OPTICAL PROPERTIES OF PLASMONIC NANOSTRUCTURES:

THEORY & EXPERIMENTS

A Dissertation in
Engineering Science and Mechanics
by
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Abstract

Metal nanoparticles and thin films enable localization of electromagnetic energy in the form of localized surface plasmon resonances (LSPR) and propagating surface plasmons respectively. This research field, also known as plasmonics, involves understanding and fabricating innovative nanostructures designed to manage and utilize localized light in the nanoscale. Advances in plasmonics will facilitate innovation in sensing, biomedical engineering, energy harvesting and nanophotonic devices. In this thesis, three aspects of plasmonics are studied: 1) active plasmonic systems using charge-induced plasmon shifts (CIPS) and plasmon-molecule resonant coupling; 2) scalable solutions to fabricate large electric field plasmonic nanostructures; and 3) controlling the propagation of designer surface plasmons (DSPs) using parabolic graded media.

The full potential of plasmonics can be realized with active plasmonic devices which provide tunable plasmon resonances. The work reported here develops both an understanding for and realization of various mechanisms to achieve tunable plasmonic systems. First, we show that certain nanoparticle geometries and material compositions enable large CIPS. Second, we propose and investigate systems which exhibit coupling between molecular and plasmonic resonances where energy splitting is observed due to interactions between plasmons and molecules.

Large electric field nanostructures have many promising applications in the areas of surface enhanced Raman spectroscopy, higher harmonic light generation, and enhanced fluorescence. High throughput techniques that utilize simple nanofab-
Fabrication are essential their advancement. We contribute to this effort by using a salting-out quenching technique and colloidal lithography to fabricate nanodisc dimers and cusp nanostructures that allow localization of large electric fields, and are comparable to structures fabricated by conventional lithography/milling techniques.

Designer surface plasmons (DSPs) are surface waves that are localized to the interface between a structured perfect electric conductor (PEC) surface and dielectric medium. Terahertz (THz) DSPs excited on microscale structured PEC are localized in the out-of-plane direction, with negligible in-plane localization. We addressed this problem by subjecting DSPs to a parabolic graded-index structure. Lateral confinement such as focusing, collimation, and waveguiding of DSPs is demonstrated. Such control will pave the way towards THz energy concentration, diffusion, guiding, and beam aperture modification.
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Publications

Accepted

1. B. K. Juluri\textsuperscript{1}, Y. B. Zheng\textsuperscript{1}, L. Jensen, L. Jensen and T. J. Huang, Dynamically Tuning Plasmon-Exciton Coupling in Arrays of Nanodisk-J-aggregate Complexes, \textit{Advanced Materials}, Vol. 22, pp. 3603-3607, 2010. (Selected for cover image)


7. Q. Hao, B. K. Juluri, Y. B. Zheng, W. Bei, I. Chiang, L. Jensen, V. Crespi, P. C. Eklund, T. J. Huang, Effects of Intrinsic Fano Interference on Surface Enhanced Raman Spectroscopy: Comparison between Platinum and Gold, \hfill \footnote{Authors have equally contributed in this project.}


**Under Review/To be submitted**


2. N. Chaturvedi\(^1\) & B.K. Juluri\(^1\) *et al.*, Plasmonic Snowman Nanostructures with Tunable Plasmon Resonances, *ACS Nano*.


5. B.K. Juluri *et al.*, Enhanced Figure of merits in plasmonic Clusters for Biosensing, *Nanoletters*.


\(^1\)Authors have equally contributed in this project.
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Dedication

Dedicated to my family and friends
Motivation and Overview

1.1 Motivation

Plasmonics is an emerging branch of nanophotonics that examines the properties of the optical properties of noble metallic thin films and nanostructures. These structures when exposed to electromagnetic radiation of suitable energy and momentum support oscillations of sea of electrons. In the case of metallic nanostructures, oscillations of sea of electrons can results into an oscillating dipole, whose dipole moment can be resonantly enhanced at certain energy. These resonances are commonly called as localized surface plasmon resonances (LSPR) and are analogous to mechanical resonances in spring-mass systems (Fig. 1.1). In the same way, mechanical resonances can be tuned by controlling the spring stiffness and mass, LSPR can also be tuned by changing one of the following: 1) size[1, 2], 2) shape [1–4], 3) inter-particle distance[3, 5, 6] and 4) dielectric constant of the surrounding medium; [2, 7–10].

Two important effects are observed at plasmon resonance, 1) there is large extinction of light by nanoparticle as shown in Fig. 1.2 a (extinction is equal to sum of scattering and absorption) and 2) there is large localization of electric field near the nanoparticle as shown in Fig. 1.2 b. The phenomenon of enhanced extinction by nanoparticles has been used for many centuries by Romans who used gold nanoparticles in stained glass to give them different colors in transmission and reflection. But much interest in metal nanoparticles started with the advent of powerful theoretical tools and fabrication techniques over the last three decades.
Research in metallic nanostructures has shown that the effects of plasmon resonance can be harnessed for numerous applications that include bio-sensing,[11, 12], energy harvesting[13], higher harmonic light generation[14], data storage[15], contrast-enhanced imaging,[16, 17] and nanoelectronic devices.[18]

Recently, researchers have proposed an idea of next generation computer processors that process information using light instead of electrons[18]. A major motivation to this proposal is the ultimate achievable speed of light, $2.989 \times 10^5$ km/sec and one can envision that such system would work $100,000 \times$ faster than current electronic processors. Most plasmonic devices demonstrated thus far, including filters and waveguides, are passive components. Before the full potential of plasmonics can be realized, active or functional plasmonic devices such as switches and modulators have to be developed. However, most of these active plasmonic materials and devices are induced by microscale or even macroscale behavior that occurs in bulk materials, and thus are too big to be integrated into the future nanoscale plasmonic circuits. One part of this thesis is aimed towards understanding and realizing various mechanisms of achieving tunability in nanoparticle systems that can be used for active systems in future nanoscale plasmonic circuits. Firstly, we theoretically investigate charge-induced plasmonic shifts (CIPS) in metal nanoparticles. Charge-induced plasmonic shifts are plasmonic shifts that occur due to injection or removal of electrons in metal nanoparticles. There is a need to establish governing rules to maximize the magnitude of CIPS. Secondly, we have worked on tunability that can be achieved by resonant coupling of plasmonic...
resonances with molecular resonances. This type of resonant coupling can be realized in metal-molecule complexes when excitons spectrally and spatially overlap with plasmon modes. By taking advantages of interactions between plasmon modes and exciton modes, it is possible to significantly tune the LSPR. The dramatic change in the plasmon mode associated with the transition from weak to strong resonant coupling makes the metal-molecule complexes an ideal candidate for active molecular plasmonic circuits. Another aspect of this thesis is about scalable, rapid and inexpensive fabrication of nanoparticle systems that exhibit large electric fields. Nanostructures that can localize large electric fields are of great interest in plasmonic community. For examples, these structures will enable single molecule detection, higher harmonic light generation, and control of molecular fluorescence and absorption. High throughput and simple nanofabrication techniques are essential for the practical implementation and advancement of large E-field nanostructures for real-life applications. Currently, the fabrication of large electric field nanostructures is done by electron beam lithography or focused ion beam milling. Both of these methods are expensive, not scalable and are slow. In this thesis, we demonstrate a rapid, inexpensive and scalable fabrication method based on the salting-out quenching technique and colloidal lithography for the fabrication of two types of large E-field nanostructures: nanodisc dimers and cusp nanostructures.

The last part of this thesis deals with designer surface plasmons (DSPs). DSPs are surface waves that are localized at the interface between structured perfect
electric conductor surface and a dielectric (Fig. 1.3 a). DSPs are very similar to propagating surface plasmons in terms of localization and dispersive properties (Fig. 1.3 b). However, DSPs on micron scaled PEC structures will allow excitation of THz waves (Fig. 1.3 b) and in addition, dispersion relations can be tuned with geometry and material used in structured PEC. One major limitation of DSPs is that they are not localized in the in-plane direction and spread out in the in-plane direction. There is requirement to control the propagation of DSPs in the in-plane direction and basic functions such as focusing, collimation and waveguiding need to be achieved. We address this by using graded media in structured PEC, such graded media will change the effective refractive index which the DPSs perceive and enable control over the propagation of DSPs. Successful control of propagation of DSPs will advance THz energy concentration, diffusion, guiding, and beam aperture modification.

1.2 Overview of the Dissertation

Chapters 2, 3, 4, 5 and 6 are taken directly from, or are expanded versions of published, submitted or soon to be submitted technical research manuscripts. A literature review is given at the beginning of each thesis chapter, as Introduction sections, specific to the subject of that particular chapter. In some cases, calculations were also done mostly to guide the experiments. Chapter 7 outlines the summary of this work. All relevant copyright information and publishing rights conclude each
chapter. References from each chapter are also provided towards the end of each chapter. The remaining sections of this chapter contain summaries of each thesis chapter.

1.2.1 Chapter 2: Charge-induced Plasmonic Shifts: Effect of Geometry and Material Composition

In this work the influence of geometry and composition on the charge-induced plasmonic shifts (CIPS) of gold nanoparticles are systematically studied using Mie scattering theory and the discrete dipole approximation. The sensitivity of nanorods and nanodiscs with different aspect ratio and nanoshells with different volume fractions and compositions are studied using different charging levels. The electrodynamics calculations were performed by changing the internal electron density in the Drude model for the dielectric constant of gold. We show that for a constant volume, Nanodiscs and nanorods exhibit CIPS with a linear dependence on aspect ratio. Geometries having higher aspect ratio show larger CIPS. In nanoshells, increasing the volume fraction of the core causes a slow increase of CIPS at first followed by a rapid increase for larger volume fractions. In addition, we find that nanoshells with the same volume fractions exhibit larger shifts when the refractive index of the cores is larger. Furthermore, the electrodynamics results are interpreted using analytical approximations based on quasistatic theory. The qualitative understanding of geometric and composition effects on the CIPS of gold nanoparticles obtained in this work can hopefully be used to realize highly tunable charge-based active plasmonic devices.

1.2.2 Chapter 3: Resonant Coupling between Molecular and Plasmonic Resonances

In this work, we show using both experiments and classical electrodynamic simulations that plasmon splitting in resonant molecule-coated nanoparticles (plasmon-exciton systems) increases linearly as the square root of absorbance of the molecular layer. This linear relationship shows the same universal behavior established in analogous systems such as cavity-polaritron and surface plasmon polariton systems.
To explain this behavior, a simple physical mechanism based on linear dispersion and absorption is proposed. The insights obtained in this study can be used as a general principle for designing resonant molecule-coated nanoparticles for realizing tunable nanophotonic devices and molecular sensing.

1.2.3 Chapter 4: Dynamically Tuning Plasmon-Exciton Coupling in Arrays of Nanodisc-J-aggregate Complexes

Spectral overlap between plasmon and exciton is prerequisite to observe plasmon-exciton states, researchers have used tunable plasmon mode associated with geometry change to demonstrate variable strength of plasmon-exciton coupling. However, they require the fabrication of a large number of nanoparticles with different geometry to establish plasmon-exciton coupling. Not only does the large number of samples complicate the experimental procedures and introduce deviations, this method is not implementable in active nanophotonic devices, where the geometry of the nanoparticles will be fixed. We demonstrate dynamic tuning of plasmon-exciton resonant coupling in arrays of Nanodisc-J-aggregate complexes. The angle-resolved spectra of an array of bare Au Nanodiscs exhibit continuous shifting of localized surface plasmon resonances. This characteristic enables the production of real-time, controllable spectral overlaps between molecular resonance and plasmonic resonance. In this work we explore resonant interaction strength as a function of spectral overlap. In experiments where we changed the incident angle of a probe light, the coupling strength changed; this result matched with the simulated data based on a coupled dipole approximation method.

1.2.4 Chapter 5: Plasmonic Nanodisc Dimers and Cusp Nanostructures: Fabrication using Salting-out Quenching method and Colloidal Lithography

In this work, we demonstrate a rapid, inexpensive and scalable fabrication method based on the salting-out quenching technique and colloidal lithography for the fabrication of two types of large E-field nanostructures: nanodisc dimers and cusp nanostructures. Our proposed technique relies on fabricating polystyrene
doublets from singlet beads by controlled aggregation and later using them as soft masks to fabricate metal nanodisc dimers and nanocusp structures. Both of these structures have a well-defined geometry for the localization of large electric fields comparable to structures fabricated by conventional lithography/milling techniques. We also show that various parameters in the fabrication process can be adjusted to tune the geometry of the final structures and control their resulting plasmonic properties. With several advantages, including an inexpensive, rapid, and scalable process that can demonstrate good geometric tunability, our proposed fabrication method provides a promising potential to facilitate the advancement of large E-field nanostructures in various practical applications.

1.2.5 Chapter 6: Propagation of Designer Surface Plasmons in Structured Conductor Surfaces with Parabolic Gradient Index

In this work, we investigate the propagation of designer surface plasmons in planar perfect electric conductor structures that are subject to a parabolic graded-index distribution. A three-dimensional, fully vectorial finite-difference time-domain method (FDTD) was used to engineer a structure with a parabolic effective group index by modulating the dielectric constant of the structure’s square holes. Using this structure in our simulations, the lateral confinement of propagating designer surface plasmons is demonstrated. Focusing, collimation and waveguiding of designer plasmons in the lateral direction is realized by changing the width of the source beam. Our findings contribute to applications of designer surface plasmons that require energy concentration, diffusion, guiding, and beam aperture modification within planar perfect electric conductors.

1.2.6 Summary of Appendices

The appendices add more detail to the content of the main thesis and provide supplementary information. Appendix A documents the instrumentation common to multiple chapters, including the description of the clean room nanofabrication instruments and dark field micro-spectroscopy. Appendix B outlines the origins of
angle dependent plasmon spectra through coupled dipole approximation calculations.
References


Chapter 2

Charge-induced Plasmonic Shifts: Effect of Geometry and Material Composition

2.1 Introduction

Charge-induced plasmonic shifts (CIPS) of extinction spectra due to changes in the free electron density of gold and silver nanoparticles have been demonstrated in recent years. Nanoparticles in a colloid or immobilized on a substrate were charged either by adding a reducing agent or by applying an electrochemical potential. For an applied electrochemical potential, the amount of charge or discharge, or the number of electrons transferring in or out of the nanoparticle was proportional to the double-layer capacitance across the solid-liquid interface. The direction of the shift was controlled by the electrochemical polarization and the amount of charge injection was limited only by the evolution of hydrogen or oxidation of the solvent at higher potentials. An increase in internal free electron density caused a blueshift of the extinction spectra, while a decrease caused a redshift [1, 2]. Ung et al.[1] controlled the resonance position of colloidal silver by electrochemical processes. Based on the observed spectral shifts, they reported a charge density change of 6.2%/V/particle. Chapman et al.[2] and Daniels et al.[3] have demonstrated CIPS in silver nanoparticles immobilized on an Indium Tin Oxide (ITO) substrate. Similar
work was performed by Baum et al.\cite{4} on gold nanospheres adsorbed on ITO. Gold nanospheres were immobilized by Toyota et al.\cite{5} with an amine-terminated, siloxane-linking monolayer. This configuration was used to study the effects of both constant and modulated potential on the transmission and absorption properties of the nanoparticles. All these studies were performed with nanoparticles of spherical shape and concluded that changes in free electron density alter the optical constants of the nanoparticles and thus the resonance positions.

In recent years, the increase of research in plasmonic applications has led to the synthesis of new nanoparticle geometries. Wet chemistry has been used to synthesize nanoparticle geometries such as nanorods,\cite{6-8} nanodisks,\cite{9} nanoshells, \cite{10, 11} hexagonal prisms,\cite{12} etc. On the other hand, certain applications of plasmonics which require a supporting substrate have led to the fabrication of nanoparticles on the substrate using electron beam lithography\cite{13-15} and colloidal lithography\cite{16, 17}. In these methods, arrays of nanoparticle geometries like nanodisks,\cite{18, 19} nanotriangles,\cite{16, 20, 21} nanorings,\cite{17, 22} nanoprism\cite{23} etc. are directly fabricated on a substrate, resulting in a more uniform and controlled distribution of nanoparticles unlike the monolayer linking of nanoparticles synthesized by wet chemistry. Moreover nanoparticles fabricated by colloidal lithography are extremely stable to positive potentials applied on ITO surface.\cite{24} We believe that the resonance position in new geometries fabricated both by the bottom-up and top-down methods can be tuned by charging and discharging.

Recently, Mulvaney et al.\cite{25} have experimentally demonstrated that gold nanorods exhibit drastic blueshifts in optical resonance position when their free electron density increases. They also showed that CIPS strongly depends on the nanorod aspect ratio (AR). Geometries such as nanodisks, nanorods and nanoshells can be tailored to obtain the desired CIPS. CIPS in these new geometries will find applications in building electrochemically tunable nanophotonic devices such as electrochromic devices and active waveguides. CIPS can also be potentially used to detect redox activity in the vicinity of nanoparticles and should find applications in sensing. Realizing these applications entails the understanding of optical effects of charging and its dependence on geometry and composition of nanoparticles.

In this direction, we report the effects of electron charging on both composite (hollow and solid nanoshells) and nonspherical nanoparticle geometries (nanodisks
and nanorods) using electrodynamic simulations. Based on plasmonic shifts, comparison of these geometries, and influence of AR, volume fraction (VF) and composition within specific geometries are presented systematically for different levels of charging. Furthermore, the calculated CIPS sensitivities of various nanoparticle geometries and compositions are rationalized in terms of approximate analytical expressions based on quasistatic theory. It is shown that the CIPS sensitivity of nanoparticle is significantly affected by the AR and composition of the nanoparticle, and should be taken into account to maximize the nanoparticle CIPS sensitivity.

Section 2.2 outlines the various theoretical methods to calculate CIPS in nanoparticles. Section 2.3 presents the electrodynamic results for various geometries and compositions and the analytical expressions based on quasistatic theory to correlate with results obtained from the electrodynamic methods. Finally, section 2.4 concludes this work.

