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Design, Fabrication and Fundamental Studies of Plasmonic Materials

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Abstract

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Nanoplasmonics is an emerging branch of photonics that studies the optical properties of noble metals. Nanostructured noble metal materials, which can strongly interact with light and support various plasmon modes, are exceptional candidates for nanophotonic devices. This work describes the latest advances in the fabrication of ordered silver nanoparticles or nanowell arrays using both nanosphere lithography (NSL) and electron beam lithography (EBL). More specifically, three types of new NSL-derived materials are addressed in this thesis: (1) the application of electrochemistry to “fine tune” the structure of silver nanotriangles and the wavelength of their localized surface plasmon resonance (LSPR), (2) the fabrication of ordered arrays of in-plane, triangular cross-section nanowells with the aid of reactive ion etching (RIE), and (3) the anchoring of the truncated tetrahedrons for a more stable sensing surface. Furthermore, utilizing EBL, studies looking deeper into the fundamental coupling interactions in both one and two dimensional arrays were performed. All of these studies will allow for the logical design of novel plasmonic devices for an array of applications.

Prof. Richard P. Van Duyne
Research Advisor

Prof. Kenneth G. Spears
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I did it!!

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List of Common Abbreviations

AFM – Atomic Force Microscope

CDA – Coupled Dipole Approximation

DDA – Discrete Dipole Approximation

EBL – Electron Beam Lithography

EF – Enhancement Factor

FON – Film Over Nanosphere

FOW – Film Over Nanowell

LSPR – Localized Surface Plasmon Resonance

NSL – Nanosphere Lithography

PL – Photolithography

RIE – Reactive Ion Etching

SAM – Self-Assembled Monolayer

SEM – Scanning Electron Microscopy

SERS – Surface Enhanced Raman Scattering

SHG – Second Harmonic Generation

SPR – Surface Plasmon Resonance

TEM – Transmission Electron Microscopy

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Chapter 1

Introduction to Nanoparticle Fabrication and Optical Properties

1.1 Fabrication of Noble Metal Nanostructures

If you have ever looked at a piece of gold bar and a deep red stained glass window stained with gold nanoparticles, you notice a distinct difference in their color, even though they are both the same material. This is because there is a distinction between many of the macro- and micro- scale properties of materials. Because of the vast difference between the two size regimes, size dependent properties have garnered a significant interest in recent years. As in the example above, one of these size dependent properties of interest has been the optical properties of noble metal nanoparticles, particularly the localized surface plasmon resonance (LSPR), the details of which will be described in a later section (Sections 1.2, 1.3, and 1.4). The ability to observe and study the LSPR is heavily reliant on the researchers ability to fabricate these structures in a systematic and precise manner. There are three main types of nanofabrication techniques available to probe all the characteristics affecting the LSPR. These techniques are: (1) wet chemical synthesis, (2) direct write lithographies and (3) natural lithographies. Wet chemical synthesis, is a popular method, although not a focus of this theses. It is commonly conducted by the chemical reaction of metal salts in the presence of surfactants and capping agents, and enables the fabrication a large variety of structures. Many groups have made structures ranging from nanocubes¹ to triangular prisms² to core-shell morphologies.³

Another class of fabrication exists where the nanoparticles are produced directly on the desired surface. This generates substrate-bound nanoparticles, as opposed to the dispersions of nanoparticles synthesized by wet chemical methods. The number of substrate-bound lithographic methods is as varied as the structures that can be made by them. Two categories exist, direct write and natural lithography. Direct write methods are those where a user defined computer aided design (CAD) file or program to tell the system the desired location of the

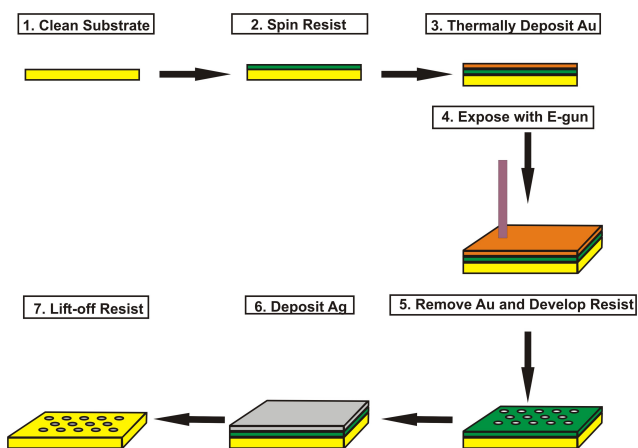


Figure 1.1 Schematic illustration of the electron beam lithography technique.

patterns. Direct write methods include:

photolithography;^{4,5} electron beam lithography (EBL);⁶⁻⁸ focused ion beam lithography (FIB);⁹⁻¹⁵ soft lithography;¹⁶⁻¹⁹ and dip-pen nanolithography.²⁰ Natural lithographies use natural assemblies of particles to be used as masks, e.g. nanosphere lithography.^{21,22} Two

fabrication methods that were used throughout the experiments in this work will be discussed in the following sections: one direct write method, electron beam lithography; and a natural lithography method nanosphere lithography.

1.1.1 Electron Beam Lithography

Electron beam lithography (EBL) is a standard approaches for making substrate-bound nanostructures. EBL patterns are made serially, produced by exposing a thin layer of electron sensitive resist to high-energy electrons from a filament in an electron gun, altering the exposed resist. The surface is then developed in a solvent to remove the chemically altered resist. After development, the masks are used to etch the surface or deposit the material of choice on the surface. The leftover resist is subsequently removed from the surface, usually with a strong base, leaving the nanostructures, see Figure 1.1. While EBL is an expensive and time-consuming nanofabrication technique, the inherent flexibility and precision in nanostructure design is a powerful asset, as has been demonstrated by the large number groups that have utilized this technique for studying nanoscale optical systems. Kauranen and coworkers used EBL to look at both the linear and non-linear properties of Au L shaped nanoparticles.²³⁻²⁶ Käll and coworkers

used EBL to fabricate pairs of Ag nanoparticles to look at the optical coupling as the distance between the two nanoparticles is varied.⁷

EBL is notoriously time consuming and expensive, but new techniques are offering ways to extend EBLs usability. Nanoimprint lithography and other soft lithographies offer a way to make EBL a massively parallel technique. With these stamping techniques, a master is made with EBL and the pattern is reproduced onto the desired substrates.

1.1.2 Nanosphere Lithography

Nanosphere Lithography (NSL) is a powerful fabrication technique to quickly and inexpensively produce nanoparticle arrays with controlled shape, size, and interparticle spacing. The NSL fabrication process starts with the self-assembly of monodispersed nanospheres of diameter, D , to form a hexagonally close packed (HCP) colloidal crystal. The two most common methods to pack the nanospheres are drop coating,²¹ and spin coating.²² The nanospheres used are in a suspension, typically aqueous. As the solvent dries on the surface a meniscus is formed that helps the nanospheres pack on the surface, through capillary forces. This meniscus also allows the nanospheres to obtain their lowest energy conformation and crystallize in the HCP arrangement. As in all naturally occurring crystals, nanosphere masks include a variety of defects that arise as a result of nanosphere polydispersity. Among these are point defects, line defects, and polycrystalline domains. Typical defect-free domain sizes are in the 10 μm range.²¹ New techniques have been developed that help reduce these defects by forcing the packing into certain geometries. Convective self-assembly²⁷ and template assisted assembly²⁸ of nanospheres use robots and pre-patterned surfaces to eliminate some of the environmental conditions that normally govern the packing of the nanospheres in the older methods. These techniques also offer a larger range of surfaces and spheres without need for special surface functionalization.

Following self-assembly of the nanosphere mask, these surfaces can be used in a multitude of ways, usually as a deposition mask. A variety of materials have been deposited through NSL masks. Fan and coworkers utilized the NSL technique on a GaN surface to grow well ordered ZnO pillars *via* a vapor-liquid-solid epitaxy method.²⁹ They were able to achieve isolated single nanocrystals by being controllably fabricating single catalytic sites. Cheng and coworkers utilized NSL to fabricate NiSi₂ nanodots.³⁰ They were able to show that NSL is very powerful for fabricating well ordered arrays for use in studying interfacial reaction of difference metals. Cai and Ocko utilized NSL to pattern lysozymes onto a silicon surface while retaining biofunctionality.³¹ The size of the proteins and patterns they were able to achieve was on order with those obtained by scanning probe techniques. An advantage of using NSL in this way over scanning probe methods is the ability to fabricate novel structures on a much faster time scale. Not only can the material deposited be varied, but the angle of deposition and the nanosphere mask can be changed as well. The shape and spacing of the nanoparticles can be varied by changing the angle of deposition³² and by shrinking or swelling the nanosphere masks.³³

The nanosphere masks can also be used in combination with other techniques. In the push to extend and refine the NSL technique, it has recently been combined with a dry etching technique, reactive ion etching (RIE). The resultant structure produced by combining these two techniques is a nanohole array. We have demonstrated the fabrication of ordered arrays of in-plane, triangular cross-section nanowells with large range in sizes of the in-plane widths and a variety of hole depths.³⁴ We kept the nanosphere mask intact by utilizing lower etch powers and pressures to create isolate structures, while Wang and coworkers fabricated high aspect ratio nanopillar surfaces by shrinking of the nanosphere mask.³⁵ Murray and workers combined NSL

and RIE to create nanopillar arrays that were used as a template to fabricate ferromagnetic structures.³⁶

1.2 Fundamental Studies of Tunable Optical Properties

Optical properties of submicron sized metal nanoparticles fabricated with nanometer precision have drawn particular interest both experimentally and theoretically because of their impact in technological applications such as bio/chemosensors,³⁷⁻⁴³ optical filters,^{12,44} plasmonic waveguides,⁴⁵⁻⁴⁸ and substrates for surface-enhanced spectroscopies.⁴⁹⁻⁵⁷ These important applications are all based upon a phenomenon known as the localized surface plasmon resonance (LSPR). The LSPR is a collective oscillation of the conduction electrons that occurs when light of a specific wavelength impinges on a surface. The LSPR resonance creates enhanced light scattering at selected wavelengths and local enhancement of the electromagnetic field around the nanoparticles. The resonance peak position and shape of the LSPR as measured in extinction spectra is governed by the nanoparticle shape, size, and dielectric environment. The composition also effects the plasmon peak position. The LSPR occurs mostly in the visible wavelength range for nanoscale silver and copper, and moves into the near and mid infrared with gold structures. Typically, noble metals are the most common material used in optical applications, but other metals e.g. Sodium, exhibit this property.⁵⁸ Excitation of the LSPR has two characteristic consequences: (1) selective absorption and scattering and (2) generation of electromagnetic fields at the surface of the nanoparticles.

Another important factor to study is the differences between individual nanoparticles and arrays of nanoparticles. When individual nanoparticles are brought close together, the LSPR also becomes dependent on the interactions between two or multiple adjacent nanoparticles. This added complexity opens new areas of research where not only do certain conditions effect

the individual nanoparticle plasmon resonances, but also there is the need to understand the effects of nanoparticle coupling on the array plasmon as the interparticle spacing, shape, and the nanoparticle environment are varied.

1.2.1 Optical Coupling and the Localized Surface Plasmon Resonance

In order to study the effect of optical coupling in nanoparticle arrays, it is necessary to methodically control all parameters that determine the array LSPR. With a sufficiently flexible nanofabrication method, like those detailed above, it is possible to manipulate all factors affecting the LSPR, varying one parameter at a time to systematically to examine the outcome. Extensive studies have been completed by Van Duyne and coworkers using NSL-fabricated substrates whereby it is possible to meticulously vary the nanoparticle size, shape, substrate, dielectric environment, effective thickness of the chemisorbed monolayer, and thickness of a deposited layer on the surface. In both cases, the experiments revealed systematic shifts in the LSPR: increasing the aspect ratio shifts the LSPR to lower energies; retraction of sharp tetrahedral tips shifts the LSPR to higher energies; increasing the refractive index of the substrate or solvent environment shifts the LSPR to lower energies; and increasing the thickness of chemisorbed or deposited layers shifts the LSPR to lower energies within the limit of the electromagnetic field decay length. One disadvantage of utilizing the NSL technique is that the interparticle spacing is fixed for a given nanosphere used to fabricate the particles. Thus, although certain factors were able to be studied, others were left untouched. Hanarp and coworkers⁵⁹ as well as Rindzevicius and coworkers both utilized colloidal lithography, a non-close packed version of NSL, to change the shape and environment of the structures produced.⁶⁰

Fundamental studies of electromagnetic coupling between nanoparticles are driven by the fact that the design of plasmonic nanodevices relies heavily on the nature of the electromagnetic

interactions between nanoparticles in the devices. These interactions can be evaluated by measuring the LSPR wavelength because an explicit LSPR peak shift occurs as the electromagnetic coupling changes, i.e., when the nanoparticles are moved closer together or further apart.

There are a variety of ways researchers have studied the topic of optical coupling between metal nanoparticles. The first is to embed nanoparticles into a polymer matrix. This is done to utilize the flexibility of polymers to change the distance between the nanoparticle systems. Chumanov and coworkers looked at the difference in the extinction spectrum as a disordered array of Ag nanoparticles on a glass surface. They observed a distinct difference in the extinction spectrum of the nanoparticles in water and in poly-dimethyl siloxane (PDMS) by seeing an increase in a sharp peak on the high energy side of a larger feature. This cooperative plasmonic coupling spurred further inquiries into its properties. They fully embedded the particles into a PDMS substrate, and used the innate flexibility of the polymer to change the interparticle spacing. As they decreased the spacing, the quadrupole band increased in intensity and sharpens, while the dipole peak disappeared. They also observed a decrease and shift in the peak as the incident angle was changed for both s and p polarized light.

Other groups have focused on studying particles on solid surfaces rather than in dielectric media. We have studied short-range coupling effects in EBL fabricated hexagonal and square arrays of triangular or circular Au and Ag nanoparticles.⁶¹ We observed a shift of the LSPR, depending on lattice spacing, and a related theoretical work explained these effects in terms of radiative dipolar coupling between the nanoparticles and retardation effects. Others have looked in more detail at two-dimensional arrays. Aussenegg and co-workers have studied extinction spectra of two-dimensional Au nanoparticle arrays with variety of nanoparticle shapes such as

cylinders,⁶²⁻⁶⁴ nanorods,⁶²⁻⁶⁵ and nanowire gratings.⁶⁶ In one study, a variety of lattice spacings were fabricated utilizing EBL.⁶⁵ After fabrication, the resonance peak was measured with white light spectroscopy and the plasmon lifetime with time-resolved collinear autocorrelation measurements. They were able to observe a red-shift with increasing grid spacing, and an increase in the plasmon damping at a critical grating constant.

Another type of coupling recently studied is the interaction between nanoparticles and molecular absorptions.^{67,68} With the versatility of NSL, Van Duyne and coworkers were able to scan the plasmon resonance over the range of the absorption peak of several chromophores and monitor the shift in the plasmon resonance. When the plasmon resonance is matched to the molecular absorption, there is almost no shift in the plasmon resonance, but if the plasmon resonance is slightly lower energy than the absorption, there is a large enhancement over the baseline in the shift in the plasmon resonance.

