNR (inset). Based on these simulations, it is evident that increasing the azimuthal angle increases both the near-electric and near-magnetic field magnitudes. Also
Figure 2.5. SEM images of SRNRs with a diameter of 500 nm and azimuthal angles of a) 135°, b) 225°, c) 315°, and d) 360° (closed ring resonator). Simulated electric field maps excited at the low energy EEL peak energy for SRNR with a diameter of 500 nm and azimuthal angles of e) 135°, f) 225°, g) 315°, and h) 360° illustrate these are $m=1$ mode. Associated maps of the magnetic field for SRNRs with a diameter of 500 nm and azimuthal angles of i) 135°, j) 225°, k) 315°, and l) 360°. m) Experimental and n) simulated aloof EEL spectra of SRNRs at 15° tilt and various azimuthal angles. The spectra show a red-shift with the increase in the SRNR perimeter. o) Plot of the experimental and simulated peak positions for the $m=1$ and $m=2$ modes as a function of varying azimuthal angles of the SRNRs. p) Plot of the maximum relative electric and magnetic field magnitudes as a function of the azimuthal angle (See Figure 2.9 for full plane wave simulation study). The scale bar is 500 nm.
Figure 2.6 a) Experimental and b) simulated aloof EELS spectra of 500 nm diameter SRNRs at 15° tilt at a series of azimuthal angles ranging from 135°-360°. The full study confirms a systematic red-shift in the m=1 mode as the azimuthal angle increases.
Figure 2.7 Simulated near field maps of the electric field for the quadrupole for SRNRs with a diameter of 500 nm and azimuthal angles of a) 135°, b) 225°, c) 315°, and d) 360° illustrate the m=2 mode.
Table 2.2 The table above shows the geometric components for the split-ring resonators investigated using EELS.

<table>
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<th>Shape</th>
<th>Azimuthal Angle</th>
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</tr>
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</tr>
<tr>
<td>45° Diamond</td>
<td>360°</td>
<td>1750</td>
</tr>
</tbody>
</table>
Figure 2.8 Plane wave simulations of 500 nm diameter SRNRs at varying azimuthal angles showing the relative intensity of the a) electric and b) magnetic fields.
included in Figure 2.5 m)-n) are the experimental and simulated 360° RR spectra, respectively. In this ring resonator geometry, instead of the Fabry-Pérot type resonance, the bonding modes\textsuperscript{93-95} of the RR emerge at \( \sim 600 \) and 1020 meV, respectively. The simulated electric field maps at these peak energies reveal that these resonances are associated with the \( m=1 \) (dipole) and \( m=2 \) (quadrupole) bonding modes, respectively (see Figure 2.5 h for dipole and Figure 2.7 d for quadrupole electric field maps). The expected blue-shift in the dipole and quadrupole modes from the SRNR to the closed RR is evident in Figure 2.5 m)-o).

To illustrate the tunability of the 3d SRNRs, Figure 2.9 a) shows low-loss experimental EEL spectra of SRNRs with different tilt angles and ring diameters all with a common azimuthal angle of 270°. As shown in Figure 2.9 a), the 15° and 45° tilt and 500 nm diameter both have similar dipole and quadrupole energies, as expected because the arc lengths are equivalent. For the smaller diameter SRNR, the first and second order modes shift to higher energy due to the decrease in the SRNR arc length. As illustrated in Figure 2.9 b), the blue-shift observed in the experimental EEL spectra agrees well with the simulated values. To further investigate the plasmonic signature of the SRNR, spectra are taken at the tip and in the gap of a SRNR grown with a tilt angle of 15° and an azimuthal angle of 45° as shown in Figure 2.9 c). (See Figure 2.6 for full azimuthal angle study for 45° tilt.) As the afoil position shifts from the tip to the center of the gap, the \( m=1 \) and \( m=3 \) modes disappear, which is consistent with the fact that careful beam positioning or tilt is required to indirectly probe electromagnetic hot spots in EELS.\textsuperscript{63, 82, 96}

Finally, to interrogate asymmetry in closed RR structures, a closed diamond and closed prolated RR structure were also grown. Table 1 lists the specific properties of each structure. Figure 2.10 a)-b) show the experimental and simulated EEL spectra, respectively, acquired at two different electron-beam positions (labeled 1 and 2) that are parallel to the short and major (long) axes, respectively. As confirmed by simulations, the resonances in this energy regime are associated with dipole and quadrupole modes of the bonding state; the antibonding state is anticipated to be at higher energies not explored here.\textsuperscript{93-95} Clearly, the experimental dipole mode red-shifts from \( \sim 530 \) meV to \( \sim 390 \) meV when probing point 2 relative to point 1, which is anticipated as the axis is elongated \( \sim 1.5x \).\textsuperscript{97} As is also expected, both simulation and experiment confirm that the quadrupole is degenerate at both positions as shown in Figure 2.10 e)-f). The effects of the asymmetric axes are illustrated in the simulated EELS maps shown in Figure 2.10 c)-d). When probed at position 1, the dipole oscillates parallel with the minor (short) axis (higher energy) while at position 2 the dipole oscillates along the major axis (lower energy). The spectra of the prolated RRs were further investigated in Figure 2.11, where the EEL spectra are shown for two
Figure 2.9. a) Experimental aloof EEL spectra for 500 nm diameter SRNRs with a 15° versus 45° tilt angle and a 300 nm diameter SRNR with a 15° tilt; all three SRNRs have a 270° azimuthal angle. The spectra are similar with variable tilt angle and a blue shift is observed for the smaller diameter. b) Simulated aloof EEL spectra of 15° tilt SRNRs with a 270° azimuthal angle and two diameters of 500 nm and 300 nm; good agreement with the experimentally observed blue-shift in the first mode is captured in the simulation. c) Experimental EEL spectra taken at the tip and in the gap of a 345° azimuthal angle SRNR. The \( m=1 \) and \( m=3 \) modes are extinguished when spectra are taken in the gap of the structure. Scale bar is 500 nm.
Figure 2.10. a) Experimental and b) simulated aloof EEL spectra of a diamond scaffold acquired at two different electron-beam positions. The dipole \((m=1)\) peak is slightly red-shifted when excited at an apex along the major (long) axis versus the minor (short) axes, whereas the quadrupole \((m=2)\) peaks have the same energy. Maps of the electric field for the dipole at positions c) 1 and d) 2 illustrate the major and minor axis excitations of the structure. Maps of the electric field for the quadrupole at positions excited at positions e) 1 and f) 2. Scale bar is 500 nm.
Figure 2.11. a) Experimental and b) simulated aloof EEL spectra of a prolated RR scaffold acquired at two different electron-beam positions. The spectra show a red-shift in the dipole peak energy when excited along the major axis versus the minor axis, whereas the quadrupole peaks have the same energy. Maps of the electric field for the dipole at positions c) 1 and d) 2 illustrate the major and minor axis excitations of the structure. Maps of the electric field for the quadrupole at positions excited at positions e) 1 and f) 2. Scale bar is 500 nm.
positions of the prolated ring structure. As was observed in the diamond scaffold, there is a slight red-shift from \( \sim 480 \text{ meV} \) to \( \sim 440 \text{ meV} \) in the dipole mode when it oscillates parallel with the major and minor axes, respectively; again, the quadrupole peak has the same energy and emerges at \( \sim 1000 \text{ meV} \) for both positions. In both the diamond and prolated ring experimental EEL spectra, an additional peak appears on the shoulder of the dipole as well as between the dipole and quadrupole. These peaks may be attributed to a rod dipole mode that propagates from the vertex down the pillar as these additional peaks appear in positions similar to what is expected to the equivalent rod lengths.