### 2.2 Theory

The extinction efficiency of nanoparticles can be numerically calculated by various methods, which include Mie Scattering Theory (MST),[26] Discrete Dipole Approximation method (DDA),[27] T-Matrix method,[28] Modified Long Wavelength Approximation (MLWA),[27] and Finite Difference Time Domain method (FDTD).[15, 29] In this work, we used DDA for nanodisks and nanorods, and MST for hollow and solid nanoshells to calculate the resonance positions ($\lambda_{\Delta N}$ and $\lambda_o$) for both charged and uncharged states. CIPS is calculated as the difference between these two wavelengths, $\Delta \lambda = \lambda_{\Delta N} - \lambda_o$. To remove the effect of particle size on CIPS, the volume of all the nanoparticles was kept constant and an effective spherical radius ($r_{eff}$) of 10 nm was chosen. The surrounding environment of all isolated nanoparticles was considered to be water with an refractive index (RI) of 1.333, as charging is generally performed in aqueous environment (double layer capacitance in water is higher than in air).
2.2.1 Drude model

An increase in free electron density affects the dielectric constant of the Au nanoparticles. To calculate the extinction spectra for various particle geometries in charged and uncharged states, we have considered a Drude type dielectric function in DDA and MST. The generalized Drude model does not account for the effects of size and shape on the particles’ dielectric constants. We modeled the nanoparticles with an effective radius equal to 10 nm, large enough to neglect size and shape effects in the Drude model.[30]. As the size of particles used in previously reported CIPS experiments is less than 50 nm, we restrict our study to particles belonging to size regime below 50 nm. In this size regime, the effect of retardation and damping are negligible [31, 32] and therefore variations of particle size affect only the line width of the spectrum.[11] Further in this work we are interested in the location of the resonance wavelength and peak broadening or sharpening is not of concern.

The analytic expressions for the Drude model with these considerations are:[31]

\[ \epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \]  

(2.1)

\[ \epsilon'(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + \frac{\gamma^2}{\omega}}, \]  

(2.2)

and

\[ \epsilon''(\omega) = \frac{\gamma\omega_p^2}{\omega^3 + \frac{\gamma^2}{\omega}}, \]  

(2.3)

where \( \epsilon' \) is the real part of the dielectric function, \( \epsilon'' \) is the imaginary part of the dielectric function, \( \epsilon_\infty \) is the contribution from the bound electrons, \( \omega_P \) is the bulk plasma frequency (\( \omega_p^2 = Ne^2/\epsilon_0m^* \)), and \( \gamma \) is the relaxation constant such that \( \gamma = Ne^2/\sigma m^* \) where, \( N \) is the free electron density, \( e \) the charge of an electron, \( m^* \) is the effective mass of an electron and \( \sigma \) is the conductivity. It should be noted that \( \omega_p \) is a function of free electron density (\( N \)), whereas the relaxation constant is independent of \( N \) as the conductivity is also proportional to \( N \). It is therefore expected that any change in free electron density will change the resonance position via \( \omega_p \). When the internal free electron density is increased by \( \Delta N \), the real and
imaginary parts of the dielectric function are given by

\[ \epsilon'_{\Delta N}(\omega) = \epsilon_\infty - \frac{\omega_p^2(1 + \frac{\Delta N}{N})}{\omega^2 + \gamma^2}, \tag{2.4} \]

and

\[ \epsilon''_{\Delta N}(\omega) = \frac{\gamma \omega^2(1 + \frac{\Delta N}{N})}{\omega^3 + \gamma^2 \omega}, \tag{2.5} \]

respectively.

Figures 2.1(a) and 2.1(b) show the real and imaginary parts of the frequency-dependent dielectric constant of gold. The solid circles are the experimental results from Johnson et al. [33] The lines represent results from the Drude model for both uncharged and charged (\(\frac{\Delta N}{N} = 14\%\)) states. The parameters \(\omega_p = 9\) eV, \(\gamma = 67\) meV and \(\epsilon_\infty = 9.84\) were used to fit the experimental data with the above-mentioned Drude model, and were obtained from the work by Sönichsen.[32] The imaginary part of the dielectric constant for wavelengths below 700 nm cannot be properly fit with the Drude model due to the contributions from interband transitions.[32] As the resonance position is dependent primarily on the real part of the dielectric function, a proper fit of the real part is required to accurately calculate the resonance position. This requirement is satisfied by the Drude model for wavelength higher than 500 nm. However, the peak intensity and width might be strongly dependent on the imaginary part. Therefore, we might not be able to describe accurately the extinction intensities and widths below 700 nm. For plasmon resonance modes below 500 nm, Drude dielectric function fails to predict the exact position of plasmon mode as the real part of the dielectric function deviates from the experimental data. Since the amount of charge injected into nanoparticles can be varied by double-layer capacitance and applied electrochemical potential, we considered a wide range of charging levels (\(\frac{\Delta N}{N} = [-7\%, 7\%, 14\%, 21\%]\)) in the electrodynamics calculations.

2.2.2 Discrete Dipole Approximation (DDA)

The Discrete Dipole Approximation (DDA) is time independent method used to calculate the extinction properties of nanoparticles with arbitrary geometry and composition. It has been extensively employed in surface plasmon resonance
Figure 2.1. (a) Real and (b) Imaginary parts of the frequency-dependent dielectric function of gold. Experimental data from Johnson et al.[33] (solid circles) and the fitted Drude model (parameters obtained from Sönnichsen et al.[32]) for uncharged state (solid line) and charged state with $\Delta N/N = 14\%$ (dotted line).

calculations. DDA was first developed by Purcell and Pennpacker,[34] and was later improved by Draine and Flautre.[35, 36] DDA calculates the extinction spectra by describing the particle shape as a collection of $M$ dipoles arranged in cubic lattice such that each dipole responds to both the incident electric field and electric fields induced by neighboring dipoles. The polarization $\mathbf{P}_j$ of a dipole $j$ is given by $\alpha_j \mathbf{E}_j$, where $\alpha_j$ is the polarizability and $\mathbf{E}_j$ is the sum of the incident electric field $\mathbf{E}_{\text{inc},j} = \mathbf{E}_0 e^{i\mathbf{k} \cdot \mathbf{r}_j}$ and the electric field arising from the $M-1$ other dipoles. The total electric field of $j^{th}$ dipole is then given by

$$\alpha_j^{-1} \mathbf{P}_j = \mathbf{E}_j = \mathbf{E}_{\text{inc},j} - \sum_{l\neq j} A_{jl} \cdot \mathbf{P}_l, \quad (2.6)$$

where the electric field from the other $M-1$ dipoles are given by
Polarizations vectors of each dipole were calculated by solving the $3M$ complex linear equations resulting from eq 2.6. In order to calculate these linear equations we used the DDSCAT program by Draine and Flateau[36] which uses Fast Fourier transformations and complex conjugate methods[37] to calculate the polarization vectors for a large number of dipoles. These calculated polarizations and incident electric fields are used to calculate extinction cross-section of the nanoparticle based on the optical theorem given by[26]

$$C_{\text{ext}}(\lambda) = \frac{4\pi k}{|E_o|^2} \sum_{i=1}^{M} \text{Im}(E_{\text{inc},i}^* \cdot P_i), \quad (2.8)$$

where $k$ is the wave vector equal to $2\pi m/\lambda$ and $m$ is the RI of the particle relative to the medium at wavelength $\lambda$. The extinction cross-section is normalized as the extinction efficiency, $Q_{\text{ext}} = C_{\text{ext}}/C_{\text{geom}}$, where the extinction cross-section is divided by the cross-section of a sphere with effective area $C_{\text{geom}} = \pi r_{\text{eff}}^2$. In this work, the lattice constant of 1 nm was taken for nanodisk and nanorod calculations to ensure accurate extinction spectra.[38]

### 2.2.3 Mie Scattering Theory (MST)

Calculations based on Mie Scattering Theory (MST) are used to investigate the extinction spectra of hollow and solid nanoshells due to the capability of MST in obtaining the exact full solution to Maxwell’s equation for the spherical nanoshells. This method involves solving Maxwell’s equations in spherical coordinates with appropriate boundary conditions. According to MST, the extinction cross-section of core-shell structure is given by

$$C_{\text{ext}} = \frac{2\pi}{|k|^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re} (a_n + b_n), \quad (2.9)$$

where the scattering coefficients $a_n$ and $b_n$ are given by
When nanorods are suspended in solution, two types of polarization modes can be defined as the ratio of length to diameter. Further, for each nanorod or nanodisk of specific AR, the influence of polarization of incident light on the CIPS is considered. In order to study the effects of geometry on CIPS in nanorods and nanodisks, we considered various AR’s but maintained a constant volume. The AR of nanodisks in this work is defined as the ratio of diameter to height, and for nanorods it is defined as the ratio of length to diameter. In order to study the effects of geometry on CIPS in nanorods and nanodisks, we considered various AR’s but maintained a constant volume. The AR of nanodisks in this work is defined as the ratio of diameter to height, and for nanorods it is defined as the ratio of length to diameter. Further, for each nanorod or nanodisk of specific AR, the influence of polarization of incident light on the CIPS is considered. When nanorods are suspended in solution, two types of polarization modes can be defined as the ratio of length to diameter. Further, for each nanorod or nanodisk of specific AR, the influence of polarization of incident light on the CIPS is considered.
Figure 2.2. Extinction spectra of (a) in-plane polarization mode of nanodisks and (b) longitudinal polarization mode of nanorods at constant $r_{eff}=10$ nm of AR’s, 2.5 (thick lines) & 4.5 (thin lines) for uncharged state (solid lines) and charged states, $\frac{\Delta N}{N} = 14\%$ (dotted lines).

Figure 2.3. (a) Calculated CIPS for $\frac{\Delta N}{N} = 14\%$ and various nanorod AR’s, longitudinal modes (triangles) and transverse modes (inverted triangles); in nanodisks, in-plane mode (squares) and out-of plane mode (diamonds). (b) Longer wavelength plasmonic mode CIPS for various charging levels, nanorods with AR = 4.5 (triangles) and 2.5 (half filled triangles); nanodisks with AR = 4.5 (squares) and 2.5 (half filled squares). Solid lines are best fits.
excited by linearly polarized or natural light. If the incident light has the electric field parallel to the longitudinal axis of nanorods, longitudinal plasmon mode is excited; and if the electric field is perpendicular to longitudinal axis, transverse modes get excited. Similarly in nanodisks, two types of modes, i.e., in-plane and out-of-plane modes, can be excited by controlling alignment between polarization of incident light and disk plane. In the in-plane polarization mode, the incident light direction is normal to the disk plane and the electric field is parallel to the diameter axis, whereas in the out-of-plane mode, the incident light direction is parallel to the disk plane and electric field perpendicular to the diameter axis.

Fig. 2.2(a) illustrates the uncharged and charged state extinction spectra of two types of nanodisks with AR’s of 2.5 and 4.5, respectively. These spectra were obtained by in-plane polarized incident light. In Fig. 2.2(a) the uncharged state’s peak resonance wavelength ($\lambda_o$) for nanodisks with AR = 4.5 is larger than that of AR = 2.5. Both nanodisks’ peak positions blueshift upon charging ($\Delta N = 14\%$).

In Fig. 2.2(b) we compare the uncharged and charged state spectra of nanorods of two different AR’s, 2.5 and 4.5, when subjected to longitudinal polarized incident light. When volume is held constant, nanorods of AR = 4.5 exhibit an uncharged state peak resonance wavelength near the infrared region, whereas nanodisks at the same AR are in the range of visible light. Similar to the nanodisks, the nanorods’ spectra blue shifts upon electron charging. Figures 2.2(a) and 2.2(b) thereby show that the CIPS in nanodisks and nanorods are dependent on their AR’s.

To quantitatively evaluate the relation between CIPS and AR of nanorods and nanodisks, our electrodynamics calculations included a fixed charge injection ($\Delta N = 14\%$) for various AR configurations. For each AR, different polarizations of incident light were also considered in order to understand the effects of polarization on CIPS. These results are summarized in Fig. 2.3(a), where the blueshifts of plasmonic resonance for various geometries and polarizations are plotted against the AR of the nanoparticles. The CIPS due to transverse polarizations in the nanorods and out-of-plane polarizations in the nanodisks remains almost constant as shown in Fig. 2.3(a). It should be however noted that the transverse modes in nanorods and out-of-plane modes in nanodisks for certain AR’s fall below 500 nm and therefore the exact position of plasmon resonance could not be calculated accurately with the Drude dielectric function. In contrast, the longitudinal polarization of nanorods
and the in-plane polarization of nanodisks result in larger CIPS, which follows an increasing linear dependence on AR. From the slopes of linear fits in Fig. 2.3(a), we observe that at a certain charging level, AR and volume, nanorods exhibit more CIPS than nanodisks; this difference in CIPS increases with AR. To further evaluate the effects of charging on the CIPS, we calculated the shifts of the longer wavelength plasmonic mode resonances (in-plane polarization mode in nanodisks and longitudinal polarization mode in nanorods) by considering different levels of charging. Fig. 2.3(b) shows the effect of charging level and AR on CIPS. From Fig. 2.3(b), we can observe that for both nanorods and nanodisks, CIPS at a particular AR follows a linear relationship at lower charging levels and this linear behavior deviates at higher charging levels. For a range of charging levels and constant volumes, geometries with higher AR result in larger plasmonic shifts, and CIPS in nanorods is larger than that in nanodisks.

2.3.2 Hollow and Solid Nanoshells

Metal nanoshells have attracted tremendous interest for their ability to obtain plasmonic resonance over a large range by controlling the shell thickness or core compositions.\cite{11,41} To understand the effect of shell composition on CIPS, we carried out a series of electrodynamic calculations using MST on hollow and solid shells. The RI of the hollow shells core was taken to be equal to the surrounding environment (water), while the RI of the solid shell was varied from 1.333 to 2.332. To understand the effect of VF on plasmonic shifts, different radius ratios, $\frac{R_c}{R_m}$, were considered, where $R_c$ is the radius of the core and $R_m$ is the total radius of the core-shell particle. The radius ratios of the nanoshells can be engineered and nanoshells of radius ratio between 0.33 and 0.92 have been fabricated and studied in the past.\cite{42}

Fig. 2.4(a) and 2.4(b) shows the uncharged and charged state ($\frac{\Delta N}{N} = 14\%$) spectra of hollow and solid nanoshells (RI = 2.332) with different VF’s. It can be seen that the peak resonance wavelength in both solid and hollow nanoshells at different VF’s blueshift on charging, a behavior similar to that of nanodisks and nanorods. It is also observed that the CIPS and uncharged state peak position ($\lambda_o$) in nanoshells are a function of composition and VF of the core.
Figure 2.4. Extinction spectra of (a) hollow nanoshells and (b) solid nanoshells at constant $r_{eff}=10$ nm; radius ratios are 0.8 (thick lines) & 0.95 (thin lines) for the uncharged state (solid lines); and for the charged states (dotted lines), $N = 14\%$. The two peaks at a certain charge state and volume fraction represent two different energy plasmonic resonances.

To evaluate the dependence of CIPS on the VF of the core, a series of electrodynamic calculations using MST was performed with various VF’s and the results are summarized in Fig. 2.5(a). The charge-induced plasmonic blueshift increases with increasing radius ratio between the core and the mantle. This increase is slow when the radius ratio is smaller than 0.7. However, as the radius ratio reaches unity, rapid increasing in CIPS occurs. It can also be observed that solid nanoshells with core RI higher than hollow nanoshells result in larger shift at a particular radius ratio.

The effect of charging level and VF’s on CIPS in both hollow and solid nanoshells is shown in Fig. 2.5(b). CIPS at a particular RI and VF of the core follow a linear relationship with the amount of charging. This linear behavior deviates after a certain value of charging, much like the behavior of solid nanoparticles (nanodisks and nanorods). From Fig. 2.5(b), it can also be observed that a higher RI of the core in conjunction with a higher VF lead to larger CIPS over a range of charging levels. The lines in Fig. 2.5(a) & 2.5(b) correspond to the shifts predicted by
Figure 2.5. CIPS of longer wavelength plasmon mode in nanoshells, by MST calculation (discrete points) and by eq’s 2.25&2.27 based on quasistatic theory (lines) for a) charging ($\Delta N/N = 14\%$) different radius ratios (0.2 to 0.95), hollow nanoshells (hollow circles) and solid nanoshells with core RI = 2.332 (solid circles); (b) different amounts of charging ($\Delta N/N = -7\%$ to $+ 21\%$) at constant $r_{eff}=10$ nm, in hollow nanoshells with different radius ratios (0.6, the smaller hollow circles; 0.95, the larger hollow circles) as well as solid nanoshells with different radius ratios (0.6, the smaller solid circles; 0.95, the larger solid circles).

quasistatic approximation described in the next section. In addition, Fig. 2.6 presents the dependence of plasmonic shifts on RI at different AR’s. It can be seen that plasmonic shifts follow a linear relationship with the RI of the core. The slopes of the linear fits indicate that higher core VF causes larger CIPS in the nanoshells.

2.3.3 Quasistatic Theory Approximation

In comparison with the electrodynamics calculations presented above, analytic expressions provide an intuitive way to understand and interpret qualitative behavior of the plasmonic shifts. In this section we focus on quasistatic theory to understand the effects of geometry and composition on CIPS in nanoparticles. In quasistatic theory, the spatial variation of the electromagnetic field is neglected and only temporal variation is considered, with the aim of calculating an approximate peak resonance wavelength.[31] Mulvaney et al.[25] have used quasistatic theory and the
Drude model to explain the dependence of nanorod AR on CIPS. In their work, as the charge injection was performed by reducing gold nanorods using NaBH\textsubscript{4} and also to simplify the formulation, they assumed that the amount of added internal free electron density is much smaller than the existing internal free electron density, (\(\frac{\Delta N}{N} \ll 100\%\)). As the amount of charge injected into the nanoparticles can be increased by applying a greater electrochemical potential or increasing the double-layer capacitance, we have considered higher levels of charging in our model. We also extend our investigation into various other nanoparticle geometries (nanodisks and nanoshells).