1.3 Applications of the Localized Surface Plasmon Resonance

Along with fundamental studies, there is a great deal of interest in using these nanosystems for practical devices. While most of these technologies are still in the beginning stages of research, the use of these optical systems as biological sensors has already been adopted by industry.^{37,69-76} Van Duyne and coworkers have exploited the high sensitivity of noble metal nanoparticle systems to changes in the local refractive index in order to sense a variety of surface bound molecules. Utilizing self-assembled monolayers as capture layers on these single nanoparticle systems, extremely high sensitivity to small biomolecules like streptavidin can be detected down to the picomolar level. These initial studies opened the door for sensing of clinically relevant analytes, such as ADDLs, a molecule believed to be crucial in the development of Alzheimer's disease.⁴⁰ Preliminary studies based on small populations of Alzheimer's patients

and aging controls showed a shift of almost 11 nm for diseased samples and less than 1 nm shift for the control in the LSPR peak position, correctly diagnosing the affected patients via spinal fluid. Van Duyne and coworkers also compared LSPR to the more commonly used SPR technique evaluating the sensitivities and detection capabilities for sugar lectins.⁷⁶ This study showed that the sensors built off of the LSPR platform had comparable sensitivity for the target analyte to SPR, but with less sensitivity to interfering non-specifically bound analytes due to smaller sensing volumes.

All of the above measurements deal with ensemble averaged signal over an array of nanoparticles. Several groups have begun to shrink this down even further and move to building single nanoparticle sensors. McFarland and coworkers were able to demonstrate zeptomolar sensitivity of single nanoparticles to changes in the refractive index, via solvents and biological molecules.⁷⁷ Halas and coworkers have used a Au core shell structure with an absorption in the near infrared and are capable of passive uptake from the abnormal tumor vasculature due to their nanoscale size.^{78,79} Under controlled conditions, nanoshells accumulate in tumors with good efficiency compared to the surrounding tissues. They were able to treat the tumors via: (1) inoculation in immune-competent mice by subcutaneous injection, (2) polyethylene glycol coated nanoshells (≈ 150 nm diameter) with peak optical absorption in the NIR were intravenously injected and allowed to circulate, and (3) the tumors were then extracorporeally illuminated with a collimated diode laser (808 nm, 2-6 W/cm², 2-4 min). Upon irradiation, the photothermal therapy was able to regress the tumors in greater than 90% of the mice.

1.4 Surface-Enhanced Raman Spectroscopy

As stated earlier, the LSPR results in two phenomenon, the first of which was described in detail above. The second property, enhanced electromagnetic fields, play a key role in related

phenomenon that also hold promise in future analytical uses. Raman scattering, an inelastic light scattered process, was first discovered by Raman and Krishnan in 1928. (ref) In the classical view of the Raman effect, the incident light is considered an electromagnetic wave that induces polarization in a molecule. This induced dipole in the molecule then emits or scatters light at the optical frequency of the incident light wave, plus or minus the energy of a molecular vibration. Raman scattering produces sharp spectral features that are useful for molecular identification. The intensity of scattering is proportional to the magnitude of the change in molecular polarizability. Thus, aromatic molecules exhibit more intense Raman scattering than aliphatic molecules. Even so, “large” Raman scattering cross sections are typically 10 orders of magnitude smaller than elastic scattering cross sections and 14 orders of magnitude smaller than those of fluorescence. Therefore, the Raman signal is still several orders of magnitude weaker than the fluorescence emission in most cases. The applications of Raman scattering were limited for many years because of the inherently small intensity of the Raman signal, the sensitivity limits of available detectors, and the intensity of the excitation sources. However, its utility as an analytical technique improved with the advent of the laser, development of inexpensive and high quality filters, and the evolution of photon detection technology.

In 1977, Jeanmaire and Van Duyne demonstrated that the magnitude of the Raman scattering signal can be greatly enhanced when the molecule is placed on or near a nanoscale roughened noble metal substrate.⁸⁰ The principal source of enhancement is the strong electromagnetic fields that are generated at the noble metal surface. These fields are produced as a result of the LSPR. When the molecule is subjected to these intensified electromagnetic fields, the magnitude of the induced dipole increases, and accordingly, the intensity of the inelastic scattering increases. This enhanced scattering process is known as surface-enhanced Raman

scattering (SERS)—a term that emphasizes the key role of the noble metal substrate in this phenomenon.

In addition to the electromagnetic enhancement mechanism, a chemical mechanism has also been posited. The relative contribution of each mechanism remains an active research topic among those in the SERS community.^{81,82} In the chemical mechanism, thought to contribute an average enhancement factor of 100, a charge-transfer state is created between the metal and adsorbate molecules.⁸²⁻⁸⁴ In a manner analogous to that observed in resonance Raman spectroscopy, the existence of this charge-transfer state increases the probability of a Raman transition by providing a pathway for resonant excitation. This mechanism is site-specific and analyte-dependent. Furthermore, the molecule must be directly adsorbed to the roughened surface to experience the chemical enhancement.

Most researchers formally consider the EM mechanism to be the more important of the two mechanisms. However, to understand the electromagnetic mechanism, one must consider nanostructure optics. As stated *supra*, the excitation of the LSPR has two consequences: selective absorption and scattering of the resonant electromagnetic radiation, and generation of large electromagnetic fields at the surface of the roughness feature. The electromagnetic mechanism is based on these amplified electromagnetic fields (E) generated by the LSPR of nanoscale features. There is a complex relationship between the surface structure and the structurally dependent optical characteristics that determines the magnitude of the electromagnetic portion of SERS enhancement.⁸⁵ The improved understanding of the nature of the EM enhancements has generated renewed interest in the use of SERS as an analytical technique.⁸⁶ Many groups continue to generate new insights as new mathematical models are coupled to more accurate characterization in the nanoscale regime.^{61,87,88}

SERS holds great potential as a sensitive and selective identification tool for both biological and chemical agents. The narrow, well-resolved bands allow simultaneous detection of multiple analytes, and the low signal strength of water simplifies investigation of biological samples. SER spectroscopy (SERS) can be exploited for sensitive and selective molecular identification. Recently, SERS has been used extensively as a sensing platform in biological and chemical sensing. Examples are trace analysis of pesticides,⁸⁹ anthrax,^{90,91} prostate-specific antigen, (ref) glucose,⁹²⁻⁹⁵ and nuclear waste. (ref) SERS has also been implemented in identification of bacteria, genetic diagnostics, and immunoassay labeling.⁹⁶⁻⁹⁹ A miniaturized, inexpensive, and portable SERS instrument makes the technique practical for trace analysis in clinics, the field, and urban settings.¹⁰⁰ Obtaining a deeper understanding the LSPR and the design of the devices will impact the reliability, repeatability, and usability of SERS in everyday applications.

1.5 Goals and Organization

The remainder of this thesis is organized as follows. Chapters two and three examine extensions of the NSL enable a wider variety of options for describe the development of novel NSL variations with an eye to enabling new sensors and applications. Specifically, chapter two describes the fabrication and optical characterization of nanoparticle arrays on an indium tin oxide (ITO) surface and consecutive electrochemical modification. Chapter three studies at the development and testing of anchored nanoparticle surfaces for their tunability and initial testing as both LSPR and SERS sensors. Chapter four begins the deep delve into optical coupling in nanosystems beginning with the fabrication and optical testing of film over nanowell surfaces. Theoretical simulations elucidate where the main contribution to the plasmon comes from, as well as the main coupling mechanism in the system as varying physical parameters are changed.

Chapters five and six focus on fundamental studies in one and two-dimensional arrays and the changing lattice parameters to maximize the diffractive coupling in the system. Finally, chapter seven looks at a comparison of a commercially available SERS active surface, Klarite, to one that is commonly used by the Van Duyne group, silver film over nanospheres (FON). This comparison sets out criteria for future evaluations to help to push the use SERS further in the commercial arena by forcing the best and most reliable surfaces to be developed and used.

Chapter 2

Electrochemical Modification on Nanoparticle Surfaces

2.1 Introduction

Nanosphere lithography (NSL) is an inexpensive, simple to implement, high throughput nanofabrication technique capable of producing a large variety of nanoparticle structures and well-ordered nanoparticle arrays.^{22,101} This letter describes our recent efforts to broaden the scope of NSL by fabricating truncated tetrahedral Ag nanoparticles on indium tin oxide coated glass electrode surfaces. The samples produced have large areas (10-100 μm^2) with low defect density. Well-ordered nanoparticle arrays on conducting transparent surfaces permit the simultaneous study of optical and electrochemical measurements. These new plasmonic materials enable the study of the effect of the electrochemical potential on the localized surface plasmon resonance (LSPR) of Ag nanoparticles.¹⁰² It should now be possible to develop electrochemical LSPR nanosensors.¹⁰³

The LSPR is excited when a specific wavelength of light impinges on a noble metallic nanoparticle and causes the plasma of conduction electrons to oscillate collectively.⁸⁵ Because this collective oscillation of electrons occurs only for light within a certain bandwidth, noble metal nanoparticles exhibit selective photon absorption and resonant Rayleigh scattering which can easily be monitored using UV-visible extinction spectroscopy. It is well established that the maximum extinction wavelength, λ_{max} , of the LSPR is strongly and systematically dependent upon the composition, size, shape, and interparticle spacing of nanoparticles.¹⁰⁴ Therefore, monitoring the LSPR λ_{max} permits *in situ* optical monitoring of changes in the Ag nanoparticle structure during electrochemical modification experiments.

Recently it has been demonstrated that the LSPR λ_{max} of chemically reduced silver nanoparticles shifts ~ 20 - 40 nm towards shorter wavelengths due to the increase in negative

surface charge density on an ITO electrode surface with the application of potentials from 0 to -2 V (vs. Ag/AgCl).^{105,106} Poly(acrylic acid)^{105,106} or aminobutylsiloxane¹⁰⁷ has been utilized to immobilize noble metal colloids onto ITO surfaces, which make it difficult to fabricate a well-ordered and repeatable surface motif, and therefore, to achieve controllable LSPR spectra.⁷ Moreover, when anodic potentials were applied to silver colloid modified electrode surfaces, total dissolution of colloids was observed.¹⁰⁸ In contrast, NSL produced nanoparticle arrays have controlled shape, size, and interparticle spacing, and are extremely stable to positive surface charge density on an ITO surface electrode. This makes NSL produced arrays a prime candidate for the use in the systematic study of electrochemical modification of nanoparticles.

This chapter addresses two goals: (1) to develop a simple electrochemical method to modify the structure of NSL-fabricated silver nanoparticles and monitor these structure changes by *in situ* LSPR; and (2) to explore the electrochemical properties of Ag nanoparticles and other nanoscale materials.

2.2 Experimental Methods

2.2.1 Surface Preparation

ITO substrates (Delta Technologies Limited, Stillwater, MN) were cleaned by 10-min sonication in Detergent 8[®] (Alconox, Inc. New York, NY). 5:1:1 H₂O: NH₄OH: 30% H₂O₂ with sonication for one hour, was used to render the ITO surface hydrophilic. Polystyrene nanospheres (Duke Scientific, Palo Alto, CA) were drop-coated onto the cleaned ITO substrates and were allowed to dry. This yielded a hexagonal close-packed monolayer of nanospheres which served as the NSL deposition mask. The samples were mounted into a Consolidated Vacuum Corporation vapor deposition chamber. A Leybold Inficon XTM/2 quartz crystal microbalance was used to monitor the mass thickness, d_m , of the metal being deposited.

Following metal deposition, the samples were sonicated for 1-2 min in ethanol (Pharmco, Evanston, IL) to remove the polystyrene nanosphere mask.

2.2.2 Scanning Electron Microscopy

Scanning electron microscope (SEM) images were collected using a Hitachi S4500 Field Emission (Hitachi, Japan) electron microscope operating at an accelerating voltage of 5 kV and an average working distance of 7 mm. As shown in Figure 2.1, a well-ordered, minimal defect, Ag nanoparticle array on ITO with an area as large as $\sim 400 \mu\text{m}^2$ can be produced. The high resolution, top-view, SEM image (Figure 2.1 inset) clearly indicates that individual truncated Ag triangular nanoparticles have sharp tips. Additionally, the SEM studies demonstrate that the drop-coating fabrication method can easily achieve $\sim 10\%$ surface coverage of Ag nanoparticle array monolayer with low defect density.

2.2.3 Electrochemistry

In this study, a BAS 100B/W electrochemical workstation was used for cyclic

voltammetry and chronocoulometry

measurements. (Bioanalytical System Inc., West Lafayette, IN). The in-house constructed spectroelectrochemical cell consists of three electrodes with a Pt wire (D. F. Goldsmith, Evanston, IL) as the auxiliary electrode. All electrode potentials are reported versus a Ag/AgCl electrolyte reference electrode.

Solutions were deoxygenated with nitrogen for a

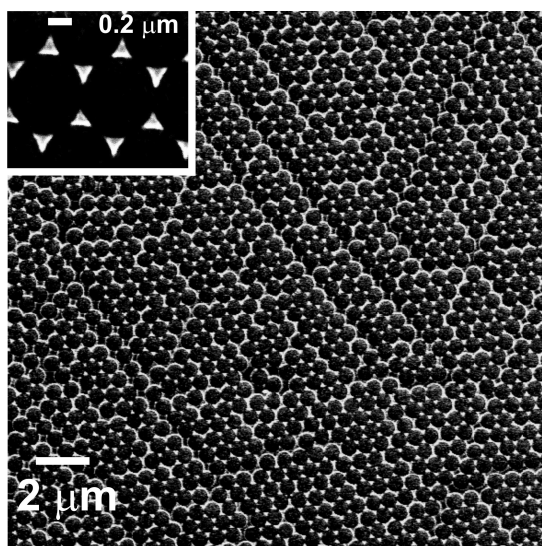


Figure 2.1. SEM images of Ag nanoparticle arrays on ITO. Nanosphere diameter $D = 590$ nm, the mass thickness of silver film $d_m = 67$ nm.

minimum of 2 min prior to electrochemical experiments. All electrochemical measurements were performed under a N₂ atmosphere.

2.2.4 LSPR Spectroscopy

Macroscale UV-visible extinction measurements were collected using a fiber optically coupled Ocean Optics SD2000 (Ocean Optics, Dunedin, FL) spectrometer. All spectra in this study were macroscopic measurements performed in standard transmission geometry with unpolarized light. The light spot diameter was approximately 1 mm. The extinction maximum of each spectrum was located by calculating its first derivative.

2.2.5 Atomic Force Microscopy

Tapping-mode atomic force microscope (AFM) images were collected using a Digital Instruments Nanoscope IV microscope and Nanoscope IIIa controller (Digital Instruments, Santa Barbara, CA). Asymmetric phosphorous n-doped silicon tips (Veeco, Santa Barbara, CA, radius of curvature = 10 nm and resonant frequency = 304-385 kHz) were used to obtain all the images.