2.5 Conclusion:

In this study, we have developed a direct-write fabrication method through a hybrid synthesis technique utilizing FEBID scaffolds. Nanoscale 3d plasmonic architectures including rod-like structures, SRNRs, and closed ring-like structures were synthesized and their full plasmonic spectra were characterized via high-resolution EELS. We dictated the frequency and field orientations of photonic and magnetic meta-atoms through the manipulation of the nanostructure geometry. EELS of various rod-like structures confirm the expected red-shift of the plasmon modes as a function of increasing the length. A series of SRNRs with increased azimuthal angle were fabricated and characterized revealing a red-shift in the plasmon modes. Simulations for the SRNRs confirm this progression, and furthermore, plane wave optical simulations show that the near-electric and magnetic fields can be maximized by increasing the azimuthal angle. The hybrid nanoscale 3d synthesis process demonstrated here enables complex 3d architectures, which provides new degrees of freedom over the tunability and coupling of plasmon modes yielding great promise for advanced photonic and magnetic metamaterials.
Chapter 3

High Spatial and Energy Resolution Electron Energy Loss Spectroscopy of the Magnetic and Electric Excitations in Plasmonic Nanorod Oligomers
A version of this chapter was originally published by Grace Pakeltis, Enzo Rotunno, Siamak Khorassani, David A. Garfinkel, Robyn Collette, Claire A. West, Scott T. Retterer, Juan Carlos Idrobo, David J. Masiello, And Philip D. Rack: Grace Pakeltis, Enzo Rotunno, Siamak Khorassani, David A. Garfinkel, Robyn Collette, Claire A. West, Scott T. Retterer, Juan Carlos Idrobo, David J. Masiello, And Philip D. Rack, High spatial and energy resolution electron energy loss spectroscopy of the magnetic and electric excitations in plasmonic nanorod oligomers. Optics Express, 2021. 29(3): p. 4661-4671.

Grace Pakeltis conducted the sample fabrication (with the assistance of David Garfinkel), TEM characterization, analysis, and wrote the manuscript. Siamak Khorassani and Claire A. West performed the eDDA/DDA simulations. Enzo Rotunno performed the boundary element method simulations. The manuscript was written through contributions of all authors. The manuscript has been modified to include supplemental material here.

3.1 Background:

The search for metamaterials that exhibit negative permittivity and permeability in the visible spectrum has led to the exploration of architectures that support coupled plasmonic elements. While standard split ring resonators (SRR) have been extensively studied and shown to be extendable to near infrared frequencies, pushing to higher frequencies is challenging. Cut SRR geometries or coupled nanospheres have been shown to be a viable solution for higher frequency applications. However, while optical and magnetic properties of coupled nanospheres and disks have been studied more comprehensively, anisotropic bi-spheres and rods have stronger polarizability and thus afford a greater opportunity for demonstrating high frequency negative permeability and permittivity. Additionally, pairs of parallel nanorods have been shown to exhibit anti-symmetric resonances that generate a magnetic field, which has also been explored for negative permeability.

Plasmonic oligomers, cyclic assemblies of plasmonic nanoparticles made up of high aspect ratio nanorods, provide another geometry for high frequency collective electric and magnetic responses that are, in addition, spectrally distinct. The hybridized energies of such oligomers depend on the edge length, gap size, and number of edges. The magnetic and electric dipole modes of triangular nanorod oligomers have been studied previously as have coupled symmetric and asymmetric pairs of triangular nanorod oligomers. Nevertheless, a comprehensive investigation of the hybridization of higher order oligomers composed of high aspect ratio nanorods is still lacking. In the following, we nanofabricate a series of such oligomers ranging from trimers to hexamers and study their spectral and spatial plasmonic responses with high-resolution monochromated and aberration corrected electron energy loss spectroscopy (EELS).
Complementary electron beam and optical simulations are used to elucidate our experimental observations.

3.2 Methods:

3.2.1 Nanorod Polygon Fabrication:

The nanorod polygons were fabricated via electron-beam lithography (JEOL 9300FS) using a lift-off process. A 300 μm Si wafer with 30 nm of LPCVD SiNₓ is spin coated with an e-beam resist, PMMA 495 A4, and exposed. Following electron-beam exposure, the pattern was then developed using methyl isobutyl ketone:isopropyl alcohol (IPA) (1:3) for 50 s. 25 nm of Au was sputter deposited via DC magnetron sputtering onto the substrate followed by soaking in a heated NMP bath for 15 min, sonicating in NMP and acetone for 10 min, and rinsing with IPA and deionized water. The backside of the wafer was then spin coated with P20 and S1818 and exposed using photolithography to create the windows for backside etching. Reactive ion etching is used to remove the backside nitride layer and the wafer is subsequently submerged in a heated KOH bath to etch away the exposed portion of Si substrate, stopping on the SiNₓ windows to create the TEM grid edges.

3.2.2 Electron Energy Loss Spectroscopy:

Low-loss EEL spectra and spectrum images were taken using a Nion aberration-corrected high energy resolution monochromated EELS-STEM (HERMES) operated at an accelerating voltage of 60 kV. The convergence and collection semiangles used for the spectrum acquisition were 30 and 15 mrad, respectively. The energy resolution (full width at half-maximum of the zero-loss peak) was approximately 20 meV. The EEL spectra presented were energy aligned and normalized to the zero-loss peak.