According to quasistatic theory, the polarizability \(\alpha_1\) of nanodisks and nanorods when approximated as oblate and prolate spheroids respectively is given by [26]

\[
\alpha_1 \propto \left( \frac{\epsilon_1 - n^2}{n^2 + L(\epsilon_1 - n^2)} \right),
\]

where \(\epsilon_1\) is the Drude type dielectric function of nanorods and nanodisks; \(n\) is the RI of the surrounding medium; and \(L\) is a geometry-dependent polarization factor for nanodisks and nanorods. The resonance condition corresponds to a wavelength at which the denominator of the polarizability equals to zero:

\[\Delta \lambda (\text{nm}) = 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80\]
\[ \text{Real}(n^2 + L(\epsilon_1 - n^2)) = 0. \]  

(2.15)

In the frequency range where \( \epsilon_1'' \) is small or changes very slowly, \( \epsilon_1 \) can be considered equal to \( \epsilon_1' \). Thus, the resonance condition is given by

\[ \epsilon_1^{\text{reso}} = \left( 1 - \frac{1}{L} \right) n^2. \]  

(2.16)

The polarizability of a solid shell, \( \alpha_2 \), characterized by a core RI \( n_{\text{core}} \), a mantle dielectric constant \( \epsilon_2 \), a mantle VF \( P \), and a surrounding RI \( n \) is given by [26]

\[ \alpha_2 \propto \left( \frac{\epsilon_2 \epsilon_a - n^2 \epsilon_b}{\epsilon_2 \epsilon_a + 2n^2 \epsilon_b} \right), \]  

(2.17)

where

\[ \epsilon_a = n_{\text{core}}^2(3 - 2P) + 2\epsilon_2 P, \]  

(2.18)

\[ \epsilon_b = n_{\text{core}}^2 P + \epsilon_2(3 - P), \]  

(2.19)

and,

\[ P = 1 - \left( \frac{\text{Rad}_{\text{core}}}{\text{Rad}_{\text{mantle}}} \right)^3. \]  

(2.20)

The poles of the polarizability expression are obtained by from the denominator of eq 2.17 as

\[ \text{Real}[\epsilon_2 \epsilon_a + 2n^2 \epsilon_b] = 0. \]  

(2.21)

The resonance condition of solid nanoshells is therefore given by

\[ \epsilon_2^{\text{reso}} = \frac{1}{4P} \left[ -(n_{\text{core}}^2(3 - 2P) + 2n^2(3 - P)) \pm \sqrt{(n_{\text{core}}^2(3 - 2P) + 2n^2(3 - P))^2 - 16P^2n^2n_{\text{core}}^2} \right]. \]  

(2.22)

In the case of hollow nanoshells, the RI of the core is equal to the surrounding RI, \( n_{\text{core}} = n \). Upon incorporating this condition in eq 2.22, the resonance condition for hollow nanoshells is given by
\[ \epsilon_3^{reso} = \frac{n^2}{4P} \left[-(9 - 4P) \pm 3\sqrt{9 - 8P} \right]. \] (2.23)

The two solutions of resonance condition in nanoshells represent plasmon modes of two different energies and correlate with two peaks (one below 500 nm and other above 500 nm) observed in the extinction spectra shown in Fig. 2.4(a) and 2.4(b). The two fundamental dipolar modes of core-shell nanoparticle can be thought to arise from the hybridization of a dipolar modes of the metallic sphere and a dielectric void in a metal substrate.[43]

The charged-state resonance wavelength (\(\lambda_{\Delta N}\)) is obtained by equating the charged-state dielectric constant of the nanoparticle (\(\epsilon_{\Delta N}^{'}\)) to the dielectric constant at resonance (\(\epsilon_i^{reso}\)). The charged-state dielectric constant of the nanoparticles is obtained from the real part of the Drude model as discussed in section 2.2.1

\[ \epsilon_{\infty} - \frac{\omega_p^2(1 + \Delta N/N)}{\omega^2 + \gamma^2} = \epsilon_i^{reso}, \quad i=1,2,3. \] (2.24)

Substituting \(\omega = \frac{c}{\lambda_{\Delta N}}\) and \(\omega_p = \frac{c}{\lambda_p}\) in eq 2.24, we obtain an expression relating the resonance wavelength to the amount of charging, geometry and composition:

\[ \lambda_{\Delta N} = \frac{\lambda_p \sqrt{A_i}}{\sqrt{1 + \frac{\Delta N}{N} - \frac{\gamma^2 A_i}{\omega_p^2}}}, \] (2.25)

where

\[ A_i = \epsilon_{\infty} - \epsilon_i^{reso}, \quad i=1,2,3. \] (2.26)

The uncharged state resonance position (\(\lambda_o\)) is obtained by substituting \(\Delta N = 0\) in eq 2.25

\[ \lambda_o = \frac{\lambda_p \sqrt{A_i}}{\sqrt{1 - \frac{\gamma^2 A_i}{\omega_p^2}}}. \] (2.27)

Furthermore, the sensitivity of the nanoparticle, defined as the ratio of CIPS (\(d\lambda = \lambda_{\Delta N} - \lambda_o\)) to the change in free electron density (\(dN\)) is obtained by subtracting eq. 2.27 from eq. 2.25 and dividing by the amount of charge injection.
\[
\frac{d\lambda}{dN} = \frac{\lambda_o}{(\frac{A_i}{\omega_p})^2} \left[ \sqrt{1 - \frac{\gamma^2 A_i}{\omega_p^2}} - 1 \right] .
\]  
\[
(2.28)
\]

where

\[
A_i = \frac{(\lambda_0\omega_p)^2}{(\lambda_p\omega_p)^2 + (\lambda_0\gamma)^2} .
\]  
\[
(2.29)
\]

Eq's 2.27 & 2.25 give the plasmonic shifts for various amounts of charging and various core VF’s in solid and hollow nanoshells; the parameters \(A_2\) and \(A_3\) incorporate the effect of the core’s VF and composition. CIPS of longer peak wavelength in nanoshells calculated based on quasistatic theory (eq’s 2.27 & 2.25) and MST are shown in Figures 2.5(a) and 2.5(b) for solid and hollow nanoshells respectively. These figures show the dependence of core VF and level of charging on the plasmonic shifts in nanoshells. In nanodisks and nanorods, the exact relationship between AR and \(L\) is unknown, but for shapes such as prolate and oblate spheroids the exact relationship between AR and L is known and it is recognized in these shapes that higher AR’s have lower L’s. From Eqs. 2.16, 2.25 & 2.27, as AR increases or L decreases, the value of \(\lambda_o\) increases as does the difference between \(\lambda_o\) and \(\lambda_{\Delta N}\). This behavior of higher CIPS at higher AR agrees with the electrodynamics calculations shown in Fig. 2.3(a). Eq’s 2.22, 2.25 & 2.27 when combined demonstrate the dependence of CIPS in solid nanoshells on the RI of core and the VF. These equations rationalize the almost linear dependence of CIPS with the RI of core as observed in Fig. 2.6.

Eq. 2.28 estimates the plasmon shift sensitivity of a nanoparticle independent of its geometric parameters. The expression shows that the sensitivity is dependent only on the uncharged state resonance wavelength (\(\lambda_0\)) and the amount of charging (\(\Delta N\)). Fig. 2.7 presents the sensitivity of the plasmonic shift as a function of uncharged state resonance wavelength for all five geometries. Fig. 2.7(a) compares the sensitivities of particles as calculated by DDA with analytic sensitivity expressions obtained from quasistatic theory. It can be observed that nanorods in general for comparable amounts of charging and volume are more sensitive than nanodisks due to the nanorods’ higher uncharged state resonance wavelength. Fig. 2.7(b) shows MST calculation results on nanoshells of various VF’s and core RI, as
well as a quasistatic analytical expression of sensitivity.

The expression for the plasmon shift sensitivity, Eq 2.28, can be further simplified by assuming low levels of charging and neglecting the contributions from relaxation constant term. Using a binomial series expansion of the right hand side of Eq 2.28 and neglecting higher order terms, we obtain

\[
\frac{d\lambda}{dN(N)} = \frac{\lambda_o}{2}
\]  

(2.30)

This equation indicates that the sensitivity of charging is approximately constant and is equal to the half of the uncharged resonance position.

To develop nanoparticle-based devices with highly tunable CIPS, one must carefully design the particles’ geometry and composition. As shown in Fig. 2.7(a) and 2.7(b), lower energy or higher wavelength resonances result in higher sensitivities. The location of the extinction band in uncharged-state solid nanoparticles can be adjusted to obtain higher sensitivities. The adjustment in the band location can be achieved through changing the particles’ shape or relative dimensions (such as AR). In composite structures, such as hollow and solid nanoshells, both geometrical variations and RI of the core can be engineered to lower the energy of the extinction wavelength.

The uncharged optical resonance position ($\lambda_o$) has been shown to redshift with an increase in the size of nanoshells and nanorods.[31, 39] Therefore, CIPS sensitivity can be enhanced by increasing the size of the nanoparticle. But variations in double layer capacitance due to changes in size must be taken into account. Electrodynamics calculations in this study were performed assuming a constant RI of the surrounding environment. An increase in the surrounding environment’s RI generally redshifts the resonance position.[18, 21, 40, 44] Choosing a higher RI of the surrounding medium before charging would reduce the uncharged state’s resonance energy and increase its CIPS sensitivity. A higher RI of the medium also increases the double layer capacitance of the nanoparticles, which increases the amount of charging per unit potential.

Nanodisks and nanorods fabricated on a substrate by top-down fabrication methods have the advantage of controllable polarization modes, unlike nanoparticles in colloids which have random polarization orientation. Control over polarization
Fig. 2.7. Dependence of CIPS sensitivity on uncharged optical resonance position ($\lambda_0$), electrodynamics calculations (discrete points) and by eq 2.28 based on quasistatic theory (line) at $\frac{\Delta N}{N} = 14\%$ for (a) nanodisks (squares) & nanorods (triangles) and (b) hollow (open circles) and solid nanoshells (solid circles).

will lead to higher sensitivity. In our electrodynamics model, the nanoparticles were surrounded by a homogenous medium (water). A substrate beneath the nanoparticles has a higher RI than the surrounding medium, and thus will cause a redshift of the resonance[31, 45] and increase the CIPS sensitivity. Sensitivity can be further enhanced by applying a polymer film on top of the nanoparticles, because the polymer film increases the capacitance of the system.[2, 46] In arrays of nanoparticles fabricated by nanosphere lithography, the interparticle distance should be optimized. Two effects should be considered for optimization: 1) dipole-coupling interactions between nanoparticles should be reduced to increase the CIPS sensitivity[2], and 2) the amount of charge injection should not be limited by charge induced Rayleigh instabilities[47].

2.4 Conclusions

Toward the development of highly sensitive, charging-based active plasmonic devices, we have studied the effects of electron injection in nanorods and nanodisks of various AR, and nanoshells of various core VF’s and RI’s. Using accurate electrodynamics
calculations, it is shown that both the nanoparticles’ geometry and composition significantly affect their CIPS sensitivities. In nanorods and nanodisks of constant volume, CIPS sensitivity can be increased by using longitudinal and in-plane polarized light respectively, and by choosing higher AR geometries. In nanoshells, the CIPS sensitivities are higher for nanoshells with higher RI and VF of the core. Irrespective of shape and composition, it was shown by quasistatic theory that the CIPS sensitivity of the particles at a particular charging level depends linearly on the resonance position ($\lambda_o$) of the uncharged state. This relationship matches with our electrodynamic calculations; from these findings we conclude that nanoparticles with higher $\lambda_o$ are more sensitive to CIPS. The particles’ CIPS can be further enhanced by increasing the size of the particles or the RI of the surrounding medium.

### 2.5 Acknowledgments and Copyright Information

Chapter 2 is a modified version of the author’s publication: B. K. Juluri, Y. B. Zheng, D. Ahmed, L. Jensen, and T. J. Huang, Effects of Geometry and Composition on Charge-induced Plasmonic Shifts in Gold Nanoparticles, *Journal of Physical Chemistry-C*, Vol. 112, pp. 7309-7312, 2008. We also acknowledge the support from the High Performance Computing Group at The Pennsylvania State University. This research was supported by the NSF NIRT grant (ECCS-0609128).
References


Chapter 3

Resonant Coupling between Molecular and Plasmonic Resonances

3.1 Introduction

The past two decades have witnessed tremendous research focused on understanding the interactions between electromagnetic radiation and metal nanostructures. The motivation stems from the promise that localized surface plasmon resonance (LSPR) will provide significant advances in areas such as molecular imaging, biological sensing and nanophotonic devices. [1–3] Many of these applications require control over LSPR wavelength, which can be achieved using changes in shape, size, [4–7] electron density, [8, 9] inter-particle distance [10, 11] and surrounding refractive index [6, 12–14]. Currently, it is widely recognized that frequency-independent dielectric material positioned on a metal nanoparticle will linearly red shift the LSPR wavelength. [3, 7, 15] However, it is only recently that a metal nanoparticle covered with a layer of resonant molecules has attracted interest in the plasmonics community. It has been shown that the presence of strongly absorbing molecules on the metal nanoparticle surface result in resonant coupling between molecular and plasmonic resonances. [16–21] Resonant coupling is characterized by the formation of new hybridized states in the extinction spectra, and the energy of these states
can be engineered significantly by controlling the spectral overlap between the plasmonic and molecular resonances, similar to the vacuum-field Rabi splitting observed in cavity-polaritron systems. Such control over hybridized states paves a way to enhance the application of plasmonics in realizing tunable nanophotonic devices, molecular sensing, and plasmonic resonance energy transfer (PRET) methods.

Kometani et al. were among the first to observe resonant coupling effects in resonant molecule-coated plasmonic nanostructures. They observed an absorption dip in the extinction spectra of J-aggregate-coated silver and gold nanoparticles. Wiederrecht et al. later explained that this observation arose from coherent coupling between molecular excitons and electronic polarizations of noble metal nanoparticles. The effects of resonant coupling as a function of spectral overlap were experimentally reported by Wurtz et al. who used J-aggregate molecules on nanowire assemblies with tunable LSPR. Ni et al. later extended these ideas to solution-bound gold nanorods. Using nanoshells and J-aggregates, Fofang et al. observed similar behavior in both dipolar and quadrupolar plasmonic resonances. From these studies, it is clear that the extinction spectra of nanoparticles covered with resonant molecules are not a simple sum of absorption contributions, but rather strongly influenced by the strength of resonant coupling which is maximized at the spectral overlap of the resonances.

The successful application of resonant coupling for various applications mentioned above relies on maximizing the splitting between hybridized states at the spectral overlap. Fofang et al. reported an increase in the splitting by controlling the concentration of dye in plasmon-exciton nanostructures. They speculated that the thickness of the molecular layer controlled the magnitude of splitting. For cavity-polaritron and other analogous systems, factors affecting the splitting have been thoroughly studied over the last decade. It has been shown both theoretically (quantum mechanical and classical) and experimentally that the splitting can be controlled by the absorbance of the absorber used in the cavities. One would therefore expect similar behavior in resonant molecule-coated plasmonic nanoparticle systems. In this work, we experimentally show that the splitting observed in resonant molecule-coated plasmonic nanostructures can be controlled by changing the absorbance, $A$, of the molecular layer. A linear relation-
3.2 Plasmon-Excitation Coupling

3.2.1 Effect of Absorbance: Experiments

To understand the plasmon splitting due to hybridization, we studied the extinction spectra of a resonant molecule-coated plasmon nanostructure that consisted of gold nanorod and J-aggregates as a function of the molecular absorbance by varying the concentration. A schematic of the J-aggregate-coated nanorods together with the molecular structure of the J-aggregate is shown in the inset of Fig. 3.1.

Figure 3.1. Extinction spectra of gold nanorods and absorption spectra of J-aggregates. The inset shows a schematic of a resonant molecule-coated plasmonic nanostructure consisting of gold nanorod and J-aggregate molecules.
Figure 3.2. (a) Experimental extinction spectra of J-aggregate-coated nanorods using different concentrations of dye solution. (b) Plasmon splitting as a function of $\sqrt{A}$. The dotted line is a linear fit of the form $y = ax$.

Bare gold nanorods with diameter 35 nm and length 90 nm were purchased from Nanopartz Co. (Salt Lake, UT) and used in the experiments without any further modification. These nanorods exhibited a transverse plasmon resonance at 533 nm and a longitudinal plasmon resonance at 692 nm (Fig. 3.1). The J-aggregate used in the experiments was 2, 2'-dimethyl-8-phenyl-5, 6, 5', 6'-dibenzothiacarbocyanine chloride, and was characterized by a strong absorption at 693 nm upon aggregation on a nanorod surface. This absorption wavelength overlaps with the LSPR of the gold nanorods (Fig. 3.1). The absorbance of the molecular layer was controlled by using various amounts of dye solutions (prepared in a mixture of water/ethanol-50/50 by volume) that were added to the nanorod solution. The mixture was stirred for 5 min and was kept undisturbed for 36 h to allow aggregation of molecules on the nanorod surface. Fig. 3.2(a) shows the extinction spectra of the J-aggregate-coated nanorods as a function of concentrations of dye solution used. From the extinction spectra, we see clearly the splitting of the plasmon band into two distinct peaks at positions different from the peak positions of the isolated molecular resonance and the plasmon band of the nanorods. It is also shown in Fig. 3.2(a) that the splitting increases as higher concentrations of the molecules are used. This increased splitting can be explained by increased coverage of the resonant molecules on the nanoparticle surface. Recently, Ni et al. [25] and Zhao et al. [32] reported plasmon shift of nanorods and nanoprisms, respectively, as a function of the concentration of resonant molecules. However, these systems did not exhibit hybridization-induced
plasmon splitting. In the case of Ni et al. [25], who used nanorods similar to the work presented here, a minor peak in the molecular adsorption precluded the observation of the splitting.

The observed larger splitting at higher molecular concentration is a result of stronger absorption of the molecular layer since more molecules are adsorbed on the nanoparticle. The molecular absorbance of a monolayer is given by $A = \sigma \times N_o \times \theta$, where $\sigma$ is the absorption cross section of the resonant molecules, $N_o$ is the saturated coverage, and $\theta$ is the coverage of the resonant molecules on the nanoparticle surface. [33, 34] The coverage follows a Langmuir isotherm given by $\theta = \frac{aC_s}{1+aC_s}$, where $a$ is the adsorption equilibrium constant and $C_s$ is the concentration of the adsorbate in solution. For a given resonant molecule and constant surface area of nanoparticles, the absorbance only varies with $\theta$ since $\sigma$ and $N_o$ are fixed. Thus, to calculate $A$ as a function of concentration we assume $N_o$, $\sigma$ and $a$ to be 1, 1, and $1.45 \mu M^{-1}$, respectively. These values were chosen to normalize $\sqrt{A}$ such that $\sqrt{A} = 1$ for $\theta = 1$, i.e. complete monolayer, and when $\sqrt{A} = 0$ no molecular layer is present. The actual values used in the calculation only change the magnitude of absorbance but not the dependence on concentration. To obtain the magnitude of splitting as a function of concentration we fitted the two peaks in the extinction spectra using two Lorentzians and a third-order polynomial function. The splitting between the two hybridized states as a function of $\sqrt{A}$ is plotted in Fig. 3.2(b). We see that the splitting is linearly dependent on $\sqrt{A}$, as expected from its similarities with microcavity-polariton systems [27–31] and surface plasmon-polariton systems [35, 36]. Therefore, by simply changing the absorbance of the molecular layer, either by increasing the coverage as demonstrated here or using dye molecules with different absorption cross sections, it is possible to tune the coupling between the plasmon and molecule resonances.