2.3 Initial Electrochemistry

To evaluate their oxidation potential, Ag nanoparticle arrays on ITO were placed in aqueous 0.1 M NaClO₄ and a single cyclic voltammetric sweep was performed (Figure 2.2A, solid line). A parallel measurement (Figure 2.2A, dashed line) was carried out on vapor deposited Ag film/ITO electrode (the mass thickness of Ag film, $d_m = 50 \pm 5$ nm). The oxidation of silver on a

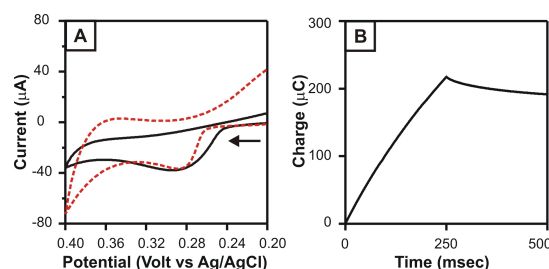


Figure 2.2. Cyclic voltamograms and Chronocoulometry plot for Ag nanoparticles on ITO on glass surfaces. (A) Single scan cyclic voltammograms of Ag film/ITO (dashed line, $d_m = 50 \pm 5$ nm) and Ag nanoparticle arrays on an ITO electrode (solid line) in 0.1 M NaClO₄ aqueous solution. Scan rate = 0.1 V/s. The arrow shows the initial scan direction. (B) Chronocoulometry plot of charge versus time for Ag nanoparticles on an ITO surface (0.64 cm²) during the oxidation of Ag. Initial potential is 0.20 V, and final potential, 0.40V. Pulse width = 250 msec. $D = 590$ nm, $d_m = 67$ nm.

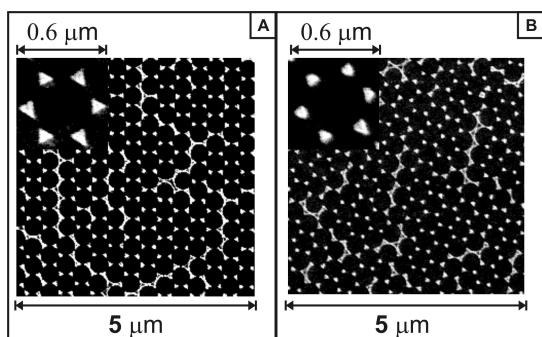


Figure 2.3. Scanning Electron Microscopy images of Ag nanoparticles. (A) SEM images of the nanoparticles before any electrochemical measurements. Sharp discrete triangles can be seen in the high resolution inset. (B) SEM images of nanoparticles after one chronocoulometry measurements (electrochemical oxidation charge density $\sim 350 \mu\text{C}/\text{cm}^2$). Rounding of the structure and a shrinking in the in-plane width of the nanoparticles can be seen. $D=390$, $d_m=54$ nm.

Ag film/ITO surface occurs around $\sim + 287$ mV, which is in agreement with previous results.¹⁰⁹ In comparison, the cyclic voltammogram of the Ag nanoparticle arrays on an ITO electrode shows a broader peak, with a less positive onset potential. Clearly, some portion of the Ag nanoparticle arrays oxidize more easily than the bulk Ag film (Figure 2.2A, black solid line). Assuming that the surface free energy is the same for metal nanoparticles and

bulk metal surfaces, then the Kelvin equation¹¹⁰ predicts that metal nanoparticles will exhibit a standard electrode potential, E° , that is shifted to more negative potentials than the E° of the bulk metal.^{111,112} A negative shift in E° of small nanoparticles means that smaller metal nanoparticles are more easily oxidized than bulk material.¹¹²⁻¹¹⁵

A potential step from $+ 200$ mV to $+ 400$ mV was used in a chronocoulometry experiment to measure the charge required to oxidize the silver nanoparticles confined on the ITO surface (Figure 2.2B). Controllable tuning of the Ag nanoparticle structure was achieved by changing the electrochemical oxidation charge over the range of 10-1000 μC . In addition, the SEM studies (Figure 2.3) reveal the continued presence of well-ordered Ag nanoparticle arrays after repeated electrochemical oxidations, demonstrating high stability of Ag nanoparticle arrays on ITO.

2.4 Optical Monitoring

A systematic study to relate electrochemically oxidized nanoparticle structures and optical properties was carried out by combining LSPR spectroscopy and AFM. Figure 2.4 shows LSPR spectra and the corresponding AFM images of a Ag nanoparticle array on an ITO electrode during a succession of two measurements. Prior to electrochemical oxidation, the Ag nanoparticle arrays on an ITO electrode exhibit a LSPR λ_{max} at 654 nm (Figure 2.4A). With each successive chronocoulometry run, the plasmon peak shifts towards shorter wavelengths due to changes in the silver nanoparticle size and shape. Correlated AFM images were obtained to further characterize this geometry change of the nanoparticles. After the first chronocoulometry run (electrochemical oxidation charge density $\sim 350 \mu\text{C cm}^{-2}$ ITO), the height of the nanoparticle remained unchanged, however, the base of the truncated tetrahedral structure became smaller and rounder, with a change of width from 126 ± 12 nm (Figure 2.4B) to 87 ± 18 nm (Figure 2.4C). This shape change is also evident in the SEM images (Figure 2.3). The 39 nm structural change in the in-plane width results in a shift in the LSPR spectra from 654 nm to 579 nm. Changes in degree of tip sharpness have already been shown to dramatically change the position of the plasmon resonance.¹¹⁶ This is because the highest electromagnetic field strength is located at the tips of the tetrahedral and triangular nanoparticles.^{116,117}

After the second chronocoulometry run ($\sim 40 \mu\text{C}/\text{cm}^2$), the nanoparticles narrow in both in-plane and out-of-plane direction and became hemispherical in shape (Figure 2.4D). The height was reduced from $52 \pm 3 \text{ nm}$ (Figure 2.4C) to $45 \pm 3 \text{ nm}$ (Figure 2.4D). The resulting plasmon at 506 nm is typical of a hemispherical nanoparticle as seen in earlier experiments.^{118,119} After further electrochemical oxidation, the height of the nanoparticles was further decreased, and the plasmon blue-shifted out of the spectral range of the spectrometer (data not shown).

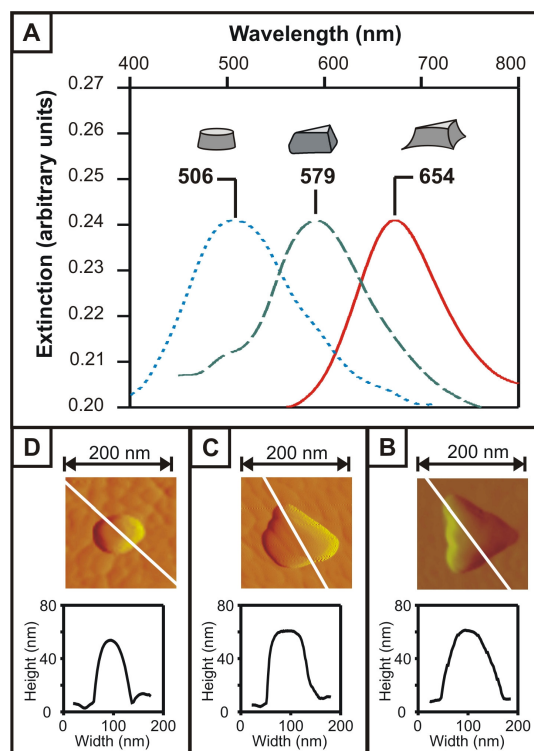


Figure 2.4. LSPR spectra and AFM images of Ag nanoparticles on ITO. $D = 390 \text{ nm}$, $d_m = 54 \text{ nm}$. (A) LSPR λ_{max} of the Ag nanoparticles shifts towards shorter wavelengths after chronocoulometry measurements. (B) AFM image before any electrochemical measurements. Average Ag nanoparticle out-of-plane height = $54 \pm 2 \text{ nm}$, and in-plane width = $126 \pm 12 \text{ nm}$. LSPR λ_{max} is 654 nm (solid line). (C) AFM image after one chronocoulometry measurement. Average Ag nanoparticle height = $52 \pm 3 \text{ nm}$, and width = $87 \pm 18 \text{ nm}$. LSPR λ_{max} is 579 nm (dashed line). (D) AFM image after two chronocoulometry measurements. Average Ag nanoparticle height = $45 \pm 3 \text{ nm}$, and width = $76 \pm 18 \text{ nm}$. LSPR λ_{max} is 506 nm (dotted line). All the LSPR spectra were collected in a N_2 environment.

From Figure 2.4, we found that the electrochemical oxidation of NSL fabricated Ag nanoparticle began with the bottom edges. To further explore the oxidation preference between top tetrahedral tips and out-of-plane height, a 590-nm nanosphere mask was selected to create larger nanoparticles which allow relatively fine electrochemical control of nanoparticle sizes.

Figure 2.5 illustrates the same series of observations presented in Figure 2.4; but, for a larger nanoparticle size. The corresponding AFM measurements indicate that larger Ag nanoparticle arrays remain constant in height (~ 68 nm) throughout the two chronocoulometry runs. After the first chronocoulometry measurement (~ 300 $\mu\text{C}/\text{cm}^2$), the base of the truncated tetrahedral structure decreased from 231 to 201 nm, creating a trigonal prism structure (Figure 2.5C) in comparison to Figure 2.5B. Further electrochemical oxidation (~ 330 $\mu\text{C}/\text{cm}^2$) removed small amounts of silver from the truncated tetrahedral tips of the nanoparticle, while not changing the nanoparticle's out-of-plane height (Figure 2.5D). Comparing the studies done for both nanosphere sizes (Figures 2.4 and 2.5), the order of electrochemical oxidation of the

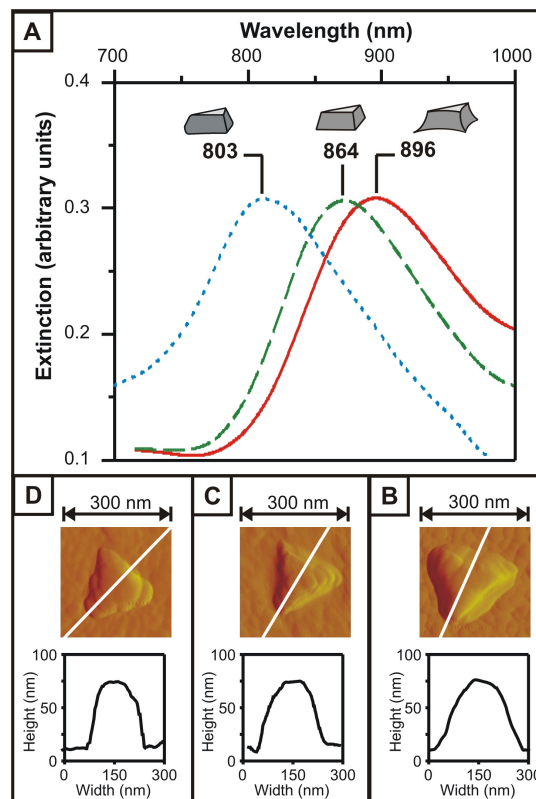


Figure 2.5. LSPR spectra and AFM images of Ag nanoparticles on ITO. $D = 590$ nm, $d_m = 68$ nm. (A) LSPR λ_{max} of the Ag nanoparticles shifts towards shorter wavelengths after chronocoulometry measurements. (B) AFM image before any electrochemical measurements. Average Ag nanoparticle out-of-plane height = 68 ± 2 nm, and in-plane width = 231 ± 16 nm. LSPR λ_{max} is 896 nm (solid line). (C) AFM image after one chronocoulometry measurement. Average Ag nanoparticle height = 68 ± 3 nm, and width = 201 ± 12 nm. LSPR λ_{max} is 864 nm (dashed line). (D) AFM after two chronocoulometry measurements. Average Ag nanoparticle height = 68 ± 3 nm, and width = 178 ± 10 nm. LSPR λ_{max} is 803 nm (dotted line). All LSPR spectra were collected in a N_2 environment.

truncated tetrahedral nanoparticles can be summarized as the following: bottom edges first, then top triangular tips, and finally out-of-plane height.

2.5 Geometric Modeling

To understand this behavior, we note that Pleith¹¹¹ and Makov et al¹²⁰ have previously studied the size-dependent electrochemical behavior of spherical nanoparticles, and they were able to rationalize their results assuming that the surface free energy makes a repulsive contribution to the electrochemical potential which varies as the inverse of the nanosphere radius. In the present context, we would expect that regions of the nanoparticle surface with the smallest radii of curvature should oxidize the most readily, so the bottom edges can precede the tips as long as the latter are sufficiently rounded (as seems to be the case from the AFM pictures).

Both the LSPR and AFM results indicate that the electrochemical oxidation method can easily modify the shape and size of silver nanoparticles confined on ITO. Moreover, the nanoparticle size/shape can be quantitatively controlled by tuning the electrochemical oxidation charge. To model this, we use Faraday's law:

$$Q = nFN \quad (1)$$

along with the following formula that relates the oxidation-induced volume change to the number of coulombs of charge passed:

$$\Delta V_s = \frac{NMW_{Ag}}{\rho_{Ag} N_A A_{ITO}} = \frac{QMW_{Ag}}{nF \rho_{Ag} N_A A_{ITO}} \quad (2)$$

Here, Q is the charge; n is the number of electrons, which is 1 for the oxidation of $Ag^0(s)$ to $Ag^+(aq)$; F is the Faraday constant; N is the quantity of oxidized silver in moles; ΔV_s is the

change in volume of a single Ag nanoparticle; MW_{Ag} is the molecular formula weight of silver; ρ_{Ag} is the density of silver; N_A is the of number of Ag nanoparticles per 1 cm² ITO, which is $\sim 7.2 \times 10^8$ Ag nanoparticles lying on 1 cm² ITO surface based on SEM measurements; and A_{ITO} is the ITO surface area in cm². Based on these expressions, after $\sim 300 \mu\text{C}/\text{cm}^2$ is passed through the Ag nanoparticle arrays on an ITO electrode ($D = 590$ nm, $d_m = 68$ nm, Figure 5B), $\sim 4.6 \times 10^4$ nm³ silver has been removed from an individual Ag nanoparticle.

We estimate the volume of the NSL-produced silver nanoparticle by assuming that the unoxidized nanoparticle has a truncated tetrahedral structure. The volume of the nanoparticle is:

$$V_{bot} = V_{tetra} - V_{top} \quad (3)$$

where V_{tetra} is the volume of the tetrahedron constructed using the nanoparticle as the bottom of the tetrahedron, and V_{top} is the volume of the top of the tetrahedron excluding the volume of the nanoparticle. V_{bot} can then be obtained by substituting the in-plane width of the nanoparticle, a_{bot} , and the out-of-plane height, h_{bot} , into the following equation (For the full derivation, refer to supporting information.):

$$V_{bot} = \frac{2\sqrt{6}}{27} [a_{bot}^3 - (a_{top})^3] \quad (4)$$

Here the in-plane width of the top tetrahedron is given by:

$$a_{top} = a_{bot} - \frac{3\sqrt{2}}{4} h_{bot} \quad (5)$$

Using $a_{bot} = 231$ nm and $h_{bot} = 68$ nm, obtained from AFM measurements (Figure 2.5B), the initial volume for an individual unmodified Ag nanoparticle is $\sim 1.5 \times 10^6$ nm³. The volume after oxidation V'_{bot} is then given by

$$V'_{bot} = V_{bot} - \Delta V_s \quad (6)$$

This volume can be used to estimate the oxidized nanoparticle structure (during the first phase of oxidation) by assuming that a_{top} and h_{bot} remain constant and the tetrahedron is oxidized only along its lower edge, converting the bottom of the nanoparticle into a trigonal prism whose in-plane width is a'_{bot} . This leads to the following expression for V'_{bot} (see supporting information for details),

$$V'_{bot} = -\frac{4\sqrt{6}}{27} a_{bot}'^3 + \frac{2\sqrt{6}}{9} a_{bot} a_{bot}'^2 - \frac{2\sqrt{6}}{27} (a_{top})^3 \quad (7)$$

Solving this equation for a'_{bot} , an in-plane width of 206 nm is calculated for the modified nanoparticle. This value is close to the AFM measurement, 201 ± 12 nm, given in Figure 2.5C.