3.2.3 Optical extinction and electron beam simulations

Optical and Electron energy loss simulations were carried out using discrete dipole approximation (DDA) and electron-driven DDA (e-DDA), respectively. These numerical methods offer flexibility for irregular shapes and are well suited to simulate oligomers with the different polygon shapes studied here. For all EELS simulations, the shape dimensions and orientations have been determined based on their experimental counterparts; the substrate is not included for computational efficiency. The primary electron beam energy was set to be 60 keV, and the impact parameter was chosen as 5 nm. All electric and magnetic field maps were generated in a plane parallel to the nanostructure located in the near-field above the structure.
3.2.4 Boundary element method calculations

In our simulations we computed the plasmon response function by solving the Maxwell's equations in the quasistatic approximation through the boundary element method\textsuperscript{34} as implemented in MNPBEM toolbox.\textsuperscript{103} As we are mainly interested in the symmetries of the different plasmon modes, we found it convenient to seek the eigenvalues and vectors of the surface derivative of the Green function, following the approach shown in Boudarham and Kociak.\textsuperscript{104} This approach has the advantage that the solutions can be interpreted in terms of eigenmodes, which, in case of plasmonic nanoparticles, are precisely given by the surface plasmons.\textsuperscript{105} The electrostatic potential associated with each plasmonic mode $V(r,\phi)$ has then been fitted according to the multipolar expansion $V(r,\phi) = \sum_{m=-\infty}^{\infty} f_m(r)e^{im\phi}$. The analysis of the multipole moment coefficients $c_m = \int |f_m(r)|^2 dr$ is a useful tool to investigate the azimuthal symmetry of the plasmonic mode in a quantitative way.

Because the size of the system considered in this paper is beyond the validity limit of the quasistatic approximation, we accounted for retardation effect solving the full Maxwell equations in some selected cases (Figure 3.1) finding that the symmetry of the calculated modes is retained when retardation effects are accounted for.

As for the dielectric function of gold we use tabulated values extracted from spectroscopic ellipsometry measurements.\textsuperscript{87} The effect of the SiN membrane supporting the metal structures has been modeled as the average between the tabulated dielectric function of SiN \textsuperscript{106} and the vacuum.

3.3 Results and Discussion

A series of oligomers composed of high aspect ratio gold nanorods are lithographically patterned with varying numbers of edges ($n=3-6$), gap length, and edge length. High spatial and energy resolution EEL spectrum images are measured, and the combined spectra and spectrum images clearly reveal the nature of the various resonant modes that are active. Note that for polygons where $n$ is even, the highest energy mode has $n$ antibonding vertices, whereas for odd number of edges, the maximum number of antibonding modes is $n-1$. As $n$ increases, the number of normal modes increases and the energy splitting of the magnetic all head-to-tail configuration and maximum head-head/tail-tail configuration increases. Depending on the resultant configuration, different net magnetic and electric fields emerge.

To characterize the oligomers' hybridization, we synthesize oligomers consisting of high aspect ratio gold nanorods with approximately the same rod length (540 nm), width (75 nm), and thickness (25 nm) and measure high spatial and energy resolution EEL spectrum images at a vertex of each polygon. Notably, the high aspect ratio minimizes coupling of the transverse/short axis
Figure 3.1 Charge distribution of the two LSPRs of the n=3 polygon calculated using the full Maxwell’s equations solution. The modal decomposition of the Green function we used in the main text is only possible within the quasistatic approximation. The size of the metallic structures we consider in this paper is however above the validity limit of the approximation. In order to check the consistency of our results we also solved the full Maxwell’s equation, including retardation effects, and calculated the charge distributions for the two main modes of the n=3 polygon. Despite the size of the system, the results obtained with the two levels of approximations are in good qualitative agreement.
surface plasmon resonance (SPR), which, for this rod dimension has an energy on the order of 2.1 eV, whereas the long axis mode has an energy of ~650 meV. Figure 3.2 a displays normalized experimental and simulated electron-driven discrete dipole approximation (e-DDA) spectra taken near a nanorod tip for each oligomer (see inset for STEM image and location for each spectrum), which illustrates the resulting hybridization of the coupled rods. Note, the e-DDA spectra have all been shifted 60 meV to lower energy to better align with the experimental spectra; the slight shift to higher energy in the simulated spectra is due to the SiN₅ substrate, which was not included in the simulations. Also included are the energies (vertical lines) of the boundary element method (BEM) simulated SPR modes. The trimer, as illustrated previously,¹⁰¹,¹⁰² consists of two non-degenerate modes, which are clearly observed in the spectrum. For the tetramer, pentamer, and hexamer, however, intermediate peaks emerge between the magnetic mode and the high-energy antibonding configuration. Figure 3.2 b is a plot of the experimental peak positions of the magnetic mode, the maximum antibonding configuration, and the energy difference illustrating that the total hybridization splitting increases progressively as \( n \) increases. Figure 3.2 c shows spectrum images of the tetramer magnetic dipole mode (top), electric dipole mode (middle), and high-energy mode (bottom) consisting of all antibonding vertices, respectively. As expected, the spectrum images confirm the head-to-tail or bonding mode with the near zero EEL intensity in the gap center for the magnetic mode. Furthermore, the high energy antibonding head-to-head/tail-to-tail configuration is characterized by a gap center that has high EEL intensity. The intermediate energy spectrum image is characterized by a mixture of the two modes, and as will be described below, this mode is the electric dipole mode of the tetramer and consists of half of the vertices with bonding and half with antibonding characteristics. The same behavior is observed in the \( n=5 \) and 6 arrangements as illustrated in Figure 3.3 c-k.

In order to elucidate and confirm the symmetry of the different plasmonic modes, information that cannot be directly extrapolated from spectrum images,¹⁰⁷,¹⁰⁸ we performed BEM numerical simulations (see Methods for details). While the oligomer geometries are outside the quasistatic limit assumed in the BEM model, the energies of the normal modes agree well with the experimental results and help reveal the general hybridization trends of the oligomers.