3.2.2 Modeling the Effect of Absorbance

In order to understand the plasmon splitting as a function of $\sqrt{A}$, we calculated the extinction spectra of a prolate spheroid covered with a layer of resonant molecules using classical electrodynamics. The nanoparticles used in this work is small enough that they had a dipolar response to incident light, thus, a quasi-static approximation
Figure 3.3. (a) Extinction spectra calculated using Eq. 3.1 for various oscillator strengths. (b) Calculated splitting as function of $\sqrt{A}$. The dotted line is a linear fit of the form $y = ax$.

is appropriate. The polarizability in the quasi-state limit for a two-layer prolate spheroid embedded in a dielectric medium is given by: [37]

$$\alpha = V \left( (\varepsilon_2 - \varepsilon_m) \left[ \varepsilon_2 + (\varepsilon_1 - \varepsilon_2) \left( L^{(1)} - f_v L^{(2)} \right) \right] + f_v \varepsilon_2 (\varepsilon_1 - \varepsilon_2) \right) / \left( (\varepsilon_2 + (\varepsilon_1 - \varepsilon_2) \left( L^{(1)} - f_v L^{(2)} \right) \right) \left[ \varepsilon_m + (\varepsilon_2 - \varepsilon_m) L^{(2)} \right] + f_v L^{(2)} \varepsilon_2 (\varepsilon_1 - \varepsilon_2) \right),$$

(3.1)

where $V$ is total volume of the system, $f_v$ is the fraction of the total volume occupied by the nanorod, $L^{(1)}$ and $L^{(2)}$ are the geometric parameters for metal and molecular spheroids, respectively, and $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$ are the dielectric functions of the gold nanorods, molecular layer and the surrounding medium, respectively. From the polarizability, the extinction cross-section is straightforwardly given by: [37]

$$\sigma(\omega) = \frac{4k}{V} \text{Im} \left[ \alpha(\omega) \right].$$

(3.2)

To model the gold nanorods, we used a spheroid with a spherical radius, $R$, of 23.97 nm with an aspect ratio of 3.14 so as to match the experimental LSPR of 692 nm. The dielectric constant of gold were described by a Drude model

$$\varepsilon_1(\omega) = \varepsilon_{\infty 1} - \frac{\omega_p^2}{\omega(\omega + i\gamma)},$$

(3.3)
where \( \varepsilon_{\infty 1} \) is the contribution from the bound electrons in the metal (9.84 eV), \( \omega_p \) is the bulk plasmon frequency of gold (9 eV), and \( \gamma \) is the plasmon relaxation constant (67 meV). [38] To compensate for various inhomogeneous broadening effects in the experimentally observed extinction spectra, the value of \( \gamma \) was multiplied by a factor of 2.4. The dielectric constant of the molecular layer was modeled as a one-oscillator Lorentzian model given by:

\[
\varepsilon_2(\omega) = \varepsilon_2(\omega)^\prime + \varepsilon_2(\omega)^\prime\prime = \varepsilon_{\infty 2} + \frac{f \omega_2^2}{\omega_2^2 - \omega^2 - i\omega \Gamma},
\]

where \( \varepsilon_{\infty 2} \) is the high frequency component of the dielectric constant (1.768), \( \omega_2 \) is the molecular excitation frequency (1.789 eV), \( \Gamma \) is the excitation linewidth (52 meV), and \( f \) is the reduced oscillator strength which we will vary in the calculations to simulate different absorption cross sections. [26] In all simulations, the surrounding medium was assumed to be water with a dielectric constant of 1.768.

In the experiments, the absorption coefficient was constant since we only studied one kind of molecule and assumed a monolayer of molecules; thus the absorption only varied with the coverage. However, in the simulations we relate the absorption to \( A = \alpha' \times t_m \), where \( \alpha' \) is the absorption coefficient and \( t_m \) is the thickness of the molecular layer. In this way, we can simulate the splitting both as a function of thickness and the absorption coefficient. The absorption coefficient is related to the imaginary part of the refractive index as, \( \alpha' = \kappa \frac{\pi}{\lambda} \), where \( \kappa = \text{Im}(\sqrt{\varepsilon_2}) \), is a function of \( \omega_2, \varepsilon_{\infty 2}, f \) and \( \Gamma \). At \( \omega = \omega_2 \),

\[
\kappa = \left[ \frac{\varepsilon_{\infty 2}^2 + \left( \frac{f \omega_2}{\Gamma} \right)^2}{2} - \varepsilon_{\infty 2} \right]^\frac{1}{2} \frac{1}{2}
\]

To investigate the relationship between splitting and \( \sqrt{A} \), we calculated the extinction spectra of resonant molecule-coated nanorods for various absorbance levels by changing the magnitude of the oscillator strength, \( f \), and the thickness of the molecular layer, \( t_m \). In Fig. 3.3(b), we plot the extinction spectra calculated using Eq. 3.1 for a gold nanorod covered with a layer of resonant molecules of thickness
Figure 3.4. Calculated splitting as function of $\sqrt{A}$ for various thickness (0.05R to 0.2R) and oscillator strength of the molecular layer (0.02 to 0.07).

$t_m = 0.06R$ (1.44 nm) at different oscillator strengths ranging from 0.02 to 0.07. The magnitudes of thickness and oscillator strength are consistent with previous reports on J-aggregate-coated nanoparticles. [24, 26] We see from Fig. 3.3(a) that the plasmon band splits into two peaks, representing the two hybridized states resulted from resonant coupling. As the oscillator strength, $f$, of the molecular layer increased, the absorbance of the molecular layer also increased and, thus, the plasmon splitting increased as well. The splitting as a function of $\sqrt{A}$ obtained from the simulations is shown in Fig. 3.3(b) where a linear dependence is found. To investigate further the dependence of the splitting on the absorption we calculated the extinction spectra using different values of molecular layer thickness for different oscillator strengths (ranging from 0.02 to 0.07). The plasmon splitting as a function of $\sqrt{A}$ is plotted in Fig. 3.4 for the different molecular layer thicknesses. We see that the splitting follows a similar linear relationship as a function of absorbance for various thickness of the molecular layer. This is expected since as the molecular
Figure 3.5. (a) Phase shift between the incoming radiation and response of resonant molecule-coated nanoparticle. The inset shows the refractive index $n_m = Re(\sqrt{\varepsilon_2})$ as a function of oscillator strength. (b) Extinction spectra of bare nanorods and nanorod covered with resonant molecules for various absorbance levels at constant $t_m = 0.06R$.

layer became thicker, the magnitude of absorbance increased, resulting in increased splitting for a given oscillator strengths. The calculated linear relationship between plasmon splitting and $\sqrt{A}$ is in excellent agreement with what is observed in the experiments.
3.3 Resonant Coupling Explained by Linear Dispersion model

The linear dependence of the plasmon splitting on $\sqrt{A}$ found in the experiments and classical electrodynamic simulations can be explained by considering the linear dispersion and absorptive properties of the resonant molecular layer. Due to incident radiation, free electrons within the bare gold nanoparticles oscillate. At specific wavelengths of radiation the response and incident radiation are 90° out of phase, which leads to the enhancement of the electric field as well as strong absorption characterized by a peak in the extinction spectrum, the plasmon peak. However, in the case of nanorods covered with resonant molecules, this phase relation happens at multiple frequencies. This is shown in Fig. 3.5, where we plot the phase shift and corresponding extinction spectra for bare nanorods covered with resonant molecules calculated using the quasi-static approximation model for different absorbance. To illustrate the phase relation, we used a molecular layer with a non-absorbing, yet dispersive resonant molecule (i.e., $\varepsilon_2(\omega) = \varepsilon_2(\omega)')$. Obviously, in reality we cannot neglect $\varepsilon_2(\omega)''$ since it is directly related to the real part using the Kramer-Kronig transformation, however, we can use this as a model to explain the plasmon splitting. In the case of the nanorods covered with resonant molecules, the dispersion of the real part of the refractive index of the molecule layer, $n_m = \text{Re}(\sqrt{\varepsilon_2})$, causes the phase to be out of phase by 90° three times due to different boundary conditions (indicated by vertical arrows). This results in three peaks in the extinction spectra and can be seen from Fig. 3.5 where the phase shift and extinction spectra are shown. The central peak position is at the spectral overlap and the other two peaks are positioned on both sides of spectral overlap. As the oscillator strength increased, the molecular layer became more dispersive, the wavelengths where the 90° phase difference occurred moved away from the spectral overlap, and thus the splitting increased. When we included $\varepsilon_2(\omega)''$ into the quasi-static approximation model, the layer of resonant molecules absorbs the incoming radiation and the central peak is cancelled. This contributes further to the shifting of the wavelength where the 90° phase difference occurred resulting in increased splitting. Therefore, as the oscillator strength of the resonant molecule increases, the molecular layers
become more dispersive and absorb more of the incoming radiation, which leads to larger splitting. On the other hand, increasing the thickness of the molecular layer leads to increased absorption of the incoming radiation, which in turn cancels the central peak more effectively and drives larger splitting. Considering these mechanisms, the end result is that an increase in absorbance will lead to larger splitting since it is directly related to both the oscillator strength and the thickness of the molecular layer.

3.4 Conclusions

In conclusion, we have demonstrated experimentally and theoretically that the magnitude of plasmon splitting in resonant molecule-coated nanoparticles due to hybridization can be controlled by the molecular absorbance. The measured extinction spectra of J-aggregate-coated gold nanorods exhibited a linear relationship between the plasmon splitting and $\sqrt{A}$, similar to that observed in systems such as microcavity-polariton and surface plasmon-polariton systems. Using electrodynamic simulations based on the quasi-static approximation, we found a similar linear dependence on absorption either by increasing the oscillator strength of the molecule or the thickness of the molecular layer. A simple physical mechanism showed that the splitting is caused by the dispersion in the real part of the molecular dielectric constant and absorption from the imaginary part, both increases as the absorption increases. The insights gained from this study will be useful in improving applications of resonant coupling, including tunable nanophotonic devices, molecular sensing and PRET methods.

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References


4.1 Introduction

Controlling the optical behavior of molecules near the vicinity of noble metal nanoparticles continues to be an active research area in nanotechnology.[1, 2] An understanding of the phenomena at such metal-molecule complexes is not only important fundamentally, but also essential for applications such as energy harvesting[3], nanoscale optical circuits[4, 5] and ultra-sensitive chemical and biological sensors.[6–13] Of particular interest is the recent discovery of mixed exciton-plasmon states in metal-molecule complexes.[14–22] Mixed exciton-plasmon states arise when excitons from a strongly absorbing dye, such as J-aggregate, resonant with the surface plasmon modes of noble metal nanoparticles. As a result new peaks, so-called hybridized states, appear in the extinction spectra; they are governed by the strength of the coupling between excitons and plasmons.[16, 17, 21] The dramatic change in the localized surface plasmon resonance (LSPR) associated with the transition from weak to strong resonant coupling makes the metal-molecule complexes a promising candidate as active plasmonic components such as switches and modulators.[23–25] The combination of these active plasmonic components[26–
with passive components[46–59] will also enable the development of nanoscale plasmonic integrated circuits.[60–63] Since resonant coupling strength varies with spectral overlap between LSPR and molecular resonance,[64] a platform with tunable LSPR is essential for understanding and harvesting mixed exciton-plasmon states. In their pioneering work, Wurtz et al. demonstrated tunable exciton-plasmon coupling in J-aggregate hybridized Au nanorods by varying the thickness of air shells that surround the nanorods.[16] In another significant work, Fofang et al. used the highly tunable LSPR observed from Au nanoshells to understand plasmon-exciton coupling as a function of spectral overlap.[17] Although these studies are demonstrations of tunable LSPR to vary plasmon-exciton coupling, they require the fabrication of a large number of different nanoparticles to establish exciton-plasmon hybridization. Such a large number of samples complicate the experimental procedures and introduce deviations. Furthermore, to change LSPR properties with these methods one must change the geometry of the nanoparticles, an impracticality for active nanophotonic devices.

In this work, we report the formation of exciton-plasmon states and the in-situ dynamic control of the coupling strength in Au nanodisc arrays coated with J-aggregate molecules. By changing the incident angle of incoming light, rather than by changing the geometry of the nanoparticles (as has been reported), we observed a continuous shift in LSPR of Au nanodisc arrays. The experimental data matched well with simulated results based on a coupled dipole approximation (CDA) method. Our approach enabled a simple yet powerful platform for dynamic control of exciton-plasmon coupling (< 2) nominal sample sizes are needed to investigate the behavior of resonant coupling and understand variations in plasmon-exciton coupling strength. This platform enables tunable resonant coupling in active nanophotonic devices.

### 4.2 Materials and Methods

**Nanodisc array fabrication:** First, an Au thin film of controlled thickness (33 nm) was initially deposited onto a glass substrate. Second, a self-assembled monolayer (SAM) of close-packed polystyrene (PS) nanospheres was deposited onto the Au surface. Third, Oxygen reactive ion etching (RIE) and Ar RIE were carried
Figure 4.1. A schematic of the arrays of Au nanodisc-J-aggregate complexes and the configuration for angular-resolved spectra. The scale bar in the AFM image is 300 nm.

out to morph the closely-packed PS nanosphere monolayer into arrays of separated nanoellipses and to selectively etch a portion of the Au and Cr film that was not protected by the nanoellipses. Removal of the PS residues with Toluene left the Au nanodiscs on the substrates. Further information on instrumentation of Au deposition and etching can be found in Appendix B.

**Formation of J-aggregates:** 2,2'-dimethyl-8-phenyl-5,6,5',6'-dibenzo-thiacarbocyanine chloride was purchased from Hayashibara Biochemical Laboratories, Japan. The aggregation of dye monomers to J-aggregates in PVA solution was obtained by a method reported earlier. In order to form J-aggregates on nanodiscs surfaces, nanodisc arrays were incubated for 24 hrs in solutions of 0.5mM dye monomers in 50/50 water/ethanol.

**UV-Vis Spectroscopy:** Extinction spectra of the arrays were recorded using HR4000 spectrophotometer (wavelength range of 350-1100 nm) from Ocean Optics Inc. All experiments were performed in air with unpolarized incident light. The area of incident light beam was approximately 2mm. The substrate surface was rotated to change the incidence angle.
4.3 Results and Discussion

4.3.1 Experiments

Fig. 4.1 illustrates the setup used to investigate the plasmon-exciton resonant coupling in arrays of nanodisc-J-aggregate complexes. The hexagonally arranged arrays of Au nanodiscs were produced on glass substrates using nanosphere lithography (NSL)[65–67]. The inset in Fig. 4.1 shows a representative three-dimensional (3D) atomic force microscopy (AFM) image of the Au nanodisc array. The nanodiscs have a mean diameter of 140 ± 14 nm, a height of 20 ± 2 nm (17 nm Au + 3 nm Cr), and a period of 320 ± 32 nm. nanodisc-J-aggregate complexes (shown in the zoomed-in part of Fig. 4.1) were formed by incubating the Au nanodiscs in a 0.5 mM solution of 2,2'-dimethyl-8-phenyl-5,6,5',6'-dibenzothiacarbocyanine chloride in a mixture of water/ethanol (50/50 by volume). The incubation time was around 24 h. Angle-resolved extinction spectra of the Au nanodisc array before and after the formation of J-aggregates were measured in transmission mode with a UV-Vis-IR spectrometer (Ocean Optics Inc.). The natural probe light was directed at the nanodisc arrays and detected at the zeroth-order transmission. For the bare disk array and the J-aggregate-covered disk array, a series of extinction spectra were recorded as the substrate was rotated out-of-plane with an angle \( \theta \). A maximum angle of 65° was achieved at intervals of 5°. We recently reported that the LSPR of Au nanodisc arrays can be tuned continuously by chemical etching.[68] Herein, we have fine-tuned the LSPR to produce a Au nanodisc array with a LSPR peak wavelength near the molecular resonance.

Fig. 4.2a shows a series of angle-resolved extinction spectra from a bare Au nanodisc array. At normal incidence (\( \theta = 0^\circ \)), a single strong in-plane LSPR was found at a wavelength of 676 nm.[51] As the incident angle was changed from 0 to 65°, the peak wavelength continuously redshifted to 710.5 nm. Further increase of the incident angle was not possible due to weak zeroth-order transmission signal. At incident angles between 40 and 65°, a second weaker LSPR band emerged blue to the strong peak at wavelengths between 550 and 600 nm. This second band is attributed to the out-of-plane dipole resonance of the Au nanodiscs.[69] The observed continuous redshift with increasing incident angle is consistent with
what is found in nanoparticle arrays as the lattice spacing is reduced.\[70–73\] Both experiments and theory have demonstrated that when the lattice spacing becomes small enough, the LSPR redshifts and broadens. This phenomenon is due to the stronger near-field coupling which leads to redshifts of the LSPR, as well as increased radiative damping that broadens the peak.

The angle-resolved extinction spectra for an array of the nanodisc-J-aggregate complexes are shown in Fig. 4.2b. The strong in-plane dipole resonance of the bare Au nanodisc array splits into two bands upon adsorption of J-aggregates on the disk surfaces, reflecting the resonant coupling between plasmons and excitons. The dip between the two extinction peaks corresponds to the absorption peak wavelength of the J-aggregates. Similar to the bare nanodiscs, we observe that the two peaks continuously redshift as the incident angle is changed from 0 to 65°. For the nanodisc-J-aggregate complexes, the out-of-plane dipole resonance of the Au nanodiscs appears at a wavelength between 550 and 600 nm when the incident angle is increased beyond 40°.