2.6 Systematic Relationships

To systematically study the relationship between nanoparticle width and plasmon λ_{max} , a set of experiments was carried out using masks created with the following nanosphere diameters: 390 nm, 510 nm, and 590 nm. This range of nanosphere sizes was chosen because the nanoparticles produced by NSL have plasmons in the range of 400 nm and 900 nm, the limiting range of the spectrometer. The initial height for the nanoparticles produced by each nanosphere mask was kept constant at 68 nm. After one chronocoulometry run, all the modified nanoparticles still remained at a height of 68 nm.

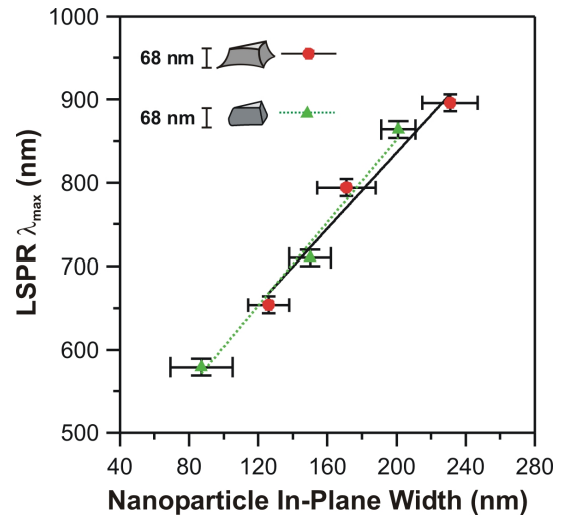


Figure 2. 6. LSPR λ_{max} versus nanoparticle in-plane width. The nanoparticles were made from sphere masks using 390, 510 and 590 nm diameter spheres. The plots show data collected before (circles, solid line) and after electrochemical measurements (triangles, dotted line). The solid line ($R^2 = 0.97$) and dashed line ($R^2 = 0.99$) are the linear fits for each data set. The nanoparticles remained fixed at a height of 68 nm.

All height data were based on AFM measurements. The results of the study can be seen in Figure 2.6. There is a linear relationship between in-plane width and $\lambda_{\max}$ of the nanoparticles before and after electrochemical modifications. There is also a consistent blue-shift in the $\lambda_{\max}$ for each nanoparticle size after a single chronocoulometry run.

2.7 Conclusions

In summary, this work demonstrates the ability to produce large areas of monolayer Ag nanoparticle arrays on a transparent conductive substrate, the stability of NSL produced Ag nanoparticle arrays on an ITO electrode in aqueous environments, the quantitative manipulation of Ag nanoparticle geometries by using chronocoulometry and using LSPR spectroscopy for monitoring the manipulation .

Chapter 3

Anchored Nanoparticle Surfaces

3.1 Introduction

Fundamental properties, fabrication, and utilization of metal nanostructures have been at the forefront of the research community in the past decade. Arrays of metal nanoparticles, which have high extinction and scattering coefficients, are important for sensitive chemical and biological detection and the development of robust microelectronic devices.^{121,122} Nanosphere lithography (NSL) is one technique offering a versatile platform to examine the properties and explore the applications of such nanoparticle structures. NSL is a parallel, inexpensive fabrication method that produces, with a high degree of reproducibility and control, periodic nanoparticle arrays with adjustable size, shape, and material properties.^{22,34,123} NSL uses ordered arrays of hexagonally close-packed nanospheres as lithographic masks on silica, mica, silicon, and other solid surfaces. Typically, a thin layer of metal is deposited over the nanosphere mask. When the nanosphere mask is removed, an ordered array of metal nanoparticles remains on the surface. Several groups have combined NSL with thermal annealing¹²⁴⁻¹²⁶ and reactive ion etching (RIE)^{34,124,127} to expand the scope of NSL by varying the shape and spacing of the metal nanoparticles. NSL has been widely used to examine optical properties of metal nanostructures,^{21,125,126,128-131} as well as to fabricate magnetic nanoparticles^{36,132,133} and photonic crystals.^{126,134} Furthermore, NSL-fabricated substrates have been used in biochemistry for protein nanoarrays³¹ and as sensors^{40,76,135,136} for various analytes.

This chapter reports the use of NSL and RIE to fabricate embedded Ag nanoparticle arrays with improved adhesion and optical tuning. These robust structures can be employed in a variety of important applications including chemical and biological sensing. Etching is used at low power to selectively etch the SiO_2 substrate with a polystyrene nanosphere mask. The resulting structure is an array of triangular nanowells beneath the mask.³⁴ After subsequent metal deposition, a portion of the nanoparticle is embedded in the substrate, thus anchoring it into the surface (Figure 3.1). While nanoparticle arrays on flat surfaces are structurally robust and stable in organic solvents, exposure to aqueous solutions (as is any biological milieu) significantly hinders their adhesion of metal to glass. The lattice mismatch between glass and silver forms an interface with a low strength of adhesion. In fact, this allows lift-off and separation of nanoparticles for applications such as tip fabrication.¹³⁷ Utilizing adhesion layers such as Ti and Cr^{40,138} is appropriate in surface plasmon resonance (SPR) measurements, where

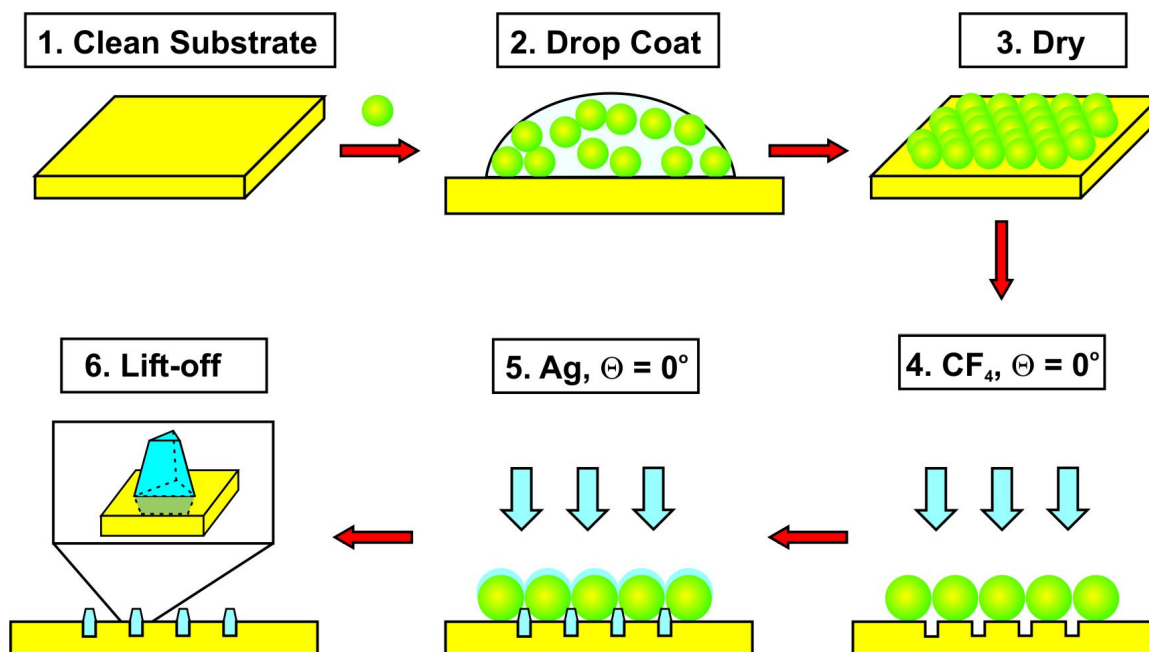


Figure 3.1. Schematic representation of the anchored nanoparticle array fabrication.

the metal film is continuous and the analyte does not interact with the adhesion layer.

However, in the case of nanoparticle arrays, exposed adhesion layers cause non-specific binding and optical interference.¹³⁹ Anchoring the nanoparticles in the substrate offers a new and unique method to improve adhesion of metal nanoparticles to the surface without utilizing additional adhesion layers or specialized surfaces like mica. This method provides a universal platform that can be used for biological and chemical sensing applications without loss of regular nanoparticle array properties and advantages.

A key feature in the ability of the metal nanoparticle arrays to be used as sensors lies in the unique optical properties of the nanoparticles, called the localized surface plasmon resonance (LSPR). LSPR occurs when a specific wavelength of light impinges on the metallic nanoparticles, producing a collective oscillation of the conduction band electrons. This collective oscillation of electrons occurs only for light within a certain bandwidth, thus metal nanoparticles exhibit selective photon absorption and resonant Rayleigh scattering, which can easily be monitored using UV-visible extinction spectroscopy. It is well established that the maximum extinction wavelength, λ_{max} , of the LSPR is strongly and systematically dependent upon the composition, size, shape, and interparticle spacing of nanoparticles.^{123,125,130,131} The LSPR of the metal nanoarray can be exploited in several ways to achieve sensing: (1) by monitoring shifts in the LSPR extinction λ_{max} due to changes in the local dielectric environment and (2) by enhancing the electromagnetic field at the surface and thus enhancing Raman scattering of molecules adsorbed to the surface by factors as large as 10^{14} .^{140,141}

Superior adhesion of the anchored nanoparticles is evaluated by applying normal forces to the nanoparticles with an atomic force microscope (AFM) and subjecting the structures to constant flow conditions. Furthermore, a systematic study of the optical properties of anchored

nanoparticles is conducted for a fixed nanoparticle height of 55 nm, while varying the depth of the nanowell. Herein we demonstrate control over the LSPR $\lambda_{\max}$ position in the wavelength range of ~ 300 nm (678 – 982 nm) for the use in the development of novel sensing modalities. As an example, we demonstrate the detection of Alzheimer's precursor ligands by monitoring the LSPR shifts, validating the potential use of anchored nanoparticles as a robust sensing platform. In addition, we show that the SERS enhancement factors from anchored nanoparticle surfaces are on the same order of magnitude as the non-anchored nanoparticle arrays. Discrete dipole calculations for the nanoparticles at various depths are conducted to elucidate the shifting behavior of the LSPR of the anchored nanoparticles. This work advances the capabilities, beyond conventional NSL methods, of nanoparticle systems in aqueous environments, where nanoparticle adhesion has traditionally been a challenge.

3.2 Experimental Methods

3.2.1 Materials

Absolute ethanol was purchased from Pharmco (Brookfield, CT). Ag pellets (99.99%, 0.125 in diameter) were obtained from Kurt J. Lesker (Pittsburgh, PA). Borosilicate glass surfaces, No. 2 Fisherbrand 18-mm circle coverslips were purchased from Fisher Scientific (Pittsburgh, PA). Polystyrene nanospheres with a diameter, D , of 500 $\pm$ 6 nm were received as a suspension in water. The nanosphere solutions were purchased from Interfacial Dynamics Corporation (Portland, OR). Millipore cartridges (Marlborough, MA) were used to purify water to a resistivity of 18 $\text{M}\Omega\text{cm}^{-1}$. 1-octanethiol, benzenethiol, 11-mercapto undecanoic acid (11-MUA) and phosphate buffered saline (PBS; pH = 7.4) were all purchased from Sigma-Aldrich (Milwaukee, WI). 1-Ethyl-3-[3-dimethyl-1-aminopropyl]carbodiimide hydrochloride (EDC)

was purchased from Pierce (Rockford, IL). Amyloid derived diffusible ligands (ADDLs) and 20C2 were obtained from the Klein lab at Northwestern University. All materials were used without further purification.

3.2.2 Surface Preparation

The glass surfaces were cleaned in a piranha solution (1:3 30 % H_2O_2 : H_2SO_4) at 80°C for 30 minutes (*CAUTION: piranha solution should be handled with great care*). Once cooled, the glass surfaces were rinsed with copious amounts of water and then sonicated for 60 minutes in 5:1:1 H_2O : NH_4OH :30% H_2O_2 . Lastly, the glass was rinsed repeatedly with water and stored in water until use. Single layer colloidal crystal nanosphere masks were prepared by drop coating the nanosphere solution onto glass surfaces. Once the nanosphere masks were assembled, the surfaces were placed in a reactive ion etcher (RIE2000, South Bay Technology, Inc. San Clemente, CA) and etched for varying times with CF_4 gas. The samples were then mounted in

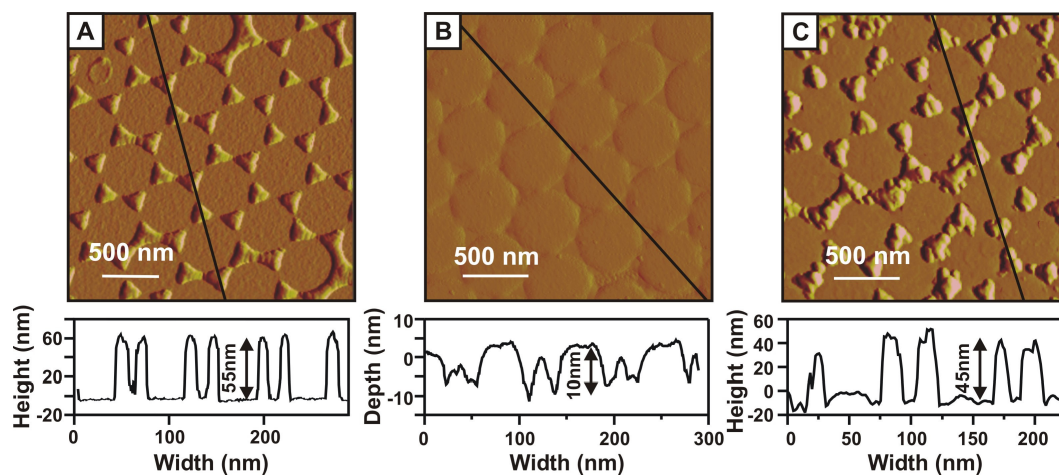


Figure 3.2. Atomic Force Micrographs of in process. (A) AFM micrograph of a nanoparticle array on a flat surface; metal thickness = 55 nm. (B) AFM micrograph of fabricated nanowells, with no Ag deposited; nanowell depth ~10 nm. (C) AFM micrograph of particles in nanowells. 55 nm of Ag was deposited onto the nanowell array giving an overall particle height ~45 nm. All arrays were fabricated using a $D = 510$ nm nanosphere mask.

an electron beam deposition system (Axxis Thin Film Electron Beam Evaporator, Kurt J. Lesker, Pittsburgh, PA). A metal thickness, d_m , of 55 nm of Ag was deposited at a rate of ~ 0.3 Å/s on all samples used in the study. After the deposition, the nanospheres were removed by sonication in ethanol for 5 minutes. Atomic force micrographs for the three different surfaces are shown in Figure 3.2: a regular nanoparticle array, the nanowell surface, and an anchored nanoparticle array.

3.2.3 LSPR Spectroscopy

Extinction spectroscopy measurements were carried out using a SD2000 spectrometer in transmission geometry coupled to a fiber probe (Ocean Optics, Dunedin, FL) and a halogen lamp (F-O-Lite H, World Precision Instruments, Sarasota, FL). The optimal wavelength range for this system is 400–950 nm.

3.2.4 Atomic Force Microscopy (AFM)

AFM images were collected using a Digital Instruments Nanoscope IV AFM and Nanoscope IIIa controller operating in tapping mode, with etched Si nanoprobe tips (TESP, Digital Instruments, Santa Barbara, CA). The resonance frequencies of the cantilevers are between 280 and 320 kHz. The tips are conical in shape with a cone angle of 20° and an effective radius of curvature at the tip of 10 nm.