We start from the case of the trimer. In Figure 3.3 a-c, we plot the induced charge distributions of the SPRs that have energy in the 300-1000 meV range. The mode energies resulting from the simulation are in good agreement with experiment, with slight differences attributed to small variations in the experimental nanorod shapes. As expected, the lowest energy mode (Figure 3.3 a) is characterized by all head-to-tail coupling of the longitudinal dipoles of the rods.
Figure 3.2 a. Experimental and simulated spectra taken at the nanorod tip for a single rod and n=3-6 oligomers. Vertical lines indicate normal modes calculated for each oligomer. Inset HAADF images illustrate the location of the beam for the spectra acquisition. b. Peak energies for the electric and magnetic dipoles as a function of the number of edges in the regular polygonal oligomers. Also plotted is the energy splitting between the high and low energy modes illustrating increased splitting as the number of edges increases. c. Spectrum images at measured at a vertex of the tetramer and are filtered to illustrate the magnetic dipole (495 meV), the intermediate electric dipole mode (630 meV), and the full antibonding mode (730 meV). Scale bar=300 nm.
Figure 3.3 a. Experimental Spectrum images for the n=3,4,5,6 arrangements illustrating the a-d) magnetic mode, e-f) intermediate mixed mode, and h-k) antibonding mode. Scale bar = 300 nm
The resulting plasmonic potential is a pure hexapole (Figure 3.3 d), which is confirmed by the multipolar expansion reported in Figure 3.4 g. The second peak in the spectrum is two degenerate modes (Figure 3.3 b-c). This mode can be described as the strong excitation of the dipole modes of two adjacent rods in a head-to-head, or antibonding configuration, plus a small excitation of the quadrupolar mode of the opposite rod to ensure charge neutrality. The two modes are rotated by a 120° angle, reflecting the symmetry of the polygon, but are otherwise identical as it is apparent from the multipole moment decomposition.

Small imperfections of the structure, such as the edge perturbations or small differences in the edge or gap length, can slightly relax the degeneracy of this electric dipole mode and thus slightly split the two modes. Additionally, the radiation damping in the magnetic mode is suppressed relative to the bright electric dipole mode. As a consequence, the higher energy peak of the experimental spectrum is broader than the lowest energy one. The associated electric field is a dipole, with a small quadrupolar component required to compensate for the odd symmetry of the particle (Figure 3.3 e-f and Figure 3.3 h-i).

Any linear combination of two degenerate modes is also a mode with the same energy, therefore, it is interesting to note the shape of the two trivial combinations, i.e. the sum and the difference, of the two modes. As reported in Figure 3.4, the difference gives an equivalent mode rotated by 120° with respect to both parent modes, completing the angular series. The sum mode is very simple from a geometrical point of view, as it can be understood as the flipping of one rod in the lowest energy mode (the bottom rod in this representation) to form two antibonding configurations and one bonding configuration. These results hold true every time we encounter a set of degenerate modes, therefore in the following we will only show one of the degenerate modes with the simplest geometrical shape.

In Figure 3.6, we show the induced surface charge distributions of the plasmonic modes (and their associated induced potentials) that have energy in the 300-1000 meV range computed for all the oligomers with n=3-6. The gray star in the top right corner denotes a set of degenerate modes for which only one representation is reported. The complete list of modes can be found in Figure 3.7, Figure 3.8, and Figure 3.9. Again, the simulations are in good agreement with the experiments. Note, as the size of the structures are large relative to the excitation wavelength, the quasistatic approximation begins to fail, and causes the observed blue-shift of the energies relative to experiment.

The lowest energy mode of each polygon (Figure 3.6 a,c,f,i) is always a multipole with the same rotational symmetry of the oligomer. As expected, it is characterized by all head-to-tail
Figure 3.4 The induced charge distributions (a-c), the associated electric potential (d-f) and its multipolar decomposition coefficients (g-i) of the first 3 plasmonic modes of the n=3 polygon. Scale bar = 500 nm.
Figure 3.5 Linear combinations of the two 743 meV mode (A and B) of the trimer. Scale bar = 500 nm
Figure 3.6 The charge density distributions and the associated electric potentials computed for the LSPRs of the n=3 polygon (a and b), the n=4 polygon (c-e), the n=5 polygon (f-h) and the n=6 polygon (i-l). The modes marked with the grey star are pairs of degenerate modes for which only a single representation have been reported. The higher energy modes of each polygon can be derived from the lowest energy mode by flipping the orientation of the dipole modes of some of the nanorods (marked with the black arrows).
Figure 3.7 The complete list of the plasmonic modes of the n=4 polygon with energy in the range [300-1000] meV. a-d) Charge distributions, e-h) the associated electric potentials and i-l) the multipolar decomposition of the potential associated with each mode. It is worth noticing the 2 degenerate modes at 663 meV and their identical multipolar decomposition. The difference between the two modes is in fact only a 90° rotation. Which one of the two modes is excited (or what linear combination of the pair) depends on the position of the electron beam. Scale bar = 500 nm.
Figure 3.8 The complete list of the plasmonic modes of the n=5 polygon with energy in the range [300-1000] meV. a-e) The charge distributions, f-j) the associated electric potentials and k-o) the multipolar decomposition of the potential associated with each mode. Scale bar = 500 nm.
Figure 3.9 The complete list of the plasmonic modes of the n=6 polygon with energy in the range [300-1000] meV. a-f) The charge distributions, g-i) the associated electric potentials and m-r) the multipolar decomposition of the potential associated with each mode. It is worth noticing the 2 pairs of degenerate modes at 642 meV and 743 meV. The difference between the two modes in every pair is a 60° rotation. Which one of the two modes is excited (or what linear combination of the pair) depends on the position of the electron beam.
coupling of the dipole modes of the rods and results in the circulating current and thus a strong magnetic field perpendicular to the plane of the oligomer. The subsequent modes are ordered in the usual way, with the electric dipole being the lowest energy configuration followed by the quadrupole and the higher electric multipoles.

The shape of the different modes can be understood by simple geometrical arguments. In order to induce an electric dipole, the charge density should be mirrored on one side of the metal structure. This is achieved by flipping, where allowed by the particle symmetry, all the dipoles of the constituent nanorods on one side of the structure. Following this argument, higher order multipoles are obtained by flipping dipoles on the opposite side of a mirror plane or alternating them along the perimeter of the polygon (see for example the hexapole mode of the n=6 polygon). The flipped dipoles have been marked with black arrows and the mirror planes with dashed lines. Note the net electric dipole is aligned along the axis of symmetry of the mirror plane.