In Fig. 4.2a we plot the LSPR peak of the in-plane dipole resonance of the bare nanodisc array (denoted by “Plasmon”) and the two new peaks after the
hybridization of the plasmon resonances and molecular excitons (denoted by “Hybrid +” and “Hybrid -” for the high-energy and low-energy peaks, respectively) as a function of the incident angle.[16] From the figure we see that the LSPR peak of the bare nanodisc array has a stronger dependence on incident angle than does that of the J-aggregate-covered nanodisc array. We also note that at angles larger than 35°, the “Hybrid +” peak has higher energy than does the corresponding “Plasmon” peak from the bare nanodisc array. The hybridization of Plasmon resonance and molecular resonance is more obvious in Fig. 4.3b where we plot the dispersion curves of the “Hybrid +” and “Hybrid -” LSPR peaks as a function of the LSPR peak of the bare nanodiscs obtained at the different incident angles. The nanodisc array has a θ-tunable range of plasmon energies (measured from the bare nanodisc array) between 1.745 and 1.833 eV. This plasmon energy range is large enough to cover the strong coupling limit due to the hybridization which occurs at 1.76 eV. However, in order to cover a wide range of LSPR peak wavelengths, which would reveal both strong and weak coupling between plasmon and exciton resonances, we fabricated a second sample with a θ-tunable range of plasmon
energies between 1.629 and 1.728 eV. To have the nanodisc arrays of the specific plasmon energies, we tuned the oxygen reactive ion etching (RIE) time in the NSL followed by the fine-tuning chemical etching process.[65, 68] The solid and dashed black lines in Fig. 4.3b represent the plasmon and exciton resonant energies without hybridization, respectively. We see the characteristic anti-crossing of the two hybrid peaks associated with Rabi splitting of the LSPR peak, where the molecular resonance and the LSPR of the bare nanodisc array overlap. We further notice that the “Hybrid +” curve crosses the solid black line instead of following an asymptotic behavior. This crossing is consistent with Wurtz et al.’s observation on the interaction of plasmon and molecular resonances in the Au nanorod and J-aggregate system.[16] The coupling strength is around 125 meV, consistent with results from nanoshells.[17] Thus, by varying the angle of incident light, it is possible to explore the complete energy range necessary for examining the hybridization by using only two samples, one for the weak coupling and one for the strong coupling.

4.3.2 Modelling Angle Dependent Plasmon-Exciton Coupling

To further understand the hybridization we used the coupled dipole approximation (CDA)[72, 74, 75] to simulate the extinction spectra of two-dimensional (2D) arrays of bare Au nanodiscs and Au nanodiscs coated with J-aggregates at various incident angles. In CDA, the nanoparticle array is described by an array of M dipoles, each with the dipole moment $P_j = \alpha_j E_j$, where $\alpha_j$ is the dipolar polarizability, and $E_j$ is the sum of the incident electric field ($E_{\text{inc},j} = E_o e^{ik \cdot r_j}$) and the electric field arising from the other $M - 1$ dipoles ($\sum_{l \neq j}^M A_{jl} \cdot P_l$). Thus, the total electric field on the $j^{th}$ dipole is given by

$$\alpha_j^{-1} P_j = E_j = E_{\text{inc},j} - \sum_{l \neq j}^M A_{jl} \cdot P_l \quad (4.1)$$

where the electric field from the other $M - 1$ dipoles are given by ,
A_{jl} \cdot \mathbf{P}_l = \frac{e^{ikr_{jl}}}{r_{jl}^3} \left[ \frac{k^2 \mathbf{r}_{jl} \times (\mathbf{r}_{jl} \times \mathbf{P}_l)}{r_{jl}^3} + \frac{1 - ikr_{jl}}{r_{jl}^2} \{r_{jl}^2 \mathbf{P}_l - 3r_{jl}(\mathbf{r}_{jl} \cdot \mathbf{P}_l)\} \right] \quad (4.2)

Dipole moment vectors of each dipole were calculated by solving the $3M$ complex linear equations resulting from Equation 4.1. These calculated dipole moments and incident electric fields were then used to calculate the extinction cross-section of the nanoparticle based on the optical theorem, [76]

$$C_{\text{ext}}(\lambda) = \frac{4\pi k}{|\mathbf{E}_o|^2} \sum_{i=1}^{M} \text{Im}(\mathbf{E}_{\text{inc,l}}^* \cdot \mathbf{P}_l)$$ \quad (4.3)

where $\mathbf{E}_{\text{inc,l}}^*$ is the complex conjugate of $\mathbf{E}_{\text{inc,l}}$, and $k = \frac{2\pi m}{\lambda}$ is the wave vector. Here $m$ is the refractive index of the surrounding medium and $\lambda$ is the free-space wavelength of incident light. The extinction cross-section is further normalized as the extinction efficiency: $Q_{\text{ext}} = \frac{C_{\text{ext}}(\lambda)}{C_{\text{geom}}}$, where $C_{\text{geom}}$ is the particle’s cross-sectional area projected onto a plane perpendicular to the incident beam.

To describe the polarizability of the Au nanodisc we approximate the nanodisc by an oblate spheroid for which the in-plane polarizability is given as[76]

$$\alpha_j = \frac{v_1(\epsilon_1 - \epsilon_m)}{\epsilon_m + L(\epsilon_1 - \epsilon_m)}$$ \quad (4.4)

where $v_1$ is the volume of the oblate spheroid, $\epsilon_1$ is the dielectric function of Au per the Drude model,[77] $\epsilon_m$ is the dielectric constant of the surrounding medium, and $L$ is the geometrical factor of the spheroid. We approximate the J-aggregate-covered Au nanodisc by a core oblate spheroid of Au covered with a shell layer of resonant molecules. The core-shell oblate spheroid has a polarizability given by[76]

$$\alpha_j = \frac{v_2 \left[ (\epsilon_2 - \epsilon_m) (\epsilon_2 + (\epsilon_1 - \epsilon_2)) (L^1 - fL^2) + f \epsilon_2 (\epsilon_1 - \epsilon_2) \right]}{(\epsilon_2 + (\epsilon_1 - \epsilon_2)) (L^1 - fL^2) (\epsilon_m + (\epsilon_2 - \epsilon_m)L^2) + fL^2 \epsilon_2 (\epsilon_1 - \epsilon_2)}$$ \quad (4.5)

where $v_2$ is the total volume of the core-shell oblate spheroid, $f$ is the volume
fraction of the shell layer, $L^{(1)}$ and $L^{(2)}$ are the geometrical factors of the core and core-shell spheroids, respectively, and $\epsilon_2$ is the frequency-dependent dielectric function of the shell layer of resonant molecules. $\epsilon_2$, expressed as $\epsilon_2(\omega)$ to indicate the frequency dependence, is given by the Clausius-Mossotti relation[78]

$$\epsilon_2(\omega) = \frac{3\epsilon_o + 2N\alpha_m(\omega)}{3\epsilon_o - N\alpha_m(\omega)}$$ (4.6)

where $N$ is the number density of the molecules, $\epsilon_o$ is the vacuum permittivity, $\alpha_m(\omega)$ is the frequency-dependent molecular polarizability, and $\omega$ is the angular frequency of the incident light. The molecular polarizability is given by a one-oscillator Lorentz model

$$\alpha_m(\omega) = \frac{\alpha_o\omega_o^2}{\omega_o^2 - \omega^2 - i\omega\Gamma}$$ (4.7)

where $\alpha_o$ is the static polarizability, $\omega_o$ is the resonant angular frequency of the molecules, and $\Gamma$ is the inverse of the effective excited state lifetime. In the simulations, the Au nanodisc array was modeled as a hexagonally arranged Au oblate spheroid array with a total spheroid number $M$ of 492, which is large enough to ensure converged results. The array had a period of 320 nm. The minor axis of the spheroid was assumed to be 17 nm while the major axis was changed between 100 and 125 nm so as to simulate the same wavelength range found in the experiments. The entire spheroid array was embedded in homogeneous surroundings with $\epsilon_m = 1.562$. The value of $\epsilon_m$ was estimated from the averaged dielectric constant of air and glass ($\epsilon_m = 1$ and 2.124 for air and glass, respectively), considering that each Au nanodisc in the experiments was immobilized on a glass substrate with the upper half of the disk exposed to air. The parameters in the Lorentz model were chosen to match the experimental absorption spectrum of the J-aggregates, i.e., $\omega_o = 1.76$ eV, $N\alpha_o = 3 \times 10^{-14}$, and $\Gamma = 0.01$ eV. To reflect the natural probe light used in the experiments, we averaged the extinction spectra over both $p$-polarized and $s$-polarized source light in the simulations.

The spectral angular dependencies are a result of two factors: 1) the periodicity of the nanoparticles and 2) the short distance between the nanoparticles. The former results in far field interactions and the latter in near field interactions. The
far field interactions arise from radiative dipole coupling. This leads to strong dipole coupling between nanoparticles and almost in-phase addition of the scattered light fields of neighboring particles causing a redshift of the plasmon resonance. These near-field effects can be understood as a change in the effective inter-particle distance between the nanoparticles both for the in-plane and out-of-plane directions when varying the incident angle. The effective inter-particle distance varies as $S \cdot \cos(\theta)$ (in-plane gap) and $S \cdot \sin(\theta)$ (out-of-the-plane gap), where $S$ is the array spacing. As the effective distance decreases the near-field coupling increases which leads to a red shift in the LSPR peak (further details are available in Appendix A). Based on CDA simulations we find that for the angular dependence is dominated by near-field interactions. While the angular dependence of nanoparticle arrays dominated by the far-field is well established, to our knowledge the details of the effect of near-field coupling on angle dependent spectra have not been reported earlier. It has been shown that the angular dependence for arrays dominated by far-field coupling lead to a non-monotonic shift in the plasmon peak. However, in our case, where the interactions are dominated by the near-field coupling we find a monotonic shifts in the plasmon peak with angle (further details are available in Appendix A). Thus, the angle dependence of the near field is better suited for studying the coupling between molecules and nanoparticles as demonstrated in this work. Furthermore, the method reported in this work is superior to fabricating many different arrays for studying the coupling as the near field is relatively insensitive to minor changes in the nanodisc geometries and spacing arising from the nanosphere lithography.

Fig. 4.4a shows a series of CDA-simulated extinction spectra for the bare Au spheroid arrays at various incident angles ($\theta$). Each spheroid has a major axis of 110 nm and a minor axis of 17 nm. The simulated results (Fig. 4.4a) are in good agreement with the experimental results (Fig. 4.2a), showing that the in-plane dipole resonance peak redshifts continuously as $\theta$ is increased from 0 to 65°. For the nanodisc-J-aggregate complexes, the simulated extinction spectra as a function of incident angles (Fig. 4.4b) are also in good agreement with the experimental results (Fig. 4.2b). We see that the in-plane dipole plasmon resonance splits into two hybrid peaks with the dip position corresponding to the absorption peak of the J-aggregates (the black short dashed line in Fig. 4.4b). Both hybrid peaks redshift
Figure 4.4. (a) A series of simulated extinction spectra of the bare Au spheroid array with incident angle $\theta$ ranging from 0 to 65° at an interval of 5°. The spheroids have a major axis of 110 nm and a minor axis of 17 nm. (b) A series of simulated extinction spectra of arrays of Au spheroid-J-aggregate complexes with $\theta$ ranging from 0 to 65° at an interval of 5°. The hybridized resonance peaks are marked with empty and solid red triangles, respectively. The dashed black line is the absorption spectrum of J-aggregates without hybridization.

as the incident angle $\theta$ is increased.

Fig. 4.5a shows the simulated LSPR peak energies of the in-plane dipole resonance before and after the hybridization as a function of $\theta$. We see that the “Plasmon” peak crosses the “Hybrid +” peak at 25°, slightly earlier than the experimental crossing (at 35°). In Fig. 4.5b we show the dispersion curves for the nanodisc-J-aggregate complexes by plotting the peak position of the two hybridized LSPR as a function of the LSPR peak of the bare spheroid arrays obtained from the simulations. In order to cover the experimental LSPR energy range between 1.629 and 1.833 eV, we had to in the simulation use six different nanoparticles arrays with the same minor axis of 17 nm but different major axes in the simulations. We see that the simulated dispersion curves (Fig. 4.5b) are in good qualitative agreement with the experimental dispersion curves (Fig. 4.3b)—both simulated and experimental results show peak splitting in the wavelength range where there is spectral overlap between the exciton and the plasmon resonances, and they exhibit the crossing of the “Plasmon” and “Hybrid +” lines at the higher plasmon energies. However, the coupling strength found from the simulations is significantly underestimated as
Figure 4.5. (a) The peak position of LSPR (in eV) as a function of $\theta$ for the Au spheroid arrays before (“Plasmon”) and after hybridization (“Hybrid +” and “Hybrid -” for high-energy and low-energy peaks, respectively). (b) The dispersion curves of the “Hybrid +” (empty triangles) and “Hybrid -” (solid triangles) LSPR peaks as a function of the LSPR peak of the bare spheroid arrays (“Plasmon”) obtained at different incident angles $\theta$. Different colors of the triangles indicate spheroid arrays with different major axes: 100, 105, 110, 115, 120, and 125 nm (with decreased energies of “Plasmon”). The rest of the parameters for all arrays are the same. The solid and dashed black lines represent the plasmon and exciton energies of the spheroids and J-aggregates before hybridization, respectively.

compared to the coupling strength in the experiments. The discrepancy between the experimental and computational results is likely a result of the assumptions made in the CDA models, such as describing the nanodiscs as spheroids, using a quasi-static approximation for the polarizability of the spheroids, and describing the substrate as a homogeneous surrounding with an average dielectric constant of glass and air.

Further experiments and simulations reveal that increased sensitivity of the LSPR peak to the angle of incident light can be obtained by changing either the diameter of the nanoparticles or the spacing between them (data not shown). This increased sensitivity reflects an increase in the near-field coupling. By increasing the diameter of the nanoparticle we effectively decrease the distance between the particles and thus increase the near-field coupling between the particles. Therefore, one can increase the angle sensitivity of the nanodisc array simply by either increasing the dimensions of the nanoparticles or reducing the spacing between
the nanoparticles. However, increasing the near-field coupling also leads to larger redshifts in the LSPR peak position, which might not be desirable for some molecules.

4.4 Conclusions

In conclusion, we have experimentally and computationally studied the angle-resolved spectra of Au nanodisc arrays with and without J-aggregates. The angle-resolved LSPR for the disk arrays is particularly well-suited as a platform to study the interactions between molecular and plasmonic resonances. Hybridization of LSPR and exciton resonances has been demonstrated in the nanodisc-J-aggregate using only two samples, one for the weak coupling and the other for the strong coupling. Our method enables efficient measurement of the plasmon-exciton coupling as a function of wavelength, without the need to fabricate new nanoparticle arrays of different LSPR wavelengths. With this tunable plasmonic system, one can also study how optical properties of molecules change with the LSPR of the nearby nanoparticles. Such optical properties include fluorescence properties and surface-enhanced Raman spectroscopy (SERS), which require strict control of the overlap between the LSPR of metal nanoparticles and the excitation or emission wavelength. An understanding of these interactions will enable optimization of metal nanoparticle-molecule complexes and have a profound impact on active nanophotonic devices, SERS and biosensors.

4.5 Acknowledgments and Copyright Information

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References


5.1 Introduction

The optical resonances of individual metal nanoparticles can also be significantly altered through near-field electromagnetic coupling between neighboring nanoparticles. This has been demonstrated in the simple case of two nanoparticles separated by a small gap, commonly referred as nanoparticle dimers. Not only is the extinction (scattering + absorption) of nanoparticle dimers different from individual nanoparticles, but there is also a large enhancement in electric field intensity in the nanogap between nanoparticles.[1, 2] These enhancements in electric field are very important, as they have the ability to enhance various non-linear processes, such as surface enhanced Raman scattering (SERS)[3, 4], fluorescence spectra reshaping[5], higher harmonic light generation[6], and two photon induced photoluminescence[7] and absorption[8]. Experimental and theoretical work related to the plasmonic properties of these large E-field nanostructures remains an active research area.

Nanoparticle dimers generally have been fabricated by e-beam lithography[9, 10]
or focused ion beam milling[6]. These top-down fabrication methods provide a controlled, precise means to fabricate nanoparticle dimers. Using these methods, nanodisc dimers[11], nanorod dimers[10] and nanoprism dimers[9] (bowtie structure) have been previously reported. However, these methods are expensive, time consuming, not scalable. Alternatively, cheaper and scalable bottom-up methods have been reported. Methods that involve the assembly of nanoparticles to nanoparticle dimers using surface modification by organic molecules (multivalent thiol linkers) or biological molecules (DNA linkers) have been reported by various groups.[12–15] However, DNA based methods require careful separation using an electrophoresis method to attain high yield. Moreover the effect of molecular linkers may not be suitable for SERS, as they might interfere with the Raman signals from the molecule of interest. Solid phase synthesis techniques that utilize a solid substrate to synthesize metal nanoparticle dimers have been used by Worden et al.[16] and Sardar et al.[17] Recently, Chen et al.[18] used controlled aggregation, encapsulation, and purification to synthesize metal nanosphere dimers with large yield. Although this process is scalable, the presence of an encapsulation layer could prevent any large SERS enhancement. Xia et al.[19] recently reported silver nanosphere dimer formation with a yield of 58% by adding salt during synthesis. The above mentioned bottom-up fabrication methods are primarily applied to metal nanosphere dimers which are limited in the tunability of their plasmon resonance wavelength. In addition, the fabricated nanoparticle dimers are loosely attached to substrates and may not be appropriate for some applications. Here, we report a combination of bottom-up and top-down methods to fabricate nanodisc dimer structures (two nanodiscs separated by small gap) over a large area with good plasmonic tunability and reasonable yield. We use “Salting out-Quenching” (SQ), a novel bottom-up technique, to synthesize colloidal doublets from polystyrene (PS) singlets and use them as templates for top-down fabrication of nanodisc dimer structures. In addition to nanodisc dimers, cusp nanostructures with sharp tips, i.e., two nanoholes in thin film with a separation smaller than their diameter, can be fabricated by simple alterations in our method. Compared to single nanohole structures, cusp nanostructures exhibit both large transmission and magnitudes with significantly larger electric field intensity. The proposed method has the advantages of being rapid, scalable, inexpensive, and highly geometrically tunable.
Figure 5.1. Schematic showing a) synthesis of doublets from polystyrene (PS) singlet beads using salting-out quenching (SQ) technique and b) fabrication of nanodisc dimers using colloidal lithography, where polystyrene doublets are used as soft masks during etching processes.