3.2.5 Mechanical Stability Study

A Digital Instruments Nanoscope IV AFM in contact mode with etched silicon tips (spring constant, 0.187 N/m) was used to study the stability of both the standard nanoparticle array and the anchored nanoparticle array. The sensitivity of the detector used for these experiments was 0.833 nm/V. Calibration of the AFM tips was performed on a clean glass slide.

Normal force was applied at deflection setpoints of 0 – 5.75 V to produce a force calibration plot.

3.2.6 Solution Stability

Stability in aqueous environment under constant flow rate was assessed for bare and self-assembled monolayer (SAM) functionalized nanoparticles. Anchored nanoparticle arrays were fabricated by etching for 3 minutes such that nanoparticles were anchored 6.6 nm into the surface. SAMs were utilized since they are commonly used to bind target analytes in the SPR and LSPR bio-sensors.^{40,73,74,138,142-144} The surfaces were incubated in a 3:1 solution of octanethiol and 11-MUA for 24 hours. Both functionalized and non-functionalized nanoparticle arrays were then subjected to a constant flow of PBS. An automated syringe pump (New Era Pump Systems, Inc., Farmingdale, NY) was programmed to inject and withdraw fluid at a constant rate of 1.5 mL/min. The samples were exposed to the flowing environment for 1 hour. LSPR spectra were collected in N₂ before the flow was turned on and after being subjected to constant flow for 1 hour.

3.2.7 ADDLs Detection

Anchored nanoparticle samples were fabricated by etching for 3 minutes, anchoring the nanoparticles 6.6 nm into the surface. These samples were then incubated overnight in a 9:1 solution of octanethiol and 11-MUA. Prior to the initial spectrum, the samples were rinsed in ethanol and dried in nitrogen. A mixture of 500nM ADDLs and 1mM EDC solutions was then injected into the flow cell and allowed to incubate for 1 hour. The sample was then rinsed with PBS and pH balanced water and dried in nitrogen for spectrum collection. Finally, a 100nM solution of the 20C2 antibody was injected and allowed to bind to the ADDLs. After a 30

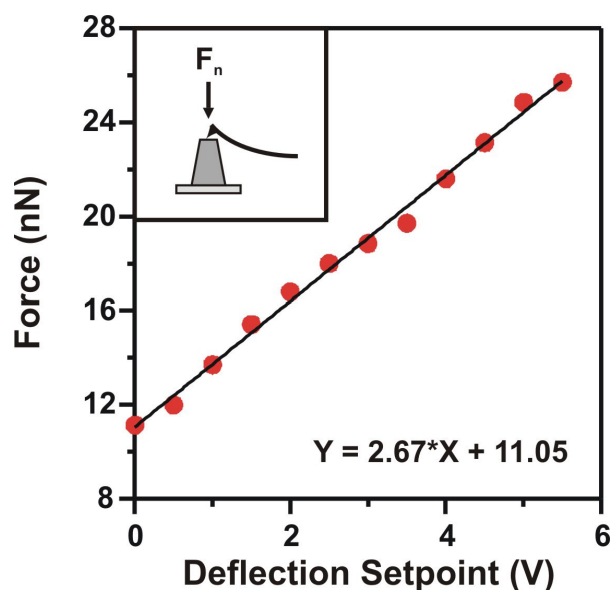


Figure 3.3. Force Calibration Plot. Normal force applied by the AFM cantilever as a function of deflection setpoint on a clean glass surface. The setpoint was varied between 0 and 5.75 V, and the corresponding force was calculated. The linear regression fit allows calculation of the force applied to the particles at setpoints outside the 0 - 5.75 range. The inset shows a schematic of the force applied by the cantilever.

minute incubation, the sample was again rinsed with PBS and pH balanced water and dried in nitrogen for final spectrum collection.

3.2.8 Surface-enhanced Raman Spectroscopy

All optical measurements were performed using a Nikon Eclipse TE300 inverted microscope (Fryer Co.,

Huntley, IL) equipped with a 20x objective (NA = 0.5). Substrates were mounted on a piezoelectric stage (model P-517.3CD, Polytech PI, Auburn, MA) to allow for sample positioning and raster-scanning during spectral acquisition. The light scattered by the samples was analyzed with a TriplePro three-stage spectrograph equipped with a liquid nitrogen-cooled, deep-depletion Spec-10:400BRCCD detector (Roper Scientific, Trenton, NJ). A color video camera was also attached to the front port of the microscope to facilitate laser alignment and positioning of the samples. Laser excitation was provided by the Spectra-Physics (Mountain View, CA) Millennia Xs ($\lambda_{\text{ex}} = 532 \text{ nm}$) and a Spectra-Physics Tsunami with GWU harmonic generator ($\lambda_{\text{ex}} = 350\text{-}500, 700\text{-}1000 \text{ nm}$). The laser light from the tunable laser systems was filtered using Pellin-Broca prisms or a diffraction grating to ensure monochromatic illumination

of the sample. For the NSL-fabricated triangular nanoparticles, in-situ measurement of the LSPR spectrum was achieved by illuminating the sample with the microscope lamp and analyzing the transmitted light with a fiber-optically coupled miniature spectrometer (model SD2000, Ocean Optics, Dunedin, FL).

3.3 Nanoparticle Adhesion

Anchored nanoparticles provide a more robust, mechanically stable substrate for sensor applications. Adhesion of the nanoparticles to the surface was examined by the AFM normal force measurements. Normal force applied by the AFM cantilever can be calculated by

$$F = k \cdot DS \cdot z$$

where k is the spring constant of the cantilever measured in N/m, DS is the detector sensitivity reported in the units of nm/V, and z is the deflection of the cantilever given in volts. The force calibration plot is shown in Figure 3.3. The linear fit to the data allows the calculation of forces applied to the samples outside of the calibration range.¹⁴⁵

Normal force, although not a direct measure of adhesion, gives a relative qualitative characteristic of the nanoparticles' stability. It is vertical component of the force applied by the cantilever as it scans the surface of the substrate (Figure 3.3 inset), which is proportional to the deflection of the cantilever. The normal force needed to remove metal nanoparticles from an unetched glass surface was determined for comparison. The nanoparticles were fabricated using a 510 nm nanosphere mask. The resulting particles had an out-of-plane height of 55 nm Ag. A $100 \mu\text{m}^2$ area of the substrate was scanned using contact mode AFM with an incrementally increasing deflection setpoint (Figure 3.4A) from -2 V to 0.5 V. The nanoparticles began to be displaced from the surface at -1.5 V, a setpoint corresponding to a normal force of 7.05 nN. Moving nanoparticles are characterized on the image by the trail left behind after being dragged

by the tip. Most of the nanoparticles were removed at a setpoint of 0.5 V, which is equivalent to a normal force of 12.39 nN. A second scan of the same area was acquired at a low deflection

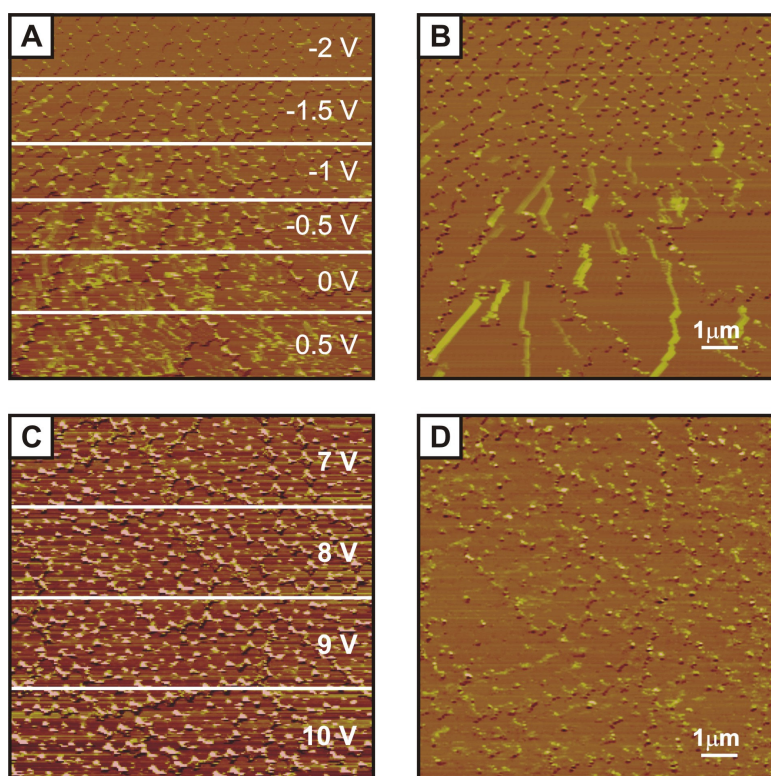


Figure 3.4. Atomic Force Micrographs illustrating the movement of the Nanoparticles under increasing forces. (A) Contact AFM image of nanoparticles on a glass substrate with increasing setpoint during the scan. Normal force is proportional to the setpoint, so with increasing force, nanoparticles are removed. At -1.5 V (7.05 nN), the nanoparticles just begin to move, and at 0.5 V (12.39 nN), most particles have moved. (B) Contact AFM image of the same area at a fixed low setpoint of -2 V. Most nanoparticles in the bottom section have been removed, and more nanoparticles shifted as a low force was applied to them in the consecutive scan. (C) Contact AFM image of anchored particles on a glass substrate with increasing setpoint during the scan. At 5 V (24.4 nN), the particles just begin to move (data not shown), and at 9 V (35.08 nN), most particles have moved. (D) Contact AFM image of the same area at a fixed low setpoint of 1 V. Most particles in the bottom section have been removed, and more nanoparticles shifted as a low force was applied to them in the consecutive scan.

setpoint of -2 V to view the resulting structure (Figure 3.4B). The metal structures formed from line defects in the nanosphere mask remain on the surface. Several nanoparticles appear to be displaced even at this low setpoint due to the stress applied by the cantilever in the previous scan. The normal force calculated agrees with previously reported normal force measurements needed to displace metal nanoparticles.^{138,146}

Anchored nanoparticle substrates were examined in the same manner. The anchored nanoparticles were fabricated using a 510 nm sphere mask with a 3 min etch at 25 W, and 55 nm of Ag was deposited. The nanoparticles were embedded into a well 10 – 15 nm deep. Contact

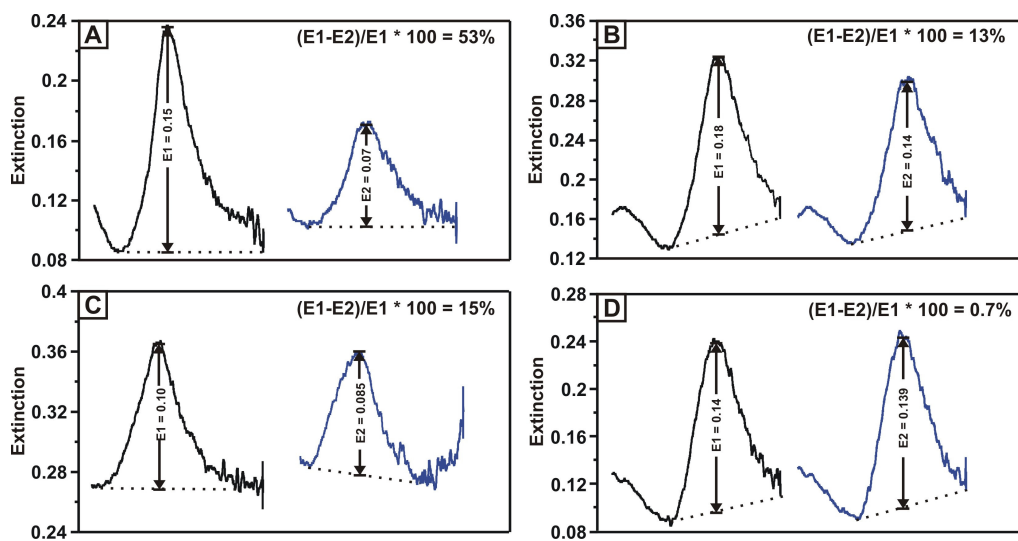


Figure 3.5. The solution stability of both anchored and non-anchored nanoparticles with and without and SAM layer. (A) A non-etched nanoparticle array with no SAM; (B) A non-etched nanoparticle array with overnight SAM incubation; (C) An etched nanoparticle array with no SAM; (D) An etched nanoparticle array with overnight SAM incubation. All samples had a mass thickness of metal of 55 nm. All samples were exposed to a constant flow rate of 1.5 mL/min by an automated syringe pump that pushed and withdrew pH balanced water for a total of 1 hour. In all graphs, the initial LSPR spectra in N₂ are shown in black and the spectra following the 1 hour exposure to fluid flow dried and acquired in N₂ are shown in blue.

force AFM scans over a $100\ \mu\text{m}^2$ area were acquired with incrementally increasing deflection setpoints. For each deflection range, a new area was scanned to maintain uniform conditions. The anchored nanoparticles were not displaced with deflection setpoints between -2 V and 4 V. They began to move with a deflection setpoint of 5 V (24.4 nN (data not shown)). Most of the nanoparticles were removed at a deflection setpoint of 9 V (35.08 nN (Figure 3.4C)). Another image of the same area was acquired at a low deflection setpoint of 1 V to view the resulting structure (Figure 3.4D). The metal structures formed from line defects in the nanosphere mask remain on the surface. These results indicate that the anchored nanoparticles provide a more robust surface for sensors than nanoparticle arrays on flat glass substrate. Anchoring the

nanoparticles results in a 3-fold improvement in mechanical stability of the structure. This increase in mechanical stability allows the anchored nanoparticle arrays to be placed in harsh environments where traditional arrays would become damaged or delaminated.

3.4 Solution Stability of Nanoparticle Arrays

Mechanical stability of anchored and non-anchored

Table 3.1 Embedded particle arrays and corresponding properties.

Etch Time (min)	Etch Depth*	Out-of-plane particle height*	Plasmon λ_{max} *
0	0	55	678
1	2.57	52.43	701
3	6.57	48.43	739
5	8.77	46.23	759
7	12.67	42.33	790
9	14.96	40.04	843
11	18.07	36.93	851
13	20.62	34.38	909
15	24.27	30.73	930
17	27.37	27.63	965
22	35.12	19.88	982

* measurements in nm

For all particles: etch power, P = 15 W; sphere mask diameter, D = 500 nm; material – Ag; Ag mass thickness, d_{Ag} = 55nm

nanoparticle arrays was further examined by subjecting the substrates to flow conditions for an extended period of time similar to the biosensing assays involving incubation and rinsing steps. Both, bare and SAM-functionalized nanoparticle arrays were examined. Figure 3.5 details a study performed on 4 different samples: (1) non-anchored bare nanoparticles, (2) non-anchored nanoparticles with SAM, (3) anchored bare nanoparticles, and (4) anchored nanoparticles with SAM. Extinction spectra before and after the rigorous flowing environment were collected to assess the extinction efficiency of the substrate, which corresponds to the number of nanoparticles that can scatter and absorb the incident light. The most dramatic effect can be seen in the samples fabricated on a flat surface (Figure 3.5A, 3.5B). In Figure 3.5A, it is evident that a large number of nanoparticles have come off the surface. This is illustrated by a 53% drop in the extinction intensity. Functionalizing the nanoparticles with a SAM helps to stabilize the nanoparticles, yet there is still a 13 % decrease in extinction intensity. The bare anchored nanoparticles (Figure 3.5C) are significantly more stable in solution as there is only a 15 % decrease in the LSPR intensity of the nanoparticle array under the same constant flow conditions. The extinction from the SAM-functionalized anchored nanoparticles does not decrease in intensity, showing that with a SAM as a protective layer, the nanoparticles are completely stable in an aqueous environment. This makes the anchored nanoparticle arrays an ideal platform for the engineering of LSPR chemo- and bio-sensors.