To further explore hybridization trends in nanorod oligomers, tetramers with various gap spacing are investigated. Studies on trimers composed of spherical particles have shown that increasing the gap size decreases the energy of both the electric and magnetic hybridized dipole modes and total splitting due to reduced capacitive coupling.110 Figure 3.10 a shows the EEL spectra and Figure 3.10 b the energy positions and energy difference in the two modes as a function of gap spacing (see Figure 3.11 for spectrum images). The spectra also show that as the gap length increases, the energy splitting decreases linearly from 235 meV to 95 meV over the gap range studied (Figure 3.10 b). Similar to the n>3 polygons, an intermediate mode is discernible in gaps below 100 nm. As the gap increases above 100 nm, the coupling decreases and spectrum progresses towards the single rod.

The effect of rod length on coupling is also studied. Nanorod tetramers are synthesized with a rod length ranging from 345 nm to 1100 nm with a constant gap spacing of ~50 nm. The spectra are shown in Figure 3.10 c, and clearly show the splitting into the magnetic and high-energy maximum antibonding mode, which are confirmed by the spectrum images (see Figure 3.12). As expected, Figure 3.10 d shows a linear blue-shifting of the magnetic and high-energy modes as the rod length decreases.111 Additionally, a clear increase in the magnitude of the energy splitting is also observed as the rod length decreases. Note the higher energy quadrupolar mode hybridization is also evident in Figure 3.10 d at higher energy for all but the 300 nm edge length tetramer as its quadrupolar mode is shifted to beyond what is measured.

Optical DDA simulations are used to determine the extinction efficiencies associated with the modes of the oligomers. Figure 3.13 a is a plot of the simulated extinction efficiency for each
Figure 3.10 EEL data for tetramer oligomers with varying gap size and edge length.  a) Spectra taken at the rod tip for gap sizes 30 nm, 45 nm, 75 nm, 100 nm, 185 nm, and 240 nm.  b) Peak energies for the low and high energy modes and energy splitting of the modes as a function of gap size.  c) Spectra taken at the rod tip for rod lengths 345 nm, 540 nm, 825 nm, and 1100 nm.  d) Peak energies for the low and high energy modes and energy splitting of the modes as a function of rod length.
Figure 3.11 a-f) HAADF images of the synthesized polygons with variable gap sizes. g-l) Spectrum images filtered at the magnetic dipole for the various gap sizes. k-g) Spectrum images filtered at the full antibonding mode various gap sizes. Scale bar=300 nm
Figure 3.12 a-f) HAADF images of the synthesized tetramers with variable edge length and e-h) Spectrum images filtered at the magnetic dipole for the n=3-6 polygons. i-l) Spectrum images filtered at the full antibonding mode for each length. Scale bar=300 nm
oligomer for oblique s-polarized excitation where the magnetic field is oriented perpendicular to the oligomer plane (note the specific polarizations for each oligomer next to each spectrum). The extinction efficiency peak confirms the magnetic field coupling of the light field to the oligomers’ magnetic modes. The excitation of the n=3 mode is expected to be a bright mode, note that the high energy modes of the other oligomers are also excited under this polarization. Electric field maps of these excited modes, confirm that these modes are the full antibonding modes, as previously illustrated in Figure 3.6 b, e, h and l. Thus, while these modes are expected to be dark, phase retardation effects are apparently operative when the wavevector is aligned along the plane of the oligomer. Figure 3.13 b is a plot of the magnetic mode extinction efficiency as a function of n, which illustrates that the extinction efficiency is a maximum for the n=4 oligomer. A circular current loop generates a resultant magnetic field perpendicular to the loop according to the Biot-Savart Law. The SPR plasmon frequency is set by the monomer length and the maximum magnetic moment is dictated by $\mu = iA$, where i is the current and is governed by plasmon damping/losses and A is the oligomer area. As the number of edges increases, the oligomer area increases. Consequently, the peak in the extinction coefficient for the n=4 oligomer suggests that the losses in the SPR are likely at the oligomer gaps. For n>4 this results in a lower extinction efficiency. Figure 3.13 c is a plot of the simulated extinction efficiency for normal incidence excitation where the light electric field is aligned to the dipolar axes of symmetry in Figure 3.6 b, d, g, j). This polarization excites the electric dipole mode of the system. Figure 3.13 c is a plot of the extinction efficiency peak for the n=3-6 oligomers. Similar to the magnetic mode, the electric dipole also peaks at n=4, though the magnitude change is much smaller. Interestingly, for the oligomers that have an odd number of edges (n=3 and 5), do not have mirror symmetry along the axis perpendicular to the dipole and thus the extinction efficiency is lower than the equivalent even modes which have this mirror symmetry. Note that at normal incidence, the phase retardation does not excite the highest energy full antibonding mode.

3.4 Conclusion:

In summary, we synthesize and characterize the hybridization of longitudinal dipole modes in nanorod oligomers with n=3-6 number of edges. High spatial and energy resolution EELS reveals that the splitting of the magnetic SPR mode and the SPR with maximum number of antibonding vertices increases with increasing number of edges. Intermediate modes for n>3 emerge where the energy ordering increases with increasing multipoles. Simulations of the EEL spectra agree well with the experimental spectra and SPR modes determined assuming the quasistatic limit, combined with multipole analysis, help reveal the symmetry/coupling of the nanorods in the oligomer. A
Figure 3.13 a. Extinction efficiency spectra of a single rod and n=3-6 oligomers with the wave vector in the plane of the oligomer (note polarization next to each spectrum). b. Peak extinction efficiency values for the magnetic mode as a function of n. c. Extinction efficiency spectra of the electric dipole mode n=3-6 oligomers using normal incidence light (note polarization next to each spectrum). d. Peak extinction efficiency values for the electric dipole mode as a function of n.
study of the tetramer reveals that the energy splitting also increases with decreasing gap spacing and linearly blue-shifts with decreasing rod length. Finally, optical simulations show efficient magnetic coupling of the light field to the oligomers' magnetic modes, and for the dimensions studied here, the extinction efficiency has a maximum value in the extinction efficiency for the $n=4$ arrangement. Furthermore, the full antibonding mode is also excited when optically excited with the wave vector aligned along the oligomer plane, which is attributed to phase retardation effects. When optically excited with normal incidence and the electric field aligned with the dipole mode, the extinction efficiency also peaks at the $n=4$ oligomer.
Chapter 4

Hybridization of Planar and 3D Coupled Split Ring Resonators
4.1 Background:

Metamaterials have garnered great interest in the field of photonics for their ability to realize intriguing new properties that are unable to be achieved in naturally occurring materials. One of the fundamental building blocks in high frequency magneto-optical metamaterial design is the split ring resonator (SRR) because on resonance it can couple to light and the circular oscillation can lead to negative permeability as well as possess a negative refractive index.\(^{53}\) Split ring resonators have been used in a variety of applications including biosensors,\(^{109, 110}\) antennas,\(^{111, 112}\) and absorbers & filters.\(^{113, 114}\) When arranged in an array, individual SRRs act as “meta atoms” in a lattice resulting in a “metamaterial.” The coupling interactions between the SRR “atoms” play a vital role in the overall response of the array architectures.