5.2 Materials and Methods

5.2.1 Doublets Fabrication by Salting-out Quenching Technique

Monodisperse, surfactant-free, amine-functionalized polystyrene latex (APSL) microspheres (average molecular weight, 70000 g/mol) were purchased from Invitrogen. Specifically, 100 nm and 200 nm APSL microspheres (2% w/v) were used in the experiments described in this paper. In order to fabricate 100 (200) nm amine-functionalized polystyrene latex (APSL) doublets, 5 µL of APSL colloids were added to 1 mL of 100 (250) mM KCl solution in a centrifuge tube. The rapid flocculation time for this system is approximately 10 sec. This estimate provided a good starting point for forming doublets, and a few rounds of refinement showed that a reaction time of 60 sec for the salting out technique provided enough time for
a significant number of doublets to form. The centrifuge tube, with the particles in high ionic strength solution, was rolled for 60 sec, after which 100 mL DI water was added to quench the aggregation, thereby making mostly doublets while limiting the formation of higher order aggregates. Substrate Preparation: Glass substrates were precleaned by immersion in piranha solution (H2SO4:H2O2 = 3:1) at 80°C for 30 min and later rinsed with DI water. Samples were further sonicated in H2O:NH4OH:H2O2 (35%) = 5:1:1, rinsed with DI water, and dried with N2 gas.

5.2.2 Fabrication of Nanodisc dimers

Gold was deposited with a Chromium adhesion layer on cleaned glass slides at normal incidence using E-beam evaporation method (Semicore E-gun evaporator). 15 mL of the APSL doublet solution were added to a petridish that contained a cleaned gold coated slide, and the particles were allowed to settle for 12 hours. The excess liquid and unsettled particles were decanted off, and the dish was washed 8 to 10 times with de-ionized (DI) water to remove any particles not strongly attached to the surface. The resulting monolayer of APSL singlets and doublets adhered electrostatically to the gold coated glass slide. Oxygen RIE (Plasma-Therm 720) was performed at 20 sccm gas flow, 100 mT and 100 W power density for different durations of time. Ar RIE (Plasma-Therm 720) was performed at 30 sccm of argon plasma for 200 sec at 10 mT pressure and 300 W RF generated power. Finally, the slides were sonicated in Toulene/DI Water. The nanodisc dimers were then imaged using Field Emission Scanning Electron Microscope (FESEM JOEL 6700F).

5.2.3 Fabrication of Nanocusp structures

15 mL of the APSL doublet solution was added to a petridish that contained a cleaned glass slide, and the particles were allowed to settle for 12 hours. The excess liquid and unsettled particles were decanted off, and the dish was washed 8 to 10 times with de-ionized (DI) water to remove any unadhered particles. Oxygen RIE was performed to etch the polymer colloids at 20 SCCM gas flow, 100 mT and 100 W power density for different time periods. Gold, and a Chromium adhesion layer, were deposited at normal incidence using E-beam evaporation method (Semicore E-gun evaporator). Finally, the slides were sonicated in Toulene/DI Water. Cusp
Nanostructures were imaged using Field Emission Scanning Electron Microscope (FESEM JOEL 6700F)

Further information on instrumentation of Au deposition, etching and scanning electron microscopy can be found in Appendix B.

5.2.4 Finite Difference Time Domain Method (FDTD)

Plasmonics properties such as size/gap dependent scattering in nanodisc dimers, enhanced transmission in cusp nanostructures, and electric field enhancements in both types of nanostructures were calculated by FDTD method using commercially available software (Lumerical Solution Inc., British Columbia). A mesh size of 2 nm was used in the case of nanodisc dimer simulations and 4 nm in the case of nanocusp structures. Perfect matching layers were used to absorb non-physical reflections from the boundaries and symmetry relations were used to reduce the simulation time. Scattering cross-sections in the case of nanodisc dimers were calculated by a total-field-scattering-field formulation. Both nanodisc dimers and cusp nanostructures were simulated on glass substrates (n=1.45) and exposed to a surrounding environment of water (n=1.33). Plane wave sources were incident from the glass slide and scattering/transmission monitors were placed in the surrounding medium. The experimental dielectric function of gold[20] was fitted by a polynomial with 10 coefficients and used for all the simulations.

5.3 Results and Discussion

The nanodisc dimers are fabricated in a two step method. In the first step, doublets of polystyrene latex beads are fabricated in solution. Doublets of polymeric colloidal particles have been previously synthesized using a variety of techniques,[21–25] with challenges existing in either extending the doublet formation to variety of materials (metals, polymers, semi-conductors) or easily scaling the synthesis process with reasonable yields. Recently, a simple and robust technique, salting-out quenching (SQ) was developed in our lab to synthesize sub-micron/micron size colloidal doublets by controlled aggregation of colloidal particles[26]. This rapid and easily scalable method relies on controlling the interparticle forces[27–30] temporally to
achieve doublet formation and has been successfully utilized to synthesize doublets of various materials. The DLVO forces between similarly charged colloidal particles can be made attractive by increasing the ionic strength of the solution, due to the dominance of the van der Waals forces. The attractive forces lead to aggregation of the particles, which would give large clusters if not properly controlled. However, control over the aggregation is obtained by adding de-ionized water, thus bringing back the electrostatic repulsion and “quenching” the aggregation at the desired time. As shown in Fig. 5.1a, the SQ process involves increasing the ionic strength of an otherwise stable colloidal solution of positively charged polystyrene latex beads (typically of 200/100 nm in diameter), by initiating a salt stimulus. The increased ionic strength decreases the Debye length of the electric double layer and weakens the inter-particle repulsive forces. During the Brownian aggregation process between the polystyrene beads, beads adhere due to the attractive van der Waals forces. A simple estimate of the time for the particles to aggregate (and form doublets) is given by the Smoluchowski rapid flocculation equation \[\tau_{agg} = \frac{\pi \eta a^3}{2kT\phi W},\] where \(\eta\) is the viscosity of the solution, \(a\) is the radius of the colloidal particles, \(k\) is the Boltzmann constant, \(T\) is the temperature of the solution, \(W\) is the stability ratio (which identifies how many times particles must collide on average, before they adhere), and \(\phi\) is the volume fraction of particle in the solution. After allowing the diffusion-limited aggregation for a specific duration of time, the “stimulus” is quenched by mixing in a large quantity of deionized water, which lowers the ionic strength and prevents further aggregation by restoring the electrostatic repulsion. At this point, the suspension consists primarily of singlets and doublets. In the second step (Fig. 5.1b), we use the doublets fabricated using the SQ technique to make nanodisc dimers by colloidal lithography. Colloidal lithography uses colloidal beads as masks to fabricate nanoparticles and is scalable, rapid, and inexpensive. Various plasmonic nanoparticle geometries, including nanoprisms, nanorings and nanodiscs have been fabricated using colloidal lithography. However, these particle geometries were fabricated from isolated beads or with closely packed hexagonally arranged monolayers of beads that do not support large electric fields. Doublets made from the SQ technique, when used in colloidal lithography, can be used to fabricate nanodisc dimers by transferring the shape of doublets onto a thin film. The process involves using electrostatic interactions to settle polystyrene
**Figure 5.2.** FESEM images of polystyrene doublets synthesized using SQ technique from beads of 200 nm diameter (a) and 100 nm diameter (b). (c) Yield as function of cluster size after SQ technique for 200 nm beads. (d) FESEM image of nanodisc dimers fabricated from polystyrene doublets after colloidal lithography. Inset shows enlarged images.

doublets on a glass slide coated with a thin layer of gold (typically 30 nm) and reducing their diameter by oxygen reactive ion etching (RIE). During the oxygen RIE process, the gold beneath the beads and the distance between the center of the beads remains unaffected. The reduction of diameter, however, opens up a narrow gap between the polystyrene beads. This is followed by Argon reactive ion etching where the colloidal doublets act as etch masks and the gold is removed in the regions where there are no beads. Finally, the beads are removed by sonication to expose nanodisc dimers on glass substrates. Representative field emission scanning electron microscopy (FE-SEM) images of SQ synthesized polystyrene doublets made from 200 nm diameter and 100 nm diameter polystyrene beads are shown in Fig. 5.2a and 5.2b, respectively. Clear contact between two polystyrene beads is seen in all the doublets. Using the SQ method, we have achieved a reasonably high yield of doublets (36%), compared to (1%) yield without SQ technique,
Figure 5.3. (a) Control over nanogap size as a function of oxygen etching time. Insets show representative FESEM images of the nanodisc dimers at various etching times. (b) Calculated electric field intensity distribution in Au nanodisc dimer within in-plane cross-section (top) and out-of-plane cross-section (bottom) for nanodisc dimer corresponding to 30 sec of oxygen RIE (190 nm diameter, 30 nm height and 10 nm gap) with incident light polarized along the axis of disc dimers. c) Calculated maximum electric field intensity in nanodisc dimer as a function of nanogap length for various diameter of nanodiscs.

The magnitude of the electric field enhancement and position of plasmon resonance wavelength in nanodisc dimers strongly depends upon the gap and nanodisc diameter. For surface enhanced applications, it is essential to achieve large electric field enhancements, while simultaneously tuning the plasmon resonance wavelength to match the Raman excitation laser wavelength. Our method allows control of the gap/diameter ratio by varying the oxygen RIE time. Longer etch times correspond to smaller beads and subsequently larger gaps between the beads.
(See supplementary information for details on decrease in polystyrene bead size as a function of etching time). Fig. 5.3a shows the dependence of the nanogap size on the etching time. In the absence of oxygen etching, the nanodiscs touch each other and thus in the conducting coupled regime[11]. Such structures are potentially useful for broad-band energy harvesting applications as proposed by Aubry et al.[38, 39] As the RIE time increases, the gap between nanodiscs increases from 10 nm to 40 nm with a reasonable standard deviation. To determine the effects of particle size on electric field intensity with a constant gap, we calculated the electric field intensity distribution and maximum electric field in the nanodisc dimers for various diameters using finite different time domain (FDTD) methods[40]. Fig. 5.3b shows electric field distribution at the plasmon resonance frequency for incident light polarized along the dimer axis for a nanodisc dimer geometry corresponding to 30 sec of etching (180 nm discs and separated by 10 nm gap). The figure shows approximately three orders of enhancement in the electric field intensity due to dipole-dipole interaction plasmon modes. Fig. 5.3c shows the variation of the maximum electric field in the nanogap as function of the nanogap size for various particle diameters. The maximum electric field enhancements occur in nanodisc dimers that have large disc diameters and separated by smaller gaps. These requirements are satisfied in the proposed method when larger polystyrene beads are used with short oxygen RIE times.

We further investigated the plasmonic resonances of nanodisc dimers using dark field micro-spectroscopy (details on this technique can be found in Appendix B). It is well known from previous studies that as the gap/diameter ratio of nanodisc dimers decreases, the dipolar plasmon resonance redshifts due to a decreased restoring force between the charge separations in individual particles.[41] To understand the nature of plasmon resonances in these structures, we fabricated nanodisc dimers from 100 nm polystyrene. Although, nanodisc dimers fabricated from 200 nm PS beads and with short oxygen etch time possess large electric field enhancements, their plasmon resonances are in the infrared (1200 nm), making their characterization difficult. Fig. 5.4a shows the dark field scattering spectra of nanodisc dimers with various gap/diameter ratio fabricated from 100 nm polystyrene beads and 30 nm thin gold films with light polarized along the axis of dimer. We can see that the longitudinal plasmon peak position blueshifts from 800 nm to 700 nm with
Figure 5.4. (a) Experimentally obtained scattering intensity vs. wavelength for nanodisc dimers resulting from 100 nm polystyrene doublets and etched for different time periods (10 sec, 15 sec, 20 sec). b) Corresponding FDTD calculated scattering cross-sections. Incident light is polarized along the axis of the dimer.

increased etch time, a result of increased gap/diameter ratio. To characterize the experimentally observed scattering responses, we performed FDTD simulations of nanodisc dimers with corresponding gap/diameter geometry. The peak positions and widths of the experimentally observed scattering responses match very well with the FDTD results (Fig. 5.4b). In the case of larger disk diameters with smaller gaps, a quadrapolar plasmon mode at 600 nm emerges in the scattering response of both the experiments and simulations. Plasmon resonances of nanodisc dimers can be also shifted by adjusting the thickness of the film (results not shown here). We also investigated the effect of polarization on the plasmon resonance of the nanodisc dimers. It is known that the plasmon resonance blueshifts as the polarization is
Figure 5.5. (a) Experimentally obtained scattering intensity vs. wavelength for different polarization angles of incident light (from normal to along the dimer axis in 10° steps) in nanodisc dimer resulting from 100 nm polystyrene doublets with 20 sec of oxygen etching. B) Corresponding FDTD calculated scattering cross-section.

changed from parallel to the dimer axis to perpendicular to the dimer axis. Our results from polarization dependent dark field spectroscopy are consistent with previous reports as shown in Fig. 5.5a and agree well with FDTD simulations (Fig. 5.5b).

In addition to the fabrication of nanodisc dimers from polystyrene doublets synthesized by salting-out quenching (SQ) technique, our method can be easily modified to fabricate cusp shaped nanostructures. Such structure, fabricated by creating two nanoholes of the same diameter with center-to-center distance smaller
Nanoholes in thin metal films have attracted immense interest among researchers after the discovery of extra-ordinary transmission in nanohole arrays by Ebessen et al. Various methods both theoretical and experimental have been reported in an attempt to understand the origin of this enhanced transmission through single nanoholes in thin films. A common understanding is that interactions between localized surface plasmons and propagating plasmon modes in these systems dictate the optical performance of the nanoholes. Recently, more interest has been shown in differences in optical properties due to changes in nanohole shape. The cusp shaped nanostructures, when compared to separate nanoholes, exhibit larger electric fields and transmission are similar to bowtie slot nanoantennas. Reuven Gordon and colleagues fabricated arrays of cusp nanostructures by focused ion beam milling in these studies. Large electric fields in cusp nanostructures were also studied by Onuta et al. using second harmonic generation imaging. In their study, cusp nanostructures were obtained by random formation of colloidal doublets by using large concentrations of polystyrene beads followed by gold evaporation.

To fabricate cusp shaped nanostructures (Fig. 5.7a), polystyrene doublets
fabricated using the SQ technique are settled on a glass slide and then etched by oxygen RIE. This etching opens up a gap between the polystyrene beads. A thin film of gold is deposited and the beads were later removed by sonication. Opening a gap between polystyrene beads allows the metal to deposit between beads resulting in the formation of smaller separation between sharp tips in the aperture. Fig. 5.7b and 5.7c show FESEM images of cusp nanostructures fabricated from 200 nm polystyrene beads using this method without and with oxygen RIE respectively. In the case without oxygen RIE, sharp tips in the aperture are separated by a larger distance than the ones with oxygen etching. Control of the tip separation is important as it dictates the magnitude of the electric field intensity and transmission peak position. To understand the magnitude of electric field enhancements and transmission improvements, we performed FDTD calculations on isolated cusp nanostructures. When excited with an incident light polarized along the axis of the sharp tips, these structures exhibit a sharp transmission peak at 1860 nm with a shoulder at 905 nm (Fig. 5.7a). We also calculated the maximum electric field intensity as a function of wavelength and see that they also peak near these wavelengths. Plots of electric field distribution in the nanostructures at these wavelengths show distinct plasmon modes and represent different charge density distributions as shown in Fig. 5.7b and 5.7c. The strong transmission peak at lower energy (1860 nm) corresponds to a superradiant plasmon mode with electric field spreading throughout the nanostructure, whereas the small shoulder at 905 nm represents a subradiant plasmon mode that is tightly confined to the tips. The electric field at the higher energy shoulder peak is stronger than that of the lower energy mode due to reduction of radiative losses, a characteristic of subradiant plasmon modes\[50].

5.4 Conclusions

In summary, we have demonstrated the fabrication of nanodiscs dimers and nanocusp structures by the controlled aggregation of polystyrene beads through the salting-out quenching technique and further soft-lithography processing. The proposed method allows various means of control, such as bead diameter, etch time, and film thickness, which can be employed to finely tune the geometry of
Figure 5.7. Calculated (a) transmission intensity and electric field intensity vs. wavelength for a nanocup structure made of nanoholes of 208 nm diameter, 30 nm height and separated by 200 nm gap with incident light polarized along the sharp tips. (b) Electric field intensity distribution in the x-y plane at 1790 nm (top) and 900 nm (bottom)

the structures and subsequently control their plasmonic properties. Numerical simulations were found to be in good agreement with the experiments. Both of these structures provide large electric field localization that is geometry and polarization dependent. The proposed method has several advantages, as it is being rapid, scalable, inexpensive, and has the ability to obtain structures attached to any kind of substrate (conducting/non-conducting). We believe that these advantages make this method a promising technique to fabricate nanodisc dimers and nanocup structures. These structures can be readily applied for applications in single molecule detection, second harmonic generation, and broad wavelength energy harvesting.

5.5 Acknowledgments

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6.1 Introduction

Extraordinary optical transmission (EOT) is the enhanced transmission of incident electromagnetic radiation through sub-wavelength-scale holes in metallic films. [1, 2] EOT in real metals is based on two types of surface waves: 1) conventional surface plasmons (SPs) that are excited at a metal-dielectric interface, and 2) surface-bound states that exist on structured perfect electric conductor (PEC) surface. Although a PEC generally does not support any surface-bound states since an electromagnetic field cannot penetrate the surface, highly localized surface-bound states appear when the PEC is periodically modulated with arrays of sub-wavelength square or circular holes. Both theoretical [3–6] and experimental [7–10] studies suggest that surface-bound states and SPs exhibit similar dispersion relationships. The similarity has earned such surface-bound states the names ‘spoof’ or ‘designer’ surface plasmons (DSPs).