3.5 Optical Properties of the Anchored Nanoparticles

The optical properties of the anchored nanoparticle arrays produced by NSL and RIE were examined as a function of varying nanowell depth. The power used in the etching process is directly proportional to the etch rate of the material. Thus, at higher powers, etching occurs faster and can adversely affect the integrity of the polystyrene nanosphere mask. Polystyrene

undergoes etching at a much slower rate than silicon. However, the nanospheres are visibly affected as the power and time of the etch are increased. Rather than forming an array of discrete nanoparticles, at high powers, the process results in a continuous metallic network, which does not produce a well defined LSPR band. The connection of the nanowells is a byproduct of the shrinking nanosphere mask (caused by etching of the nanospheres). Slower etch rates result in more uniform nanowells, even for longer etch times.

The etch time controls the depth of the nanowells and thus how deeply the nanoparticles

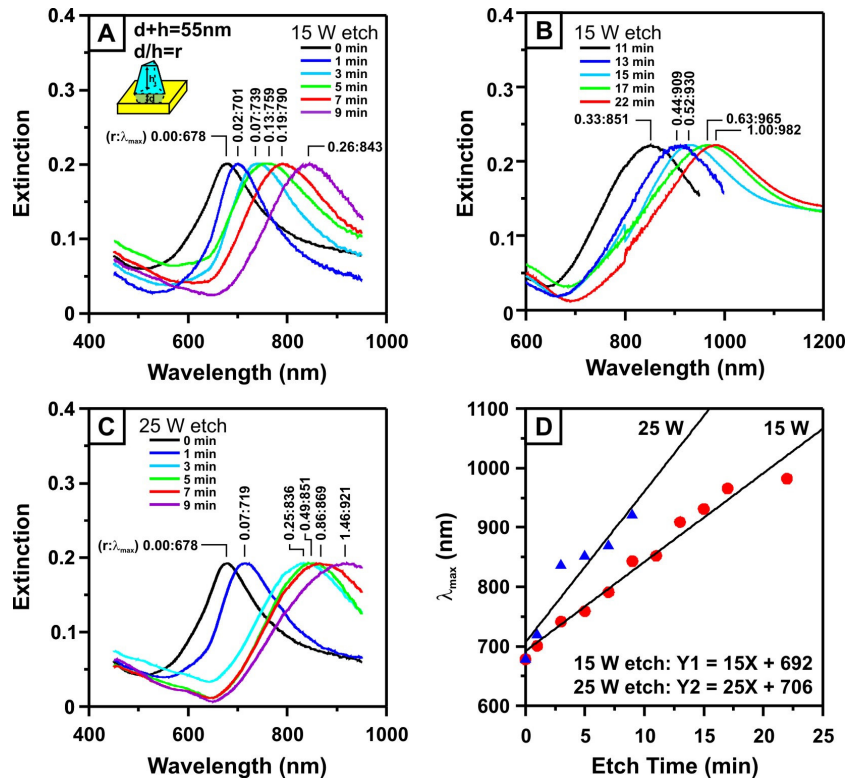


Figure 3.6. LSPR extinction spectra of anchored nanoparticles on glass substrates for different etch times and etch power. As the etch time increases, the depth of the well increases, making the metal nanoparticles more embedded in the glass. A corresponding LSPR red shift is observed with increasing etch time. LSPR spectra are shown for 15 W etch for 0 - 9 minute etch (A) and 11 - 22 minute etch (B). LSPR spectra for 25 W etch for 0 - 9 minute etch. Linear shift in LSPR $\lambda_{\max}$ is observed as a function of etch time (D). For the fitted trend lines, $R^2_{15} = 0.97$, $R^2_{25} = 0.90$ for the 15, 25 W etch, respectively. CF_4 etch, pressure = 10 mTorr, $D = 500$ nm, $d_m = 55$ nm, deposition rate = $0.4 \text{ \AA/s}$.

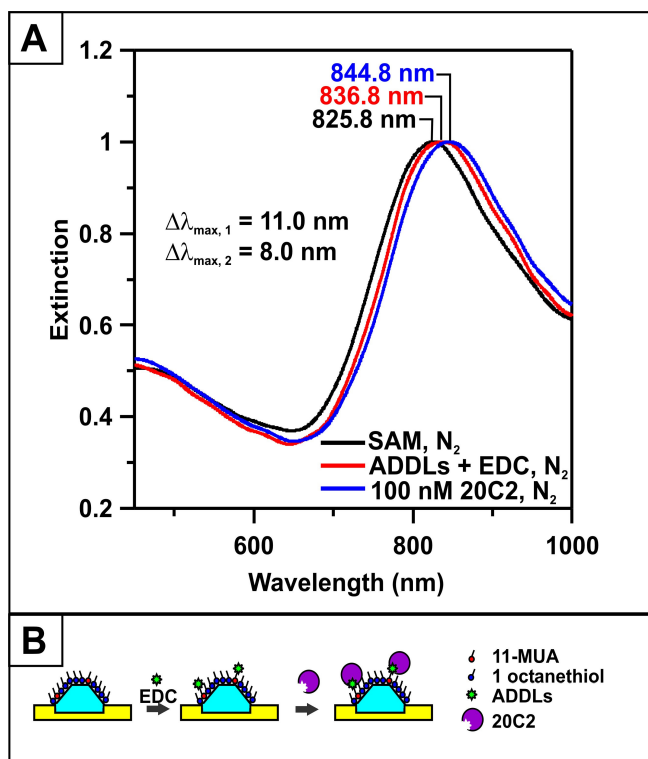


Figure 3.7. Detection of ADDLs using anchored nanoparticles. The SAM-functionalized anchored nanoparticle array has the LSPR λ_{max} of 825.8 nm. With the addition of ADDLs and EDC, the plasmon red shifts 11 nm to 836.8 nm. The second red shift of 8 nm is observed upon the addition of 20C2 antibody. The final LSPR λ_{max} = 844.8 nm. All spectra were acquired in N_2 .

are embedded into the substrate. The etch times ranged from 1–25 min and from 1–9 min for the

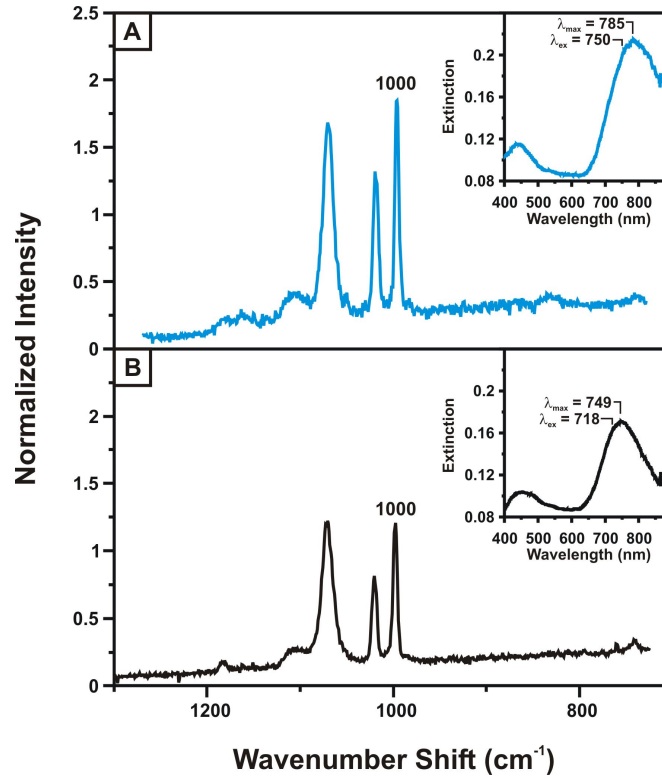


Figure 3.8. Anchored nanoparticles as a surface-enhanced raman substrate. SERS spectra of benzenethiol on non-anchored (A) and anchored (B) nanoparticle arrays.

Intensity is normalized with respect to normal Raman scattering intensity of cyclohexane at both wavelengths. The insets show corresponding extinction spectra for structures tested. The intensity of the 1000 cm⁻¹ band of benzenethiol is 1.6 for the non-anchored particles and 1.1 for the anchored particles. (A) $\lambda_{ex} = 750$ nm, $P = 10$ mW, $t = 150$ s, normalized intensity of 1 corresponds to 6600 counts. (B) $\lambda_{ex} = 718$ nm, $P = 8.25$ mW, $t = 150$ s, normalized intensity of 1 corresponds to 13300 counts.

15 W and 25 W power etches, respectively. Table 1 summarizes well depth, out-of-plane nanoparticle height, as well as the LSPR maximum wavelength, λ_{max} , for the substrates etched with 15 W. The LSPR λ_{max} shifts red as the depth of the nanowell increases (Figure 3.6). This systematic shifting is explained by the fact that glass has a higher refractive index than air ($RI_{glass} = 1.5$, $RI_{air} = 1.0$). As the nanoparticles are embedded further into the glass substrate, more of the nanoparticle interacts with the higher refractive index material, thus red shifting the LSPR λ_{max} . This feature provides a method to tune the LSPR peak position by controlling the depth of the nanowell in addition to the size of the nanoparticle and its out-of-plane height. The

broadening of the LSPR bands can be attributed to the merging of the nanoparticles as the polystyrene mask is etched away with the increasing etch times. For 15 W etches (Figure 3.6A, 3.6B), the continuous network is formed after 25 min of etching (LSPR spectrum not shown). In the case of the 25 W etches (Figure 3.6C), the LSPR range is more limited since the nanoparticles merge faster, and no LSPR spectra were obtained for etches longer than 9 min. Both sets of data show linear relationship between $\lambda_{\max}$ position as a function of etch time (Figure 3.6D).

3.6 LSPR Biosensing Platform

We have carried out an initial biosensing experiment to demonstrate the detection of ADDLs, an Alzheimer's precursor, as shown in Figure 3.7A. A depiction of the binding events being probed is also shown in Figure 3.7B. First, the nanoparticles are functionalized with the SAM, such that the LSPR $\lambda_{\max} = 825.8$ nm. When ADDLs are injected, they bind to the nanoparticles with the aid of EDC and cause the $\lambda_{\max}$ to red shift to 836.8 nm. The shift of 11 nm is due to the increase in the refractive index around the nanoparticles. Attaching the 20C2 antibody to the ADDLs results in an addition red shift of 8 nm with the final LSPR $\lambda_{\max} = 844.8$ nm. As can be seen in Figure 3.7A, anchoring the nanoparticles only 6.6 nm into the surface keeps them very stable throughout the incubation and rinsing procedure with no decrease in plasmon intensity as the experiment continues (data not shown). Furthermore, the shifts seen in the plasmon resonance are typical for this type of experiment.⁴⁰ With no decrease in plasmon intensity and the same sensitivity, the anchored nanoparticle systems successfully illustrate their viability as a new platform for fabricating LSPR chemo- and bio-sensors.

3.7 SERS Sensing Platform

Benzenethiol was used as a

probe molecule to test the potential of the anchored nanoparticles for use as a SERS platform. SERS signal intensities on anchored nanoparticle arrays and non-anchored nanoparticles arrays on flat substrates were compared to access the enhancement capabilities. Benzenethiol was chosen due to its large Raman cross-section and ease of binding to the Ag surface. The substrates were functionalized with a benzenethiol SAM and SERS spectra were acquired at an optimal

excitation wavelength to maximize the enhancement (Figure 3.8). The optimal wavelengths were determined by the LSPR $\lambda_{\max}$ of the nanoparticle arrays, which are

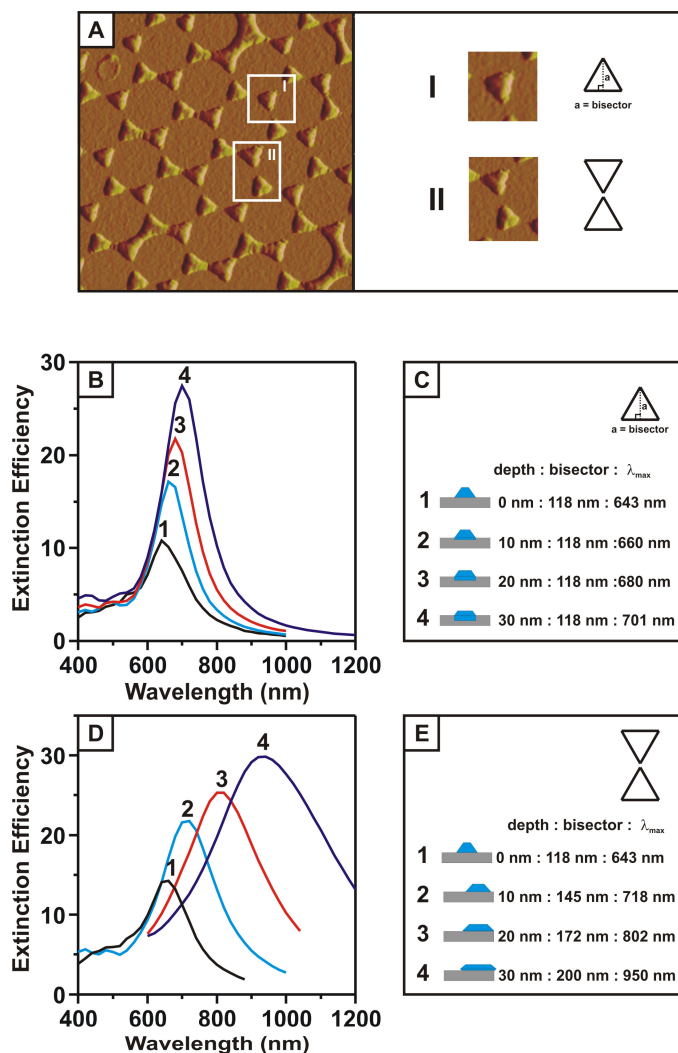


Figure 3.9. Discrete dipole simulation results. AFM images and schematics of the nanoparticles modeled (AI, AII). Initially, prism shaped wells with increasing well depth are modeled (B, C). Particle height, b , and bisector, a , is kept constant at 54 nm and 118 nm, respectively. For a more accurate representation, dimers of particles with increasing bisector were modeled (D, E). Particle height is kept constant at 54 nm, while the bisector increases from 118 nm to 200 nm at the rate of 2.7 nm per nm of embedded depth.

shown in the insets in Figure 8A and 8B for the non-anchored and anchored nanoparticles, respectively. The optimal wavelength needs to be blue-shifted from the LSPR $\lambda_{\max}$ such that the

average of excitation wavelength and the scattered photon wavelength is equal to LSPR $\lambda_{\max}$.⁸⁶

Optimal excitation wavelength for non-anchored nanoparticles was determined to be 750 nm, and for anchored nanoparticles 718 nm. The spectra of benzenethiol were scaled with respect to the normal Raman spectra of cyclohexane at both wavelengths to correct for detection system efficiency, power, and ν^4 dependence in Raman scattering. The intensity of the 1000 cm^{-1} band was analyzed to assess the Raman enhancement from the nanoparticle arrays. The intensity of the band on non-anchored nanoparticles is 1.6 while the intensity on anchored nanoparticles is 1.1, 31 % lower. The enhancement factors for both substrates are the same order of magnitude, and only a slight decrease in intensity is observed. The decrease can be attributed to a decreased number of benzenethiol molecules binding to the nanoparticles since part of it is embedded into the glass substrate. Furthermore, fewer nanoparticles are probed, since the amplitude of the LSPR spectrum of the anchored nanoparticle array is slightly lower at the sampled spot than that of the non-anchored nanoparticle array.¹⁴⁷ In summary, anchored nanoparticles provide a robust sensing platform with enhancement factors comparable to the ones of nanoparticles on flat substrates but with superior mechanical and solution stability.