While significant work has been done investigating the coupling interactions of planar SRRs via optical excitation,\(^{53, 62, 115}\) fewer studies have been performed using electron energy loss spectroscopy (EELS). EELS allows for high resolution spectra and spectrum images which can reveal modes unattainable using optical far-field spectroscopy. An EELS study has shown the progression from distinct optical bright and dark eigenmodes in small arrays (ie 2-4 SRRs) to the formation of a quasi-continuum of modes in the interior and edge modes at the boundaries of a large array.\(^{84}\) Additionally, an investigation of adjacent coupled Au SRRs arranged to be 0°, 90°, and 180° reveals the hybridization schemes of the fundamental modes. EEL spectra and numerical calculations were able to resolve the energy splitting of the modes and derive the electric and magnetic moments to show the role of dipole moments in the hybridization scheme.\(^{83}\)

Moving beyond planar SRRs, very little work has been done on SRRs in the third dimension. One study investigated single, vertical SRRs using cathodoluminescence and EELS to reveal the fundamental magnetic mode and coupling behavior between the arms.\(^{116}\) As was discussed in Chapter 2, two series of 3D nanoresonators were fabricated to investigate the affect of azimuthal angle and tilt on their plasmonic behavior. A red shift in the m=1 mode was observed as a function of azimuthal angle, while the behavior of the nanoresonator was independent of tilt. The hybrid synthesis approach used to investigate these systems can be exploited to further investigate the affect of tilt on the coupling dynamics in metamaterial design.

In this study, we fabricate a series of planar SRRs with varying rotational angle to provide a baseline to measure and model our coupled systems. The experimental results are then confirmed with eDDA simulations and fit with our collaborators numerical model. Coupled 3D SRRs are arranged with two rotations and characterized to investigate the effect of tilt on the coupling
strength. Finally, we investigate a series of SRR trimers in a planar and 3D arrangement to reveal the behavior in a more complex system.

4.2 Methods:

4.2.1 Planar Split Ring Resonator Fabrication

The planar split ring resonators were fabricated via electron-beam lithography (JEOL 9300FS) using a lift-off process. A 300 μm Si wafer with 30 nm of LPCVD SiNx is spin coated with an e-beam resist, PMMA 495 A4, and exposed. Following electron-beam exposure, the pattern was then developed using methyl isobutyl ketone:isopropyl alcohol (IPA) (1:3) for 50 s. 25 nm thick Au was sputter deposited via DC magnetron sputtering onto the substrate followed by soaking in a heated NMP bath for 15 min, sonicating in NMP and acetone for 10 min, and rinsing with IPA and deionized water. The backside of the wafer was then spin coated with P20 and S1818 and exposed using photolithography to create the windows for backside etching. Reactive ion etching is used to remove the backside nitride layer and the wafer is subsequently submerged in a heated KOH bath to etch away the exposed portion of Si substrate, stopping on the SiNx windows to create the electron transparent and lithographically patterned membranes.

4.2.2 3D Split Ring Resonator Fabrication

3D split ring resonators were fabricated using a hybrid synthesis approach utilizing focused electron beam induced deposition (FEBID) as scaffold for plasmonic materials as outlined in Section 2.2.46 The FEBID scaffolds were subsequently coated with SiO2 and Au. The 22 nm conformal SiO2 layer was deposited via ALD to enhance the structural integrity of the scaffolds, which also isolates the Au layer from the PtCx scaffold to minimize possible plasmon damping. Due to its well-known plasmonic properties as well as its stability in atmosphere, ~25 nm Au was subsequently deposited on the scaffolds via DC magnetron sputtering (7 W, 3 mTorr).

4.2.3 Electron Energy Loss Spectroscopy

Low-loss EEL spectra and spectrum images were taken using a Nion aberration-corrected high energy resolution monochromated EELS-STEM (HERMES) operated at an accelerating voltage of 60 kV.43,85 The convergence and collection semiangles used for the spectrum acquisition were 30 and 15 mrad, respectively. The energy resolution (full width at half-maximum of the zero-loss peak) was approximately 20 meV. The EEL spectra presented were energy aligned and normalized to the zero-loss peak.

4.2.4 Electron Beam Simulations

Optical and electron energy loss simulations were carried out using discrete dipole approximation (DDA)76 and electron-driven DDA (e-DDA), respectively. These numerical
methods offer flexibility for irregular shapes and are well suited to simulate oligomers with the different polygon shapes studied here. For all EELS simulations, the shape dimensions and orientations have been determined based on their experimental counterparts; the substrate is not included for computational efficiency. The primary electron beam energy was set to be 60 keV, and the impact parameter was chosen as 5 nm. All electric and magnetic field maps were generated in a plane parallel to the nanostructure located in the near-field above the structure.

4.2.5 Analytical Model

An analytical model was created by collaborators at the University of Washington (C. Praise Anyawu & David Masiello) to derive a simple description of the EELS observable for coupled Au SRRs. A single SRR is assumed to be a circular conductive ring and is mapped unto an $LRC$ circuit. Utilizing an extended circuit model, we describe the interaction potential of the magnetic and electric fields via the multi-pole expansion, where we make the dipole approximation. That is, we approximate mutual interactions as a pairwise, dipole-dipole interaction of the magnetic and electric fields keeping only the fundamental mode. We derive a solution for the driven oscillator of the dipole coordinate, $Q_i$, in the frequency domain, as

$$Q_i(\omega) = \frac{-F_{el}(R, \omega) \cdot d}{eL} \frac{1}{\Omega^2_0 - \omega^2 - i\gamma_1 \omega - \frac{g^2}{\Omega^2_0 - \omega^2 - i\gamma_2 \omega}}$$

Where $\Omega_0$ is the resonate frequency, and $g$ is the coupling constant. It should be noted that $g$ is the cumulative effect of the mutual interactions from the magnetic and electric fields. To express the EELS observable of a coupled SRR dimer, we derive the polarizability for the dipole in the coordinate expressed in $Q_i$ as

$$\alpha(\omega) = \frac{dQ_i(\omega)}{E_{el}(R, \omega)}$$

Which allows us to express the EELS observable as

$$\Gamma_{EEL}(\omega) = \frac{|E_{el}(R, \omega) \cdot d|^2}{\pi\hbar} Im[\alpha(\omega)]$$