Structured PEC surfaces and the excited DSPs have recently garnered interest
within the photonics community, as they are a new platform to engineer surface-bound states of a wide frequency range. [11–14] An important example is the guiding of terahertz-range radiation [15, 16] in the form of DSPs - this enables applications of terahertz plasmonics [17] in near-field imaging, sensing, and spectroscopy. A prime advantage of DSP is that, unlike conventional SP, the propagation of these waves can be controlled by engineering the material-independent, perceived group index. [3] PEC structures have been engineered to guide DSPs of specific terahertz-range frequencies. For example, periodically corrugated metal wires have been developed for guiding and focusing terahertz-frequency pulses [18–20]. By placing two optimized metallic grating structures on opposite sides of a narrow slit, Gan et al. were able to selectively guide terahertz-range waves along the two desired directions. [21] Similarly, metallic gratings have been found to significantly decrease the group velocity near the cutoff frequency. [22] Gan et al. [23] extended this notion by using graded metallic gratings to slow the propagation of wide-bandwidth, terahertz-range DSPs.

Successful applications of the propagation of DSPs on planar structures include waveguiding, imaging and sensing. Such applications require both vertical and lateral confinement of DSPs. To realize the latter, Oh et al. [24] exploited the anisotropic variation of the effective group indices of DSPs with frequency. Ruan et al. [25] achieved self-collimation and focusing/imaging by negative refraction. These methods work only at wavelengths comparable to the periodic spacing of the apertures, where the isofrequencies have zero or negative curvature. Another approach to realize lateral confinement was proposed by Maier et al. in which a defect mode was realized by gradually increasing the hole size, leading to evanescent decay along the lateral direction. [26]

In this study, we realize the lateral confinement of DSPs by engineering planar PEC structures as parabolic graded media. The parabolic gradient of a lens’ refractive index $N$ when transverse to the propagation $Y$ of an incident beam causes beam to propagate in a periodic fashion, as illustrated in Fig. 6.1(a). [27, 28] The parabolic gradient forces the beam to propagate periodically and can be explained by Snell’s law. Electromagnetic energy emanating from a line source is focused in the first quarter pitch and later expand/collimate in the second quarter pitch of lens (opposite for a point source). A similar effect has been observed for bulk waves
in graded metamaterials of negative refractive indices [29] as well as for photonic crystals [30–32]. However, to-date no one has reported the propagation of surface waves like DSPs for perfect electric conductors using media of parabolic gradient index. Such engineered structures would enable lateral confinement of DSPs at frequencies in the isotropic dispersion region, and they would function as on-chip optical devices after the DSPs are excited and being guided.

To establish such a parabolic gradient in the effective group index along the direction transverse to the propagation of DSPs, we modulate either the size of the holes \( a \) or the dielectric constant \( \epsilon_h \) of holes in the PEC structure, as shown in Fig. 6.1(b)-(c). Using a three-dimensional (3D) finite-difference time-domain (FDTD) method, we confirmed the effect of the parabolic gradient on the propagation of DSPs by achieving focusing, collimation, and wave-guiding (depending on the width of the light source). Our FDTD simulations agreed with analytic models from standard Gaussian optics.

Figure 6.1. (a) Principle of a gradient index based lens. A parabolic gradient (green line) of the group index \( N \) along the transverse direction of the propagation (Y-axis) enables the focusing or collimation of incoming beam (red arrows). PEC structure with periodic array of square holes with varying (b) size of square holes and (c) dielectric constant, along the transverse direction of propagation (Y-axis) enables the focusing or collimation of DSPs (red arrows).
6.2 Design of the PEC structure with Graded Media

For a PEC structure with arrays of square holes having a lattice constant \( d \), hole depth \( h \), hole size \( a \), and a dielectric constant \( \epsilon_h \), one can approximate the isotropic dispersion relation where \( \lambda \gg d > a \), as [4]:

\[
\frac{\sqrt{k_x^2 - k_0^2}}{k_o} = \frac{S^2 k_o}{\sqrt{\pi^2/a^2 - \epsilon_h k_o^2}} \left( \frac{1 - e^{-2|q_z|h}}{1 + e^{-2|q_z|h}} \right), \tag{6.1}
\]

where \( k_x \) is the propagation constant, \( k_o = \omega/c \), \( S = 2a\sqrt{2}/\pi d \), and \( q_z = i\sqrt{\pi^2/a^2 - \epsilon_h k_o^2} \). Using this equation one can solve for \( \omega \) and differentiate with respect to \( k_x \) to obtain an expression for the effective group index:

\[
N_g = \frac{c}{d\omega/dk_x} = \frac{\omega}{ck_x} \left[ 1 + \frac{2A\omega^2}{(\omega_{pl}^2 - \omega^2)} + \frac{A\omega^4}{(\omega_{pl}^2 - \omega^2)^2} - \frac{4A\sqrt{\pi\epsilon_h}\omega^4}{e(\omega_{pl}^2 - \omega^2)^{3/2}} \left( \frac{e^{-2h|q_z|}}{1 - e^{-4h|q_z|}} \right) \right], \tag{6.2}
\]

where \( \omega_{pl} \) is the cutoff frequency such that \( \omega_{pl} = \pi c/\sqrt{\epsilon_h a} \). \( A \) is given by

\[
A = \frac{64a^4}{\pi^4d^4\epsilon_h} \left( \frac{1 - e^{-2h|q_z|h}}{1 + e^{-2h|q_z|h}} \right)^2. \tag{6.3}
\]

Fig. 6.2 shows dispersion relations for various \( \epsilon_h \) and \( a \) calculated per Eq. 6.1. The frequency and the wavevector are presented in normalized units of \( \omega d/2\pi c \) and \( k_x d/2\pi \), respectively. An increase in \( a \) or \( \epsilon_h \) will lead to a decrease in the cutoff frequency, \( \omega_{pl} \), thus decreasing the range of propagating modes. In order to realize periodic focusing of DSPs, the effective group index encountered by the DSPs should be modulated parabolically in the transverse direction. In principle a change in either \( a \), \( h \) or \( \epsilon_h \) can be used to engineer the parabolic variation of \( N_g \). For the application of this concept in the terahertz range, where \( a \) is in the range of 100’s of \( \mu m \), structured PEC material can be achieved by patterning a polymer using standard lithography and followed by electroplating the PEC material. Changes in \( a \) and \( h \) within PEC structures can be achieved by controlling the polymer pattern and time of electroplating respectively. To control the dielectric constants, various refractive
index oils can be filled in different holes using a precision fluid dispensing system coupled to a micro-positioner. However, resolving the small changes in $a$ or $h$ in a three-dimensional FDTD simulations is computationally challenging; we therefore focused our investigation on changing $\epsilon_h$. Because both types of PEC structures can be fabricated and have similar behavior (as confirmed from the dispersion curves shown in Fig. 6.2), we believe that knowledge we obtained from one structure can be applied to the other. Although one could calculate the dispersion relationships for various $\epsilon_h$ using Eq. 6.1, a mismatch at wavelengths comparable to the feature size was expected since the expression was derived for feature sizes much smaller than the wavelength of light. [6] Therefore, to obtain a more-accurate dispersion relation and modulation of $\epsilon_h$ with parabolic variation in $N_g$, we used a 3D FDTD method [33] to solve Maxwell’s equations for homogeneous structures of different $\epsilon_h$.

The dispersion relations were obtained by considering a single unit cell, as shown in the inset of Fig. 6.3(a), with Bloch periodic boundary conditions in the X and Y directions and perfectly matching layers (PMLs) along the Z direction. A grid size of $\delta x = \delta y = \delta z = d/15$ was used in the calculations. Excitation was achieved with a wide-band Gaussian source arbitrarily placed within the unit cell. Harmonic inversion of time signals [34] was used to extract the resonance modes for different $\epsilon_h$ with fixed $d$, $a = 0.85d$, and $h = 1.2d$. The FDTD calculations were performed using the open software package MEEP, wherein sub-pixel smoothing was used for increased accuracy. [35]

Fig. 6.3(a) shows the dispersion relations calculated for different $\epsilon_h$ ranging from 1.25 to 3 in increments of 0.25. Keeping in view the practical importance of the proposed work in THz plasmonics research, we used an operating frequency of 1.122 THz, which for a hole depth of $d = 100\mu m$ yields an operating frequency of 0.3742 normalized units. For this operating frequency, the variation of $N_g$ with respect to different $\epsilon_h$ was obtained by numerical differentiation and is shown in Fig. 6.3(b). The variation of $N_g$ can be approximated with an exponential increase, as shown by the best fit (solid line) to the data points obtained by FDTD (dotted line).

Having established the relationship between $N_g$ and $\epsilon_h$ at a certain operating frequency, we proceeded to design the graded index media and simulate via FDTD
Figure 6.2. Dispersion relations calculated using Eq. 6.1 for a PEC structure filled with (a) different \( \epsilon_h \) and fixed \( a = 0.85d \), \( h=1d \), and (b) different \( a \) and fixed \( \epsilon_h=2 \), \( h=1d \). (c) different \( h \) and fixed \( \epsilon_h=2 \), \( a= 0.85d \).

Figure 6.3. (a) Dispersion relations calculated using FDTD for a PEC structure filled with different \( \epsilon_h \). Inset shows the unit cell. (b) Variation of \( N_g \) with \( \epsilon_h \) at an operating frequency of 0.3742 normalized units obtained from FDTD (dotted line) and a best fit to the data (solid line).
the propagation of designer plasmons. The 3D model used for FDTD consisted of a rectangular box of size $83d \times 23d \times 7d$ which included a PML thickness of $1d$ in each dimension, as shown in Fig. 6.4(a)-(c). To achieve 2D focusing and collimation of surface waves in the X-Y plane, we chose an effective group index that changed parabolically along the transverse direction of the propagation. The effective group index was highest at the center ($Y=0$) and varied along the positive and negative $Y$ direction (-10$d$ to 10$d$):

$$N_g^2(Y) = N_o^2(1 - (\alpha Y)^2)$$  \hspace{1cm} (6.4)

where $N_o$ is the group index at $Y = 0$ and $\alpha$ is the gradient coefficient. By choosing $N_o=1.1077$ and $N_g=1.014$ at $Y = \pm 10d$, we obtained a gradient with $\alpha=0.04031$. The variation of $N_g$ with these parameters is shown in Fig. 6.4(d). To realize this group index change, the dielectric constant of the holes in the PEC-structured surface was altered by changing $\epsilon_h$ (based on a nearly exponential relationship between $N_g$ and $\epsilon_h$). The group index change is shown in Fig. 6.3(b). The exact distribution of $\epsilon_h$ along the transverse direction is shown in Fig. 6.4(d).

6.3 Results and Discussion

The propagation of Gaussian beams with different beam widths in free-space parabolic graded lens was thoroughly studied by Gomez-Reino et al. [27] It has been shown that Gaussian beams with smaller beam widths expand and collimate in the first quarter pitch of the lens. Similarly, a Gaussian beam with a larger beam width gets focused and the beam width is decreased. At a certain beam width when collimation and focusing effects cancelled each other, light will propagate at the same beam width through the structure. Our investigations focused on extending this physical mechanism from free-space optics to surface plasmons.

To investigate the efficiency of the proposed structure for lateral confinement of DSPs, we simulated the propagation of several DSPs that initiated from Gaussian beams of different beam widths relative to the lattice constant $d$. The use of Gaussian beams is appropriate in the context of THz plasmonics, since surface modes are excited on planar structures using Gaussian beams incident upon razor-
Figure 6.4. FDTD model of graded PEC structure (a) X-Y view, (b) X-Z view, (c) Y-Z view, and (d) parabolic change of the \( N_g \) (line) and distribution of \( \epsilon_h \) (dots) along the transverse direction of propagation (Y-axis) of DSPs.

blade-like structures. [36]

In the simulation the PEC was represented with a negative infinite dielectric constant, and a grid size of \( \delta x = \delta y = \delta z = d/15 \) was used in all the simulations. The negative infinite dielectric constant creates the same effect as infinite conductivity by maintaining the electric field in the PEC structure at a constant value (zero in this case) Narrow-bandwidth TM-polarized (\( E_x, H_y, \) and \( E_z \)) Gaussian beams of different beam widths \( w \) at the operating frequency were launched in the X direction from \( X=-40d \).

We first investigated the propagation of DSPs produced by a Gaussian beam of width \( 5d \) in a graded medium. As shown in Fig. 6.5(a)-(d), DSPs produced by such a wide source are focused as they reach \( X=0 \) (center of the structure) and then collimate after traveling another 40\( d \) distance from \( X=0 \). This result was expected that per Gaussian optics, electromagnetic energy in a material of parabolic graded index is guided in an oscillatory fashion with a periodic focal point. The X-Z view shows the localization of the \( E_z \) field along the surface of DSPs and also shows that the intensity increases at the center of the structure (\( Y=0 \)) due to the focusing of
the DSPs. This increase is seen in the the snapshots of $E_z$ field in the Y-Z plane at X=-40d (Fig. 6.5(c)) and at X=0, (Fig. 6.5(d)). To qualitatively analyze the focusing effect, profiles of $|E_z|$ along the transverse direction at X=-40d (dotted lines) and at X=0 (solid lines) are shown in Fig. 6.5(e). Focusing is evident from the increase in the intensity of $E_z$ at Y=0 and from the lateral confinement. We also performed numerical simulations using similar source conditions and simulation geometries but with a uniform dielectric constant, and observed no focusing or collimation behavior (data not shown).

DSPs produced by Gaussian sources of smaller widths $w = 2d$ undergo collimation instead of focusing in the first half of the structure, and they are focused in the second half of the structure (Fig. 6.6). From Fig. 6.6(e), we see that the collimation of DSPs in the first half of the structure results in a spreading of the intensity along the Y direction. In the absence of the graded media, the DSPs propagate radially (data not shown here).

In both cases of Gaussian sources beam widths ($w = 5d$ or $2d$), DSPs either get collimated (Fig. 6.5) or focused (Fig. 6.6) by traveling a distance approximately 40d. This distance matches closely with the quarter-pitch of graded lenses, $\frac{\pi}{2a}=39d$,
Figure 6.6. Propagation of DSPs excited by Gaussian beams with $w = 2d$, snapshot of $E_z$ field in a) 0.1$d$ above X-Y plane b) X-Z plane, c) Y-Z plane at X=-40$d$ (source) and Y-Z plane at X=0$d$ (midway) and d) comparison of the magnitude of $E_z$ at X=0$d$ (solid line) and X=-40$d$ (dotted line).

Figure 6.7. Propagation of DSPs excited by Gaussian beams with $w = 3.5d$, snapshot of $E_z$ field in a) 0.1$d$ above X-Y plane b) X-Z plane, c) Y-Z plane at X=-40$d$ (source) and Y-Z plane at X=0$d$ (midway) and d) comparison of the magnitude of $E_z$ at X=0$d$ (solid line) and X=-40$d$ (dotted line).
predicted by standard Gaussian optics. At intermediate widths along the incident Gaussian beam, the collimation and focusing are canceled [27]. DSPs are also guided along the length of the structure with no significant deviation in the beam width, as shown in Fig. 6.7 (a)-(e). This behavior allows one to guide energy in the form of DSPs over large distances.

Graded media can also be used to control the propagation of surface plasmons at visible and IR domains using real metals. [37–39] Such extension would require consideration of absorption loss in real metals due to dispersive nature of real metals at visible frequencies. The effects of field penetration [24] in real metals should also be considered as it lowers the band positions observed in PEC structures.

6.4 Conclusions

Using FDTD simulations we have demonstrated that one may control the propagation of DSPs in structured PEC materials with arrays of square holes by exploiting graded index media. We found that graded index media can be realized by modulating either the size of the holes or the dielectric constant. Such a structure was engineered using FDTD simulations by modulating the dielectric constant of the structure’s square holes and shown to provide lateral confinement of propagating DSPs. Focusing, collimation, and waveguiding of designer plasmons in a lateral direction were realized by changing the width of the source beam. These results will promote research in THz designer surface plasmons towards high confinement waveguiding and sensing.

6.5 Acknowledgments and Copyright Information

Chapter 6 is a modified version of the author’s publication: B. K. Juluri, S. Lin, L. Jensen, and T. J. Huang, Propagation of Designer Surface Plasmons in Structured Conductor Surfaces with Parabolic Gradient Index, Optics Express, Vol. 17, pp. 2997-3006, 2009. This research was supported by the National Science Foundation (ECCS-0824183 and ECCS-0801922), the Air Force Office of Scientific Research (AFOSR), the Penn State Center for Nanoscale Science (MRSEC), start-up funds from the Pennsylvania State University (PSU), and a seed grant from PSU’s
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References


Chapter 7

Summary

An emerging field in the area of plasmonics is active plasmonics which aims at achieving tunability of plasmonic resonances allowing the realization of plasmonic nanocircuits. We believe that integration of active molecules with plasmonic nanostructures enable tunability to plasmonic resonances with unprecedented advantages such as easier integration and various mechanisms that are involved. We have worked on plasmonic tuning that include Charge-induced Plasmonics Shifts (CIPS) and resonant coupling induced plasmonic shifts. In our study, using accurate electrodynamic calculations, we proposed geometries and material compositions of the nanoparticle that would achieve maximum CIPS. We showed that, in general, nanoparticles with geometries and materials with long wavelength resonance positions are more sensitive to charging process. The presence of strongly absorbing molecules on the metal nanoparticle surface result in resonant coupling between molecular and plasmonic resonances. However it is not well understood how to control the coupling between individual resonances and what factors determine the strength of interactions. We investigated this problem and performed experiments to show that the splitting observed in resonant molecule-coated plasmonic nanostructures can be controlled by changing the absorbance, $A$, of the molecular layer. A linear relationship between $\sqrt{A}$ and the splitting was observed. Further, using classical electrodynamic simulations, we confirmed this relationship and established a simple physical mechanism based on linear dispersion. The insights gained from this study will be useful in improving applications of resonant coupling, including tunable nanophotonic devices, molecular sensing, and PRET methods. The dra-
matic change in the localized surface plasmon resonance (LSPR) associated with the transition from weak to strong resonant coupling makes the metal-molecule complexes a promising candidate as active plasmonic components such as switches and modulators. In this regard, we reported the formation of exciton-plasmon states and the in-situ dynamic control of the coupling strength in Au nanodisk arrays coated with J-aggregate molecules. By simply changing the incident angle of incoming light, rather than by changing the geometry of the nanoparticles (a very cumbersome process that involves numerous fabrication steps), we observed a continuous shift in LSPR of Au nanodisk arrays. Our approach enabled a simple yet powerful platform for dynamic control of exciton-plasmon coupling. Nominal sample sizes (<2) are needed to investigate the behavior of resonant coupling and understand variations in plasmon-exciton coupling strength. We hope that this platform will enable tunable resonant coupling in active nanophotonic devices. Our innovation in this field lies in developing a platform that provides researchers a means to dynamically study the interaction between strongly absorbing molecules and plasmons. In summary, the research work on active plasmonics presented here will enable the idea of using light to process information one step closer to reality.