3.8 Theoretical Modeling

The systematic shifting is expected due to the fact that glass has a higher refractive index than that of air ($RI_{\text{glass}}=1.5$, $RI_{\text{air}}=1.0$). As the nanoparticles are embedded further into the glass substrate, more of the nanoparticle interacts with the higher refractive index material, thus red shifting the LSPR $\lambda_{\max}$. However, the 304 nm shift from 678 to 982 nm cannot be solely attributed to the change of the embedding depth of nanoparticles into the glass substrate. Previously, Malinsky et. al.¹³⁵ found that for a nanoparticle with a diameter of 100 nm and height

of 50 nm, the plasmon resonance shift is 150 nm when the refractive index of the environment changes by 1. That is far less than observed in the experiment.

The Discrete Dipole method¹⁴⁸ is applied to further understand the mechanism of the shifting. We first modeled a truncated tetrahedral silver nanoparticle with a bisector of 118 nm and height of 54 nm which is close to the geometry of the nanoparticle prepared in the experiments. The resonance wavelength of the nanoparticle is 565 nm in vacuum and 806 nm in glass (RI=1.52). To simulate nanoparticles sitting on or embedded in glass substrate, we treat nanoparticles above the substrate as truncated tetrahedron and embedded part as prism which has the same side length as the tetrahedron (Figure 3.9B, 3.9C). The total height (height of the embedded prism and exposed truncated tetrahedron) of the nanoparticle is always kept to be 54 nm to be consistent with the experiments. The effective medium theory was applied to the simulation to include the substrate effect. The plasmon resonance wavelength of the nanoparticle on a flat glass substrate is 643 nm, which is 35 nm shorter than the measured wavelength. When the nanoparticle is embedded into glass 30 nm, the calculated resonance wavelength is 701 nm. The simulated extinction efficiency for embedded nanoparticles at various depths is shown in Figure 9B. The calculated shift is only 58 nm, which is significantly lower than the experimental observation of a 304 nm shift when the embedded depth increases from 0 to 30 nm.

This theoretical model does not take into account the changes in the shape of the nanoparticles as the well depth increases. Due to the fact that the polystyrene mask is etched away with the increasing etch time, the sides of the nanowells are tilted, thus the embedded part of the nanoparticle needs to be treated as an upside down truncated tetrahedron which has the same side length as the exposed one. As a result, the perpendicular bisector, a , of the

nanoparticle increases with etch time thus widening the nanoparticles. In the following simulations, we treat embedded part of the nanoparticle as an inverted tetrahedron and increase the bisector of nanoparticles with the increase in nanowell depth (Figure 3.9E). The rate of widening is controlled so that when the embedded depth is 30 nm, the bisector of the nanoparticle is increased to 200 nm, which is close to the experimental record. We modeled an isolated single nanoparticle (Figure 3.9AI). When the nanoparticle is on a flat substrate, the resonance remains at 643 nm (data not shown). When the embedded depth is increased to 10 nm, the plasmon resonance wavelength red shifts to 711 nm, and when the embedded depth is increased to 30 nm, the resonance wavelength red shifts further to 899 nm. The calculated value is still almost 100 nm shorter compared to the experimental data.

In the above simulations, we consider only an isolated nanoparticle and the polarization of the incident light is taken to be parallel to one side of the truncated tetrahedron. To include the coupling between nanoparticles, we also modeled nanoparticle dimers in which two truncated tetrahedrons are arranged head to head as shown in Figure 3.9AII. When the polarization of the incident light is perpendicular to the symmetry axis, the resonance wavelength is close to that of an isolated nanoparticle. When the polarization is parallel to the symmetry axis, the strong coupling between nanoparticles pushes resonance wavelength further to the longer wavelengths when the distance between the nanoparticles is decreasing. The resonance wavelength of the dimer is 718 nm when the well depth is increased to 10 nm with the polarization of the light parallel to the symmetry axis. This shows that the coupling between nanoparticles is not strong when the embedded depth is less than 10 nm. When the embedded depth is increased to 30 nm, the resonance wavelength of the dimer with polarization of the incident wave parallel to the symmetry axis is at 1005 nm. Since the light in the experiments is not polarized, we averaged

the resonance wavelengths from parallel and perpendicular polarizations, and obtained the resonance wavelength of 950 nm, which agrees well with the experimental value of 982 nm. The simulated extinction efficiency for dimers of nanoparticles with increasing bisector at various well depths is shown in Figures 3.9D and 3.9E.

Through the theoretical model, we learned that the red shift of nanoparticle resonance wavelengths are due to the change in the index of refraction of the medium as well as the widening of the nanoparticle due to the etching of the polystyrene mask with the increasing etch time. The strong coupling between nanoparticles also plays an important role in the observed red shift with the increasing etch time. The broadening of the resonance peak can be interpreted by the widening of the nanoparticles, which results in a broader and red shifted resonance peak. The increased discrepancy between plasmon resonance wavelengths for parallel and perpendicular polarized light when nanoparticles are getting closer also contribute to the broadening of the resonance peaks. The decrease in the uniformity of the nanoparticles may also be an important factor in broadening the resonance peak with increasing the etch time.

3.9 Conclusion

In this chapter, we have demonstrated the fabrication of mechanically robust and tunable substrates for chemical and biological sensing using nanosphere lithography and reactive ion etching. A 3-fold increase in adhesion was achieved by embedding the nanoparticles only 10–15 nm into the glass surface. Nanoparticle adhesion is further evaluated in an aqueous environment with constant flow, demonstrating superior adhesion for anchored nanoparticles. This dramatic increase in the stability of the nanoparticles will allow the use of these architectures in more rigorous environments (e.g. aqueous solutions) required for biological sensing. We successfully constructed a general platform with improved stability, while maintaining a structure with

carefully controlled optical properties and electromagnetic field enhancements appropriate for sensing applications. Controlled tunability of the LSPR λ_{max} has been achieved by varying the nanowell depth of the glass substrate. This tunability will allow for fine adjustments in the plasmon peak position of the nanoparticle arrays to maximize enhancements needed for high sensor sensitivity. We demonstrated the feasibility of using the fabricated surfaces for LSPR measurements to detect Alzheimer's precursor ligands and show that enhancement factors for SERS are on the same order of magnitude as nanoparticle arrays on flat surfaces. Finally theoretical calculations were conducted to elucidate the systematic shifting behavior of the LSPR of the anchored nanoparticles.

Chapter 4

Film Over Nanowells

4.1 Introduction

The unique size-dependent properties of nanometer-scale particles and templated surfaces have received significant attention in various fields, such as microelectronics^{149,150} and medicine.^{151,152} The optical properties, especially the plasmonic properties of noble metal nanostructures are of particular interest since they exhibit selective photon absorption and scattering that are strongly dependent on their surface morphology. These plasmonic properties can be used in a variety of applications including chemical and biological sensors^{41,153-155}, surface-enhanced spectroscopies,^{156,157} and near-field microscopy.¹⁵⁸

Surface plasmons exist in two simple forms, propagating and localized. On a flat smooth film, the surface plasmon polaritons (SPPs) are propagating evanescent electromagnetic waves at the metal-dielectric interface as a result of collective oscillations of the conduction electrons in the metal. Localized surface plasmon resonances (LSPRs) are observed in isolated nanoparticles. It is possible to have both SPPs and LSPRs excited in some periodic,^{22,159} colloidal,¹⁶⁰⁻¹⁶³ or other nanosystems,¹⁶⁴ which lead to an enhancement of the electromagnetic fields around the nanoparticle surfaces. This enhancement plays an important role in the interaction between the particles and their external environment.^{104,119,165}

The plasmon excitation can be monitored using either UV-visible extinction spectroscopy¹⁶⁴ or dark field resonant Rayleigh light scattering spectroscopy.¹⁶⁶ It has been well established that the wavelength of maximum extinction or scattering ($\lambda_{\max}$) associated with the LSPR excitation is strongly and systematically dependent upon the composition, size, shape, and interparticle spacing of nanoparticles.^{119,165} When surfaces are not optically transparent, the wavelength associated with minimum reflectivity ($\lambda_{\min}$) provides an alternative measure meant to locate the LSPR.¹⁶⁷

Although single nanoparticles and nanoparticle arrays have been extensively studied,^{41,119,154,165,166} nanohole arrays have just begun to be analyzed as a new plasmonic construct since the discovery of enhanced transmission through subwavelength apertures.¹² It has been shown that these nanohole arrays exhibit characteristic transmission spectra^{9-12,168,169} that are sensitive to the polarization of the light,¹⁶⁹ the shape of the hole,^{11,169} the hole size,¹⁷⁰ the hole depth,¹¹ and the external dielectric environment.^{14,153,170} To understand the mechanism of enhanced transmission that is observed from these nanostructures, a systematic study has been performed to look at the transition from nanoparticles to nanohole arrays.⁷⁵ From this work, the mechanism behind enhanced hole transmission is thought to be dominated by SPP excitation with non-negligible contributions from LSPR excitation at the hole edges.^{75,171} Although these arrays are different, physically and optically, from nanoparticles or smooth thin film that supports SPPs, they have also shown potential as biosensors^{153,170} and surfaces for surface-enhanced Raman scattering.¹⁵⁶

Uniformity in the interhole distance and the geometry of the nanoholes is critical to the elimination of variations in electromagnetic coupling between holes. It is therefore crucial to identify a fabrication method that provides the precision and accuracy required to prevent non-coherent coupling. The methods heretofore used to create nanohole arrays are focused ion beam (FIB) milling,¹² electron beam lithography,¹⁷² photolithography,¹⁷³ and colloidal lithography.^{170,174,175} This paper describes the use of nanosphere lithography (NSL)¹⁰¹ combined with reactive ion etching (RIE)¹⁷⁵ to fabricate well ordered nanowell structures (Figure 4.1). NSL is a low cost, parallel, surface independent technique used for producing well-ordered array structures with nanometer precision.^{22,101} NSL is based on the self-assembly of polystyrene or silica nanospheres into hexagonally close-packed monolayer and multilayer structures. These

structures are then used as lithographic masks for etching or deposition, creating an array of triangular nanowells or nanoparticles. The size and interhole spacing of nanowells can be tuned by using different sphere sizes, metal thickness, and etch times.

In this paper, we systematically study the plasmonic properties of nanowell structures that have a thin silver film covering the surface. The effects of internanowell distance, mass thickness, nanowell depth, and the external dielectric environment have been studied in detail. Structures have been identified that have both extremely narrow plasmon resonances and very strong wavelength sensitivity to external dielectric constant. Theoretical modeling of the film over nanowells structures has been done using a two-dimensional array as a model system and the discrete dipole approximation. The calculated spectra are in good agreement with experiment, and we have used the results to interpret the dependence of the results on architecture of these nanostructures.

4.2 Experimental Section

4.2.1 Materials

Absolute ethanol was purchased from Pharmco (Brookfield, CT). Methanol, acetone, methylene chloride, and pyridine were purchased from Fisher Scientific (Pittsburgh, PA). Ag pellets (99.99%, 0.125 in diameter) were obtained from Kurt J. Lesker (Pittsburgh, PA). Borosilicate glass surfaces, No. 2 Fisherbrand 18-mm circle coverslips were purchased from Fisher Scientific (Pittsburgh, PA). N-doped Silicon (111) was purchased from Wacker Siltronic (Portland, OR) and cut into $\sim 10\text{-}15\text{ mm}^2$ pieces. Polystyrene nanospheres with diameters (D) of $450 \pm 4.95\text{ nm}$, $510 \pm 7.65\text{ nm}$, $590 \pm 12.98\text{ nm}$, and $720 \pm 15.12\text{ nm}$ were received as a suspension in water. All of the nanosphere solutions were purchased from Interfacial Dynamics

Corporation (Portland, OR) Millipore cartridges (Marlborough, MA) were used to purify water to a resistivity of $18 \text{ M}\Omega\text{cm}^{-1}$. All materials were used without further purification.

4.2.2 Surface Preparation

Glass and silicon surfaces were cleaned in a piranha solution (1:3 30 % $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$) at 80°C for 30 minutes (*CAUTION: piranha solution should be handled with great care*). Once cooled, the glass surfaces were rinsed with copious amounts of water and then sonicated for 60 minutes in 5:1:1 $\text{H}_2\text{O}:\text{NH}_4\text{OH}:30\% \text{H}_2\text{O}_2$. Lastly, the glass was rinsed repeatedly with water and was stored in water until used.

4.2.3 Nanowell Preparation

For these experiments, single layer colloidal crystal nanosphere masks were prepared by drop coating the nanosphere solution onto glass surfaces (Figure 4.1). Once the nanosphere masks were dry, the surfaces were placed in a reactive ion etcher (RIE2000, South Bay Technology, Inc. San Clemente, CA) and etched for varying times with CF_4 gas. The spheres were removed after etching by allowing the samples to sit in warm pirhana solution overnight. The samples were rinsed with copious amounts of ethanol and dried in N_2 before being mounted in an electron beam deposition system (Axxis Thin Film Electron Beam Evaporator, Kurt J. Lesker, Pittsburgh, PA).

4.2.4 LSPR Reflectance Spectroscopy

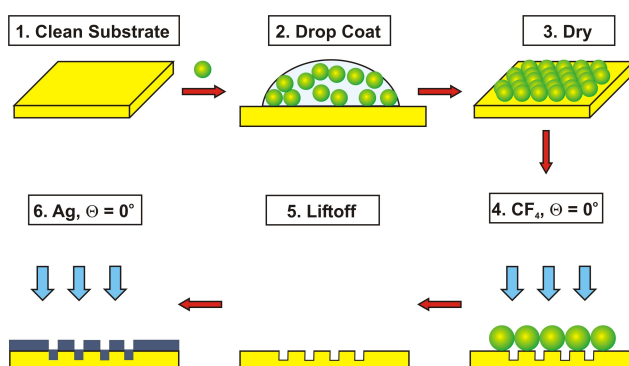


Figure 4.1. Schematic illustration of the preparation of the film over nanowell surfaces.

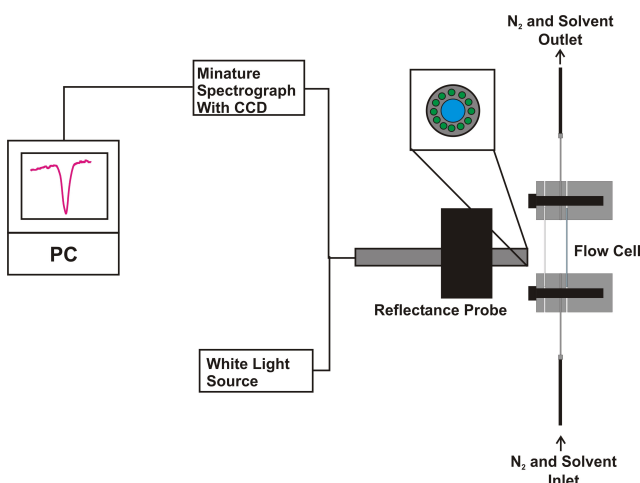


Figure 4.2. Reflectance Probe set-up. Scheme of the apparatus used for the LSPR spectroscopy in reflectance mode.