4.3 Results and Discussion

4.3.1 Planar Coupled Split Ring Resonators

To provide a baseline for our analytical model as well as a benchmark for our 3D studies, planar SRRs were fabricated. A series of Au SRRs with diameter 450 nm and $270^\circ$ azimuthal angle were lithographically patterned on a SiNx membrane. The coupled SRRs were patterned with one
SRR rotated at angles of 0°, 45°, 90°, 135°, and 180° relative to the other as shown in Figure 4.1b-f. Experimental EELS spectra (Figure 4.1 a) show a clear splitting into the bonding and antibonding modes in the 0°, 45°, 135°, and 180° and a single peak for the 90°. Complementary electron driven discrete dipole approximated simulated spectra (dashed line in Figure 4.1 a) and predicted EELS from our analytical model (dotted line in Figure 4.1) confirm the experimental results. This behavior is illustrated using spectrum images (Figure 4.1 g-p). The in-phase coupling is shown in the lower energy maps (Figure 4.1 g-h, j-k) with the signature zero EELS intensity in the gap; while the out-of-phase coupling is shown in the higher energy maps (Figure 4.1 l-o) where the electric dipole coupling has a high EELS intensity in the gap.

To further investigate the coupling behavior of the coupled SRRs, the normal mode peaks for the planar rotational study were plotted (Figure 4.2 a). The anticrossing-like plot illustrates the consistent progression of the normal mode splitting between the experimental (solid), eDDA (dashed), and model predicted (dotted) spectra as a function of in-plane orientation. The splitting is dominated by coupling of the electric dipoles. At 90° the electric dipole coupling is zero and any broadening of the monomer is due to the magnetic coupling. To confirm that the electric dipole coupling dominated, the numerical magnetic and electric coupling constants were estimated to be 0.0015 and 0, respectively. Simulated (eDDA) electric and magnetic field profiles of the systems further illustrate the progression of the normal mode splitting due to changes in coupling strength. As was observed in the experimental spectrum images, the electric field profiles of the lower energy modes (Figure 4.2 b-f) exhibit bonding mode characteristics while the higher energy modes (Figure 4.2 p-s) exhibit antibonding mode characteristics. Magnetic near field maps elucidate magnetic ordering of the hybridization in the coupled dimers. Ferromagnetic ordering is observed for the in-phase coupling (Figure 4.2 g, h) while antiferromagnetic order is observed for the out-of-phase coupling (Figure 4.2 p, q) for the dimers oriented 0° and 45°. This behavior is flipped for dimers oriented 135° and 180° where antiferromagnetic ordering is observed for the in-phase coupling and ferromagnetic ordering is observed for the out-of-phase coupling (Figure 4.2 j-k, r-s respectively).

As a compliment to the rotation about the centerline, a series of planar SRRs were fabricated and with the second SRR rotated 180 degrees with the tip gaps held constant (HAADF images of the structures shown in Figure 4.3 c-g). Experimental EEL spectra demonstrate a consistent splitting throughout the rotation series (Figure 4.3 a) with small variations due to slight differences in the gap size. When rotated about the tip, the coupling behavior is dominated by electric dipole coupling. The normal mode peaks were plotted to clearly show the peak splitting as a function of rotation angle (Figure 4.3 b).
Figure 4.1 (a) Experimental (solid) and simulated (dashed) EELS spectra taken at the SRR outer tip for planar rotational study. The progression from a splitting into the bonding and antibonding modes to a single mode (45°) reveal the transition from electric dipole-dipole coupling to magnetic dipole-dipole coupling. (b-f) HAADF images of SRR with colored dot indicating where spectra were acquired. Corresponding spectrum images reveal the bonding (g-k) and antibonding (l-p) modes in the system. Scale bar = 300 nm.
Figure 4.2 (a) Anticrossing-like plot of experimental (solid), eDDA simulation (dashed), and model prediction (dotted) EELS spectra normal mode peaks for the planar rotational study. Here we illustrate the progression of the normal mode splitting due to changes in coupling strength as a function of in-plane orientation. We show number (eDDA) electric (b-f) and magnetic (g-k) field profiles of the bonding modes and for the anti bonding modes of the electric (i-o) and magnetic (p-s) field profiles.
Figure 4.3 (a) Experimental EELS spectra taken at the SRR outer tip for planar rotational study. The progression from a splitting into the bonding and antibonding modes to a single mode ($45^\circ$) reveals the transition from electric dipole-dipole coupling to magnetic dipole-dipole coupling. (b) Anticrossing-like plot of the experimental normal modes illustrating a consistent peak splitting as a function of rotation angle. (c-g) HAADF images of SRR with colored dot indicating where spectra were acquired. Corresponding spectrum images reveal the bonding (h-l) and antibonding (m-q) modes in the system. Scale bar = 300 nm.
The anticrossing-like plot reveals that when the SRR is rotated about the tip, the coupling strength is not affected by the relative rotation. In this arrangement, coupling behavior is affected by the size and shape of the individual SRR as well as the gap size. The in-phase and out-of-phase coupling are confirmed via the spectrum images in Figure 4.3 h-i and Figure 4.3 m-q, respectively, which have the characteristic dark and bright gaps, respectively.

4.3.2 3D Coupled Split Ring Resonators

A series of 3D Au SRRs were fabricated with varying relative rotation and tilt angles. Figure 4.4 shows a tilt study where the SRRs are placed side-by-side. The top SRR in Figure 4.4 b-d is tilted at 30° and the bottom SRR is tilted 30°, 45°, and 60° (Figure 4.4 b-d respectively). Spectra were taken at the outer tip of the SRR and plotted in Figure 4.4 a. In this arrangement, the spectra are dominated by the electric dipole coupling as illustrated in the planar studies and therefore exhibits similar behavior to the planar system; the fidelity of the structures and resolution of the microscope were not able to discern the expected magnetic field coupling differences in these orientations. In the 30°-30° and 30°-45° systems, the in-phase and out-of-phase mode are more clearly seen in the spectrum images where the gaps are more intense for the out-of-phase mode (Figure 4.4 h-i). The 30°-60° system is illustrative of two uncoupled SRRs rather than a hybridized system (Figure 4.4 g, j). This is likely due to the ~150 meV difference in the dipole modes for the individual rings which is caused by differing SRR ring lengths.