Innovation in the area of fabrication in plasmonics has direct implications to the fields of physical chemistry, information technology, energy harvesting and medical diagnosis. This can be witnessed from numerous reports on the ideas related to nanotechnology fabrication in the field of plasmonics on day-to-day basis. The proposed method using salting-out quench method and colloidal lithography to fabricate large electric field nanostructures has several advantages of being rapid, scalable and inexpensive. With several advantages and large localization of electric field, we believe that these structures can be readily applied for applications in single molecule detection, second harmonic generation, and broad wavelength energy harvesting.

Structured PEC surfaces and the excited designer surface plasmons (DSPs) are a new platform to engineer surface-bound states of a wide frequency range. They are especially useful in guiding terahertz-range radiation in the form of DSPs enabling applications of terahertz plasmonics in near-field imaging, sensing, and spectroscopy. The propagation of THz DSPs waves is controlled in our work. Using FDTD simulations we have demonstrated that one may control the propagation
of DSPs in structured PEC materials with arrays of square holes by exploiting graded index media. We found that graded index media can be realized by modulating either the size of the holes or the dielectric constant. Such a structure was engineered using FDTD simulations by modulating the dielectric constant of the structure’s square holes and shown to provide lateral confinement of propagating DSPs. Focusing, collimation, and waveguiding of designer plasmons in a lateral direction were realized by changing the width of the source beam. These results will promote research in THz designer surface plasmons towards high confinement waveguiding and sensing.
Angular Dependent Spectra in Nanodisc Arrays

The angle-resolved spectra of an array of bare Au nanodiscs exhibit continuous shifting of localized surface plasmon resonances. This is primarily due to far-field and near-field coupling between nanodiscs in array. Using coupled dipole approximation method mentioned in chapter 4, the relative contributions of these near field and far field interactions were calculated and are shown in Fig A.1. The effect of near field coupling between nanodiscs is dominating the observed shifts. In the following sections, we describe in-detail the origins of the redshifts.

A.1 Effect of Near-field coupling in Nanodisc arrays

To understand the effect of near field coupling in nanodisc arrays, we first start with angle dependence of nanosphere dimers, linear arrays and 2 dimensional arrays of nanospheres. Using the understanding obtained with nanospheres we move towards understanding the resonance shifts in nanodisc dimers, linear and 2 dimensional arrays of nanodiscs as a function of incident angle.
Figure A.1. Angle dependent spectra of nanodiscs and the relative contributions of near-field coupling and far-field coupling.

![Figure A.1](image)

**Figure A.1.** Angle dependent spectra of nanodiscs and the relative contributions of near-field coupling and far-field coupling.

A.1.1 Near-field coupling in Nanospheres

The effects of near-field coupling on angle dependence spectra in nanospheres can be completely understood by the change of effective inter-particle gap in the in-plane and out-of-plane directions of dimer. Figure A.2 shows the schematic of a nanospheres dimer with an incidence angle of light at $\theta$ degrees and an equivalent normal incidence configuration with changed effective inter-particle distances, $S \cos(\theta)$ (in-plane gap) and $S \sin(\theta)$ (out-of-the-plane gap).

In the first case, angle of incident beam was changed and the particles positions

![Figure A.2](image)

**Figure A.2.** Schematic showing the equivalence of angular incidence and normal incidence with changed effective gaps in nanosphere dimers.

A.1.1 Near-field coupling in Nanospheres

The effects of near-field coupling on angle dependence spectra in nanospheres can be completely understood by the change of effective inter-particle gap in the in-plane and out-of-plane directions of dimer. Figure A.2 shows the schematic of a nanospheres dimer with an incidence angle of light at $\theta$ degrees and an equivalent normal incidence configuration with changed effective inter-particle distances, $S \cos(\theta)$ (in-plane gap) and $S \sin(\theta)$ (out-of-the-plane gap).

In the first case, angle of incident beam was changed and the particles positions
were not changed, we refer this to angle change case. In the second case, normal incidence of the particles was used and the inter-particle distance in both directions was changed with corresponding angles, we refer this to gap change case. We calculated the near field angle dependent spectra and plotted the peak positions for both these configurations to show their equivalence. Figure A.3 shows the peak position as a function of angle obtained in both these cases under longitudinal polarizations of incident light. Peak positions and their trends are similar in both cases showing that changing the angle of incidence is equal to change in the gap between them. Below 45°, the decrease in the in-plane distance caused a redshift of the two particles and after 45° the increase in the out-of-plane distance caused a blue shift of the resonance. For angles below 45°, the redshifts are similar to what has observed in nanospheres dimers where physical distance between the dimers was changed using DNA[1].

We also calculated the angle dependent spectra and plotted the peak positions for both configurations (angle change and gap change) in linear array of 50 particles and 2-d hexagonal array of 492 particles. Figure A.4 shows these results for longitudinal polarization of incident light. Similar equivalence between angle change and gap changes exists for both linear and 2-d hexagonal arrays. The redshifts (below 45°) and blue shifts (above 45°) for the longitudinal polarization are analogous to the

**Figure A.3.** Peak positions of extinction spectra due to near-field coupling in nanosphere dimer for both angle change and gap change cases.
Figure A.4. Peak positions of extinction spectra due to near-field coupling in nanospheres arrays for both angle change and gap change cases (a) Linear array of 50 nanospheres and (b) Two dimensional hexagonal array of 492 nanospheres.

one observed in dimers.

A.1.2 Near-field coupling in Nanodiscs

The effects of near-field coupling in nanodisc dimers on angle dependence spectra can also be understood by effective inter-particle gaps in the in-plane and out-of-plane directions similar to nanosphere dimers. We prove this here by showing the equivalence of changing the angle and changing the effective distance in dimers and arrays of nanodiscs. We first present data on nanodisc dimers and then extend to linear arrays and two dimensional arrays (a case relevant to this manuscript).

Figure A.5 shows the schematic of a nanodisc dimer with an incidence angle of light at $\theta$ degrees (left case) and an equivalent normal incident configuration (center case) with 1) changed effective inter-particle distances, $S\cos(\theta)$ (in-plane gap) and $S\sin(\theta)$ (out-of-plane gap) and 2) changed orientation. Unlike nanospheres where the geometry is symmetric under rotation, one has to consider the change in orientation for nanodiscs. Due to limitations of our simulation method, we cannot simulate the tilt in nanodisc in normal incidence therefore we approximated the gap change case to only change in effective distance and no tilt of nanodiscs (right case).

We calculated the near field angle dependent spectra and plotted the peak positions for both these configurations (left and right cases of Fig. A.5). Figure A.6
Figure A.5. Schematic showing the equivalence of angular incidence (left) and normal incidence with changed effective gaps and orientation (center) in nanodisc dimers. Due to limitation of our simulation method, the normal incidence with changed effective gaps and changed orientation (center) is approximated by a case with only change in effective gaps (right).

Figure A.6. Peak positions of extinction spectra due to near-field coupling in nanodisc dimer for both angle change and gap change cases.
Figure A.7. Peak positions of extinction spectra due to near-field coupling in nanodisc arrays for both angle change and gap change cases (a) Linear array of 50 nanodiscs and (b) Two dimensional hexagonal array of 492 nanodiscs.

shows the peak position as a function of angle obtained in both these cases under longitudinal polarization of incident light. The decrease in the in-plane distance in the gap change case caused a redshift of the two particles (below 45°) and the increase in the out-of-plane distance caused a slight blue shift of the resonance (above 45°). As the near field interactions of the nanodiscs in the longitudinal direction are stronger than the out-of-plane directions, the effect of gap change in the out-of-plane direction are weaker and therefore the blue shift above 45° is weaker. However, the effect of change of incident angle above 45° redshifts the peaks position and is not well described by the only change in effective distance. This is attributed to the inability of our simulation to tilt the orientation of nanodiscs under normal incidence and calculate the exact near-field interactions along the axis of dimer. The tilt of nanodiscs which is not taken into consideration increases the longitudinal (in-plane) interactions of near-fields above 45°. Similar results as observed in nanodisc dimer are also observed in the case of linear and two dimensional arrays of nanodiscs as shown in Fig A.7.

In summary, the near field interactions of nanodiscs under various incidences of angles can be explained by the change of effective distances between the nanodiscs and domination of interactions in the longitudinal direction of nanodisc dimers. The change in effective distances causes a redshift below 45° and slight blueshift above 45°. However, the blueshift above 45° is overcome by the tilt of nanodiscs
Figure A.8. (a) Schematic illustrating the relation between incident angle and the critical grating constant in an array of nanodiscs. (b) Data revealing the redshift of plasmon resonance when the critical grating constant due to the increased incident angle approaches the nanodiscs array period (320 nm) which enables stronger longitudinal near field interactions and results in monotonic redshift of the plasmon resonance.

A.2 Effect of Far-field coupling in Nanodisc Arrays

As nanoparticles are in an ordered array, they will also exhibit redshift due to far field radiative dipole coupling. For any array of nanoparticles (or grating), there is a critical grating constant ($\Lambda_C$) corresponding to a certain grating order. The $\Lambda_C$ at first grating order can be expressed as $\Lambda_C = \frac{n_1 \lambda_{sp}}{n_1 \sin (\theta) + n_2}$ as stated in Felidj et al.[2] where $\lambda_{sp}$ is the light incident angle, $n_1$ and $n_2$ are the refractive index of the array superstratum and substrate respectively (as shown in Fig. A.8 a). When the incident angle is increased, the $\Lambda_C$ is decreased continuously to approach the experimental period of nanodisc arrays (320 nm). This leads to strong dipole coupling between nanoparticles and almost in-phase
addition of the scattered light fields of neighboring particles. Due to the dipole coupling and large in-phase addition of scatter fields, plasmon resonance of array is softened causing the observed redshift of the plasmon resonance (Fig.A.8b). The red shift of plasmon resonance as critical grating constant approaching grating constant of array is a well established work studied in detail by various researchers in the field.[2]
References


Appendix B

Instrumentation

B.1 Microscopy Techniques

B.1.1 Scanning Electron Microscopy

The electron microscopy images were obtained on a ZeissSMT Leo 1530 Field Emission Scanning Electron Microscope (FE-SEM) at the Penn State Nanofabrication facility, and on a Hitachi S-3000H Scanning Electron Microscope (SEM) at the Penn State Material Characterization Laboratory.

B.1.1.1 SEM Sample Preparation

Approximately 5 µL of particle assembly sample (< 0.01% solids) were pipetted onto a silicon wafer and left to air dry. The particles were sputtered with gold for 30 seconds. SEM images were taken at an accelerating voltage of 5 kV and working distances between 6 and 7 mm.

B.1.1.2 FESEM Sample Preparation

Approximately 5 µL particle assembly samples (< 0.01% solids) were pipetted onto a silicon wafer and left to air-dry. Field emission scanning electron microscopy (FESEM) images were taken at a gun power of 1 kV and working distances between 3 and 6 mm.

SEM is a non-destructive form of microscopy that provides surface observations
Figure B.1. A picture of the (a) Leo 1530 field emission scanning electron microscope (FE-SEM) from the Penn State Nanofabrication facility, and of the (b) Hitachi S-3000H Scanning Electron Microscope (SEM) at the Penn State Material Characterization Laboratory.

down to 60 nm of resolution for SEM and to 1nm resolution for FE-SEM. Primary electrons are focused and deflected down onto the sample through a narrow beam. The electrons interact with the atoms that make up the sample producing secondary electrons that contain information about the sample’s surface topography. The working of SEM and FE-SEM is same. In a FE-SEM, there is a field-emission cathode in the electron gun that provides narrower probing beams, improved spatial resolution and less sample charging than a traditional SEM. Thus, sample imaged with FE-SEM do not require a gold sputter coating for imaging. The angle and the velocity of the secondary electrons detected relate to the surface structure of the objects (sample) and are converted into an electronic signal. This signal is amplified and then transformed into a video scan-image.

B.1.2 Dark Field Micro-spectroscopy

A transmission mode microscope (Nikon Eclipse TE-2000U) with an oil contact dark-field condenser (NA: 1.3-1.45) and a 100 wet objective with adjustable internal iris were used to obtain scattering spectra of nanodisc dimers. A polarizer was placed at the objective exit to measure polarization dependent scattering. The light from the objective was sent to an imaging monochromator (Acton Research MicroSpec 2300i) equipped with a CCD camera (CoolSnap HQ2). Spectra were obtained by
collecting samples of light from a region that contained nanodisc dimers ($I_s$) and samples from dark regions ($I_d$). Reference spectra ($I_r$) were obtained by increasing the iris of objective to allow direct coupling of incident light into the objective. The scattering spectra was obtained by following transformation, $(I_s-I_d)/(I_r-I_d)$.

**B.2 Fabrication Techniques**

The two main nanofabrication instruments used for my thesis work are Semi Core Evaporator and Reactive Ion Etcher.

**B.2.1 Thin Film Deposition Equipment**

Semi Core Electron Gun Evaporator at the Penn State Nanofabrication Facility was used for depositing thin films of metal/semiconductor on substrates. In particular, thin films of gold, silver and titania were deposited on colloidal particles. The evaporation can be at normal incidence (coat half of the particle) or conformal (coat the entire particle except the area which is in contact with the substrate). Sample Preparation: Colloidal particles were settled on a clean (piranha-etched) glass slide to form a monolayer (with or without spacing, depending on the requirement). The slide was then air-dried and mounted on the sample holder using a non-conducting krypton tape. Electron beam evaporator is a form of physical vapor deposition in which a target anode is bombarded with an electron beam given off by a charged tungsten filament under high vacuum. The electron beam causes atoms from the target to transform into the gaseous phase. These atoms then precipitate into solid
Figure B.3. A picture of the Semi Core E-Gun evaporator at the Penn State Nanofabrication facility.

form, coating everything in the vacuum chamber (within line of sight) with a thin layer of the anode material.

The evaporator in the Penn State Nanofabrication facility incorporates a 4-pocket E-beam source as well as a Thermal source for multiple material depositions. System control is semi-automated, and the vacuum is provided by a large cryo-pump and dry roughing pump. A planetary sample mounting set can handle small samples through 6” wafers along with a special holder for the lift-off process. Several materials can be evaporated, including gold, silver, iron, nickel, silicon, titania, chromium, copper etc.

B.2.2 Reactive Ion Etching

Plasma Therm 720 Reactive Ion Etch instrument at the Penn State Nanofabrication facility was used for etching materials like polystyrene and gold. Reactive Ion Etching (RIE) uses chemically reactive plasma to remove material deposited on substrates. An electromagnetic field generates the plasma in vacuum and high
energy ions from the plasma attack the substrate surface and as a result react with it.

A typical (parallel plate) RIE system consists of a cylindrical vacuum chamber, with a wafer platter situated in the bottom portion of the chamber. The wafer platter is electrically isolated from the rest of the chamber, which is usually grounded. Gas enters through small inlets in the top of the chamber, and exits to the vacuum pump system through the bottom. The types and amount of gas used vary depending upon the etch process; for instance, for my work, oxygen was used for etching polystyrene (oxygen reacts with the carbon), and argon was used for etching gold. Gas pressure is typically maintained in a range between a few millitorr (mT) and a few hundred millitorr by adjusting gas flow rates and/or adjusting an exhaust orifice.

For my work, the etch process for oxygen and argon were typically performed at 100 mT pressure and 100 W power with oxygen flow rate of 20 sccm; and 10 mT pressure and 300 W power with argon flow rate of 30 sccm, respectively. The time was set depending on the amount of colloid/film to be etched.

The RIE system at the Penn State Nanofabrication facility consists of a vacuum load lock connected to a simple parallel plate process chamber for dry etching.

**Figure B.4.** A picture of the Plasma Therm 720 reactive ion etch instrument at the Penn State Nanofabrication facility.
semiconductor, dielectric, and metal samples. The system can be used to etch small samples through full 6” wafers. It is configured with the following chemistries: $SF_6$, $C_2F_6$, $CF_4$, $CHF_3$, $Cl_2$, $O_2$, $Ar$, $H_2$. Chamber plasma cleaning procedures are implemented between each etch run to assure process reproducibility.
Vita
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Education
2011 Ph.D., Engineering Science & Mechanics
The Pennsylvania State University, U.S.A.
2004 M.S., Manufacturing Systems and Technology
The Singapore-MIT Alliance, Singapore.
2003 B.E., Mechanical Engineering
The Osmania University, India.

Awards and Honors
2011 First place in poster presentation, ESM Graduate Symposium
2010 Rustum and Della Roy Innovation in Materials Research Award
2010 Reaxys Ph.D. Prize runner-up
2010 Dr. Paul A. Lester Memorial Award
2009 Dr. Sabih & Mrs. Güler Hayek Graduate Scholarship
2006 Amelia C. Barnes, Andrew Barnes & Kevin Barnes Scholarship
2003 Graduate Fellowship, The Singapore-MIT Alliance.
2003 “Rank Certificate” for undergraduate excellence, The Osmania University.

Research Highlights
1. Three journal articles authored/co-authored by me have been highlighted as front journal cover images.
2. Paper on ordered nanodisk arrays was among the 20 most downloaded research articles in 2008 in Journal of Applied Physics.
3. Research on active molecular plasmonics was highlighted in National Science Foundation, journals Nature Materials, and >40 public media such as Science Daily, R&D Magazine and Science Mode.
4. Research on light-driven plasmonic switches was highlighted in journal Nature Photonics, ACS Nanotation, AZo Nanotechnology and Nanowerk News.
5. Review article on Biological and Biomimetic Molecular Machines was highlighted in Nanomedicine editorial.
6. Research on tunable liquid gradient refractive index lens was highlighted in National Science Foundation, and >60 public media such as US News and World Report, Science Daily, Medical News Today, and SPIE.