The SRRs were also rotated 90° to investigate how tilt affects the magnetic dipole coupling. Figure 4.5 b-d show HAADF images of SRRs rotated 90° with tilts of 30°-30°, 30°-45°, and 30°-60°. EEL spectra taken at the outer tip of the 30° SRR are plotted in Figure 4.5 a revealing a single peak for all systems. This is to be expected because when rotated in this arrangement, there is no electric dipole coupling and as determined in the planar series, the magnetic dipole coupling is very weak. Spectrum images of the coupled SRRs (Figure 4.5 e-g) exhibit similar behavior to that of the planar system. Due to the weak nature of the magnetic dipole coupling, our analytical model and eDDA simulations will be required to reveal the effects of tilt on the coupling dynamics in this system.

4.3.3 Planar and 3D SRR Trimer

The SRRs were also arranged in a trimer orientation in order to investigate the hybridization of this system. A planar trimer was fabricated with SSRs having a diameter 450 nm and 270° azimuthal angle (Figure 4.6 a). EEL spectra were acquired at a single junction (colored dots in Figure 4.6 a) and plotted (Figure 4.6 d). Spectra were taken on the inner arm to preferentially excite the bonding mode and in the gap to excite the antibonding mode. In the case of
Figure 4.4 (a) Experimental EELS spectra taken at the tip of the $30^\circ$ tilted SRR. (b-f) HAADF images of SRR with colored dot indicating where spectra were acquired. Corresponding spectrum images reveal the bonding (e-f) and antibonding (h-i) modes in the $30^\circ-30^\circ$ and $30^\circ-45^\circ$ systems. Spectrum images of the $30^\circ-60^\circ$ system illustrate the $30^\circ$ (g) and $60^\circ$ (j) acting as independent SRRs. Scale bar = 300 nm.
Figure 4.5 (a) Experimental EELS spectra taken at the SRR outer tip of the 30° tilted SRRs. A single peak is observed due to zero electric dipole coupling when the SRRs are rotated 90°. (b-f) HAADF images of SRR with colored dot indicating where spectra were acquired. (e-g) Corresponding spectrum images illustrate the single mode behavior. Scale bar = 300 nm.
Figure 4.6 (a) A planar trimer was probed (colored dots) at a single junction and (d) experimental EELS were plotted. Spectrum images and simulated electric field maps reveal the all (b,e) in-phase coupling and (d,f) out-of-phase coupling in the trimer. Magnetic field maps illustrate the (h) ferromagnetic ordering with the in-phase hybridization and (i) antiferromagnetic ordering for the out-of-phase hybridization. Scale bar=300nm.
the planar trimer, peaks are observed at 300 meV (location 1 & 3) and 400 meV (locations 1-3). Spectrum images and simulated electric field maps clearly show illustrate the hybridization of the trimer. Similar to the nanorod trimer described in Chapter 3, the lower energy mode at 300 meV consists of three head-to-tail electric dipoles characteristic of in-phase coupling (Figure 4.6 b, e). The higher energy mode at 400 meV consists of two head-to-head dipole arrangements for two adjacent SRRs, characteristic of out-of-phase coupling, plus a small excitation of the quadrupolar mode of the remaining SRR (Figure 4.6 c, f). Unique to the SRR trimer is the magnetic coupling present. Simulated magnetic field maps reveal a ferromagnetic ordering for the lower energy, in-phase coupling (Figure 4.6 h) and antiferromagnetic coupling for the higher energy, out-of-phase coupling (Figure 4.6 i).

In addition, two 3D trimers were fabricated with the SRRs having a 30° tilt (Figure 4.7 b) and 45° tilt (Figure 4.7 f). For all three trimers, spectra were acquired in three locations of a single junction (as indicated with colored dots in Figure 4.7 b, f) and plotted (Figure 4.7 a, e). In the cases for 3D trimers, the mode behaviors are not as clearly resolved due to variations in the SRR gap sizes, tilt angle, and proximity to the hole edge (Figure 4.7 a & i). For the 30° tilted system, a peak at 360 meV is observed at location one and a peak at 470 meV is strongly observed at all locations. Spectrum images at the mode energies indicate in-phase coupling at 360 meV (Figure 4.7 c) and out-of-phase coupling at 470 meV (Figure 4.7 d). For the 45° tilted trimer, two peaks are also observed, however, the lower energy 205 meV peak is very weak (Figure 4.7 e). A spectrum image at 205 meV shows a very faint excitation along the arms (Figure 4.7 h). The higher energy mode at 295 meV is clearly observed in locations 2 and 3 and faintly seen at location 1. The spectrum image shows a single SRR solely contributing to this mode (Figure 4.6 h).

4.4 Conclusions:

In summary, we synthesize and characterize rotated planar SRRs, 3d tilted SRRs, and planar and 3d SRR trimers. High spatial and energy resolution EELS, eDDA simulations and a numerical model reveal that coupling is dominated by the electric dipole coupling with only weak magnetic field coupling. Simulated and model predicted EEL spectra agree well with the experimental results. Experimental spectrum images and numeric electric and magnetic field profiles help reveal the in-phase and out-of-phase coupling in the system. Additionally, we show that when rotated about the tip, coupling between the SRRs is also dominated by electric dipole coupling and in this orientation the hybridization does not change appreciably except in the head-to-head orientation. EEL spectra and spectrum images reveal the in-phase and out-of-phase coupling which behave similarly to the planar system in 3D side-by-side arrangement as well as when SRRs are rotated 90°.
Figure 4.7 Two 3D SRR trimers with a tilt of 30° (b) and 45° (f) were fabricated and EEL spectra were acquired at a single junction (a & e). The 30° tilted system behaves similarly to the planar trimer with an all in-phase coupling (c) and out-of-phase coupling (d) revealed in the spectrum images. Spectrum images for the 45° tilted trimer reveal a faint excitation along the arms of the SRRs at 205 meV (g) and the excitation of a single SRR at 295 meV (h). Scale bar = 300 nm.
The in-phase and out-of-phase hybridization of the dimers have ferromagnetic and antiferromagnetic orderings of the magnetic fields, respectively. Finally, both planar and 3D SRRs trimers have characteristic in-phase and out-of-phase hybridization. The lower energy mode is the all in-phase coupling with ferromagnetic ordering of the magnetic fields, and the higher energy mode consists of two SRRs out-of-phase with antiferromagnetic magnetic field ordering.
References


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Vita

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