Measurements were carried out using a SD2000 spectrometer coupled to a reflection probe (Ocean Optics, Dunedin, FL) and a halogen lamp (F-O-Lite H, World Precision Instruments, Sarasota, FL). The reflection probe consists of a tight bundle of 13 optical fibers (12 illumination fibers around a collection fiber) with a useable wavelength range of

400–900 nm. (Figure 4.2) All reflectance spectra were collected against a mirror-like Ag film over glass surface as a reference.

4.2.5 Solvent Study

The experiment was done by drying the film over nanowells with nitrogen and recording an initial spectrum, filling the cell with a solvent and recording the resultant spectrum, then purging the cell with nitrogen to restore the original spectrum before repeating the process with another solvent. Each of the following solvents: ethanol, methanol, acetone, methylene chloride and pyridine, was flowed over the sample to change the refractive index (RI) surrounding the surface. Additionally, the sample was rinsed in methanol after methylene chloride to remove any excess chloride and then dried by nitrogen to restore the original spectrum. Therefore, all the solvent shifts were completely reversible, with the exception of pyridine.¹⁶⁵

4.2.6 Atomic Force Microscopy (AFM)

AFM images were collected on a Digital Instruments Nanoscope IV microscope and Nanoscope IIIa controller operating in tapping mode, using an etched Si nanoprobe tips (TESP,

Digital Instruments, Santa Barbara, CA). These tips had resonance frequencies between 280 and 320 kHz and are conical in shape with a cone angle of 20° and an effective radius of curvature at the tip of 10 nm.

4.2.7 Scanning Electron Microscopy (SEM)

SEM images were obtained using a Hitachi S-4500. For both normal and side view SEM images an accelerating voltage of 5kV was used.

4.3 Structural Characterization by AFM and SEM

Structural characterization of the samples prior to the optical measurements was conducted using both AFM and SEM. Figure 4.3 displays AFM images of three surfaces

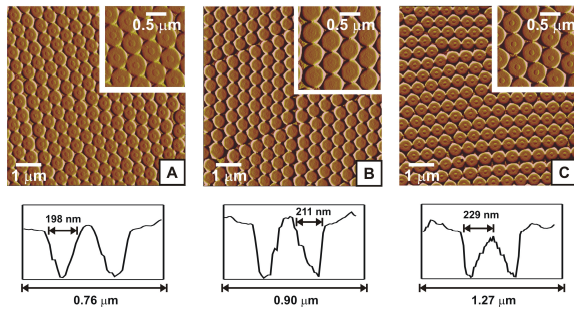


Figure 4.3. Tapping mode AFM images of three Ag film over nanowell surfaces with different nanowell depths. (A) The AFM image of the surface fabricated using a 10 min etching in CF_4 . The average nanowell width is 197.6 ± 17.3 nm and depth, 30.3 ± 2.8 nm. (B) The AFM image of the surface fabricated using a 19 min etching in CF_4 . The average nanowell width is 211.7 ± 22.2 nm and depth, 57.6 ± 3.2 nm. (C) The AFM image of the surface fabricated using a 25 min etching in CF_4 . The average nanowell width is 229.1 ± 28.8 nm and depth, 65.2 ± 2.9 nm.

fabricated with different etch times (t_e).

Figure 4.3A is a 10 minute etch, 4.3B is a 19 minute etch and 4.3C is a 25 minute etch with the corresponding line scans shows below each image. As the etch time increases, both the depth and in-plane width of nanowells increase (Figure 4.3). The nanowell width increases from 198 nm in the 10 minute etch to 229 nm in the 25 minute etch due to underetching of the polystyrene nanospheres used as a mask. The under-etching of the nanospheres is also evident in the smaller pedestal that present in the center of the larger

pedestals of the AFM images for all three etch times. The depths also increase with longer etching times, from 30 nm in the 10 minute etch to 57 nm in the 19 minute etch to 65 nm in the 25 minute etch. All of these AFM images were taken of nanowell surfaces with no Ag deposited on them.

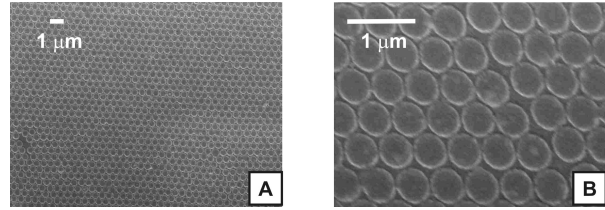


Figure 4.4. SEM images of a Ag film over nanowell surface ($D = 510$ nm, $d_m = 50$ nm, and $t_e = 10$ min). (A) shows a well packed area of over $40 \mu\text{m}^2$; and (B) is a magnified image of the same sample. The SEM accelerating voltage was 5kV.

Ag films were then deposited onto the nanowell surfaces by an electron beam deposition. The mass thickness of Ag film (d_m) was selected to be at least 50 nm to allow for efficient reflectance from the surface. Figure 4 shows the SEM images of film over nanowell surfaces fabricated from a 10 minute etch in CF_4 and deposition of 50 nm of Ag. Figure 4.4A shows the large well-packed areas that can be achieved using NSL, on the order of $40 \mu\text{m}^2$. Figure 4.4B is a zoomed in image of 4.4A, and shows more details of the surface nanostructure.

4.4 Plasmonic Properties of Film over Nanowell Surfaces

Optical characterization, by systematic variation of several structural and environmental parameters, was conducted subsequent to structural characterization of the nanoscale morphology. Specifically, the plasmonic properties of the film over nanowells were explored by varying: (1) the internanowell distance; (2) the mass thickness of the overlayer Ag; (3) the nanowell depth; and (4) the refractive index of the external environment.

4.4.1 Dependence on the Internanowell Distance

The control over the internanowell distance was achieved by varying the diameter of nanospheres, D , used as the etch mask. With an increase in D , a systematic shift of λ_{min} to longer wavelengths and a decrease in the full width half maximum (FWHM) of the plasmon peaks is observed in the reflectance spectra (Figure 4.5A). Specifically, the LSPR reflectance peak positions (λ_{min}) are 459, 487, 566, and 676 nm and the FWHMs are 0.17, 0.20, 0.13 and 0.11 eV for $D = 450, 510, 590$ and 720 nm, respectively.

Figure 4.5B plots the reflectance peak position, λ_{min} , for each film over nanowell surface as a function of D in nanometer, indicating a linear relationship with the slope close to unity ($\lambda_{min} = 0.959D$). The data points in Figure 4.5B are the averages taken over several surfaces (3-12 surfaces). The error bars represent standard deviations, which are between 1 and 5 nm,

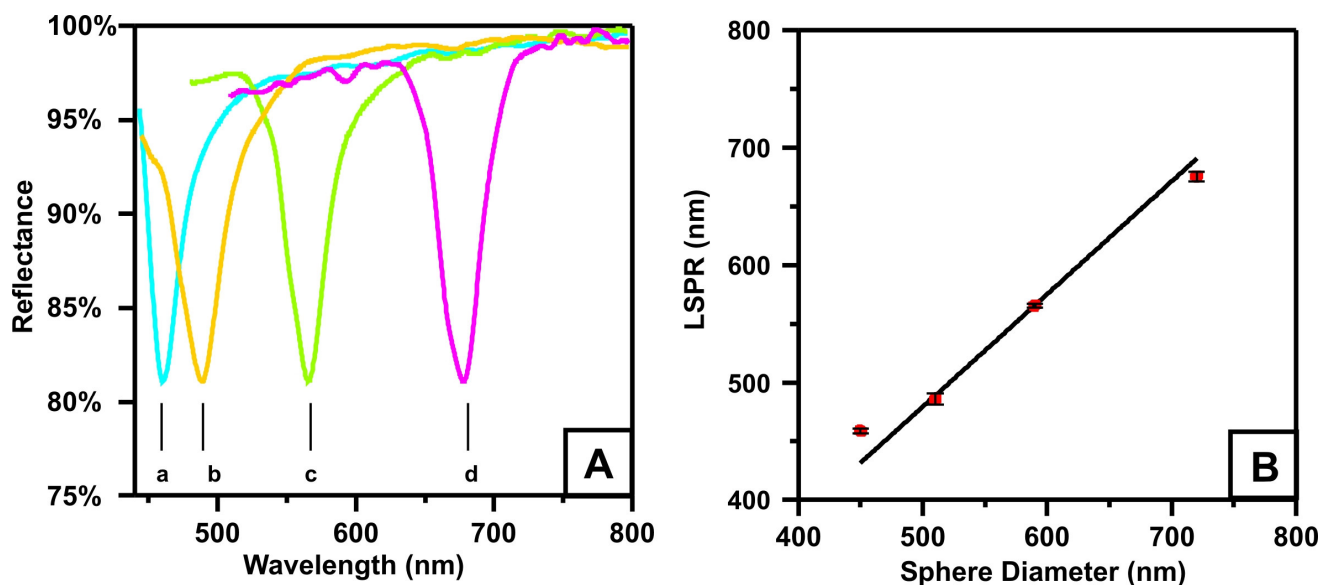


Figure 4.5. Extinction spectra of surface made with varying nanosphere diameters. (A) The reflectance spectra of a series of film over nanowell samples with different polystyrene nanosphere diameters: a) 450 nm, b) 510 nm, c) 590 nm, and d) 720 nm. For all the samples, $t_e = 10$ min and $d_m = 50$ nm. (B) A linear relationship is seen between sphere size and peak position. Linear regression was used to fit data to the line described by the equation $\lambda_{min} = 0.959D$ ($R^2 = 0.999$). Each data point represents the average value recorded from at least three surfaces. Error bars show the standard deviations.

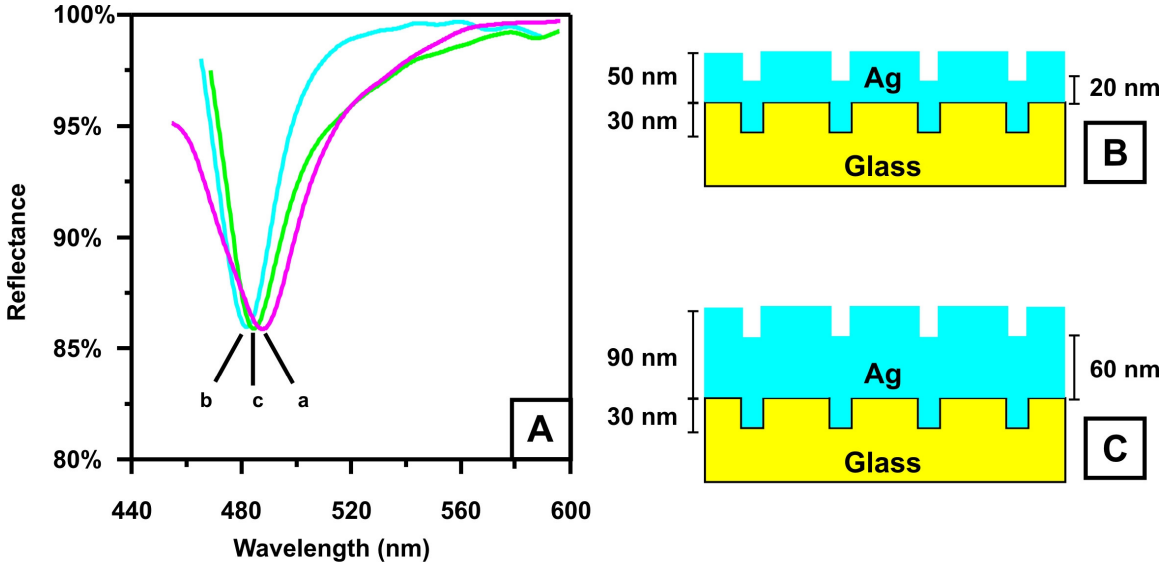


Figure 4.6. Extinction spectra of surface made with varying metal thickness. (A) Reflectance spectra of nanowell surfaces ($D = 510$ nm) with different silver film thicknesses. a) $d_m = 50$ nm, b) $d_m = 70$ nm, and c) $d_m = 90$ nm. (B) and (C) are schematic side views of the substrates, drawn to scale, with $d_m = 50$ and 90 nm, respectively.

demonstrating the high reproducibility of both the surface fabrication and the plasmon measurements. This result provides important clues concerning the nature of the coupling mechanism that is responsible for the narrow plasmons (as little as 0.1 eV FWHM). In earlier work on one- and two-dimensional nanoparticle arrays, electrodynamic calculations and analytical theories were exploited to predict that sharp plasmonic/photonic lineshapes should occur for particle arrays in vacuum ($RI = 1.0$) when interparticle distances are equal to the plasmon peak position ($\lambda_{\max} = \text{interparticle distance}$).^{176,177} When the array is embedded in a medium, this diffractive coupling effect should generalize to $\lambda_{\max} = RI \times \text{interparticle distance}$, which has been proven by experiments. Our previous work has demonstrated $\lambda_{\max} = 1.5 \times \text{interparticle distance}$ for linear arrays of Ag cylindrical nanoparticles on a glass surface and immersed in index-matched oil (for which $RI=1.5$).¹⁷⁸ In the present case, we do not have an index matched structure, so it is possible the coupling could occur through air or through glass.

However, the observed slope of the linear fit in Figure 4.5B is 0.959, indicating that the coupling through air (RI = 1.0) is dominant.

4.4.2 Dependence on the Mass

Thickness of Ag Film

Figure 4.6A shows the plasmon spectra of the Ag film over nanowell surfaces with fixed internanowell distance

and nanowell depth ($D = 510$ nm, depth = 30 nm) and various mass thicknesses. As the mass thickness increases from 50 to 70 to 90 nm, no dramatic changes in peak positions or FWHMs are observed. Schematic crosssection of the nanostructures are shown in Figures 4.6B and 4.6C. The metal film over nanowells can be mainly divided into two portions: (1) top portion, i.e., metal film with nanoholes with the depth of 30 nm and (2) bottom portion, i.e., metal nanoparticles embedded in glass. When the Ag film is thick enough, e.g. 90 nm, the penetration depth of the light is not sufficient to reach into the bottom portion. Consequently, the nanoparticles embedded in the glass substrate have no significant contributions to the plasmonic spectra, rather, it is only the top portions of the metal film over nanowell surfaces that participate.

4.4.3 Dependence on the Nanowell Depth

Figure 4.7A displays a set of reflectance spectra from a series of surfaces with various nanowell depths but fixed internanowell distance and mass thickness ($D = 510$ nm, $d_m = 50$ nm). In Figure 4.7A, as the nanowell depth increases, the peak systematically shifts to longer

Table 4.1. Reflectance data for Ag film over nanowells ($D = 510$ nm, $d_m = 50$ nm) on glass with various etch times

Spectrum	RIE time (min)	Depth (nm)	LSPR (nm)	FWHM (eV)
a	7	20	480	0.11
b	10	30	484	0.19
c	13	38	494	0.18
d	16	53	503	0.23
e	19	58	529	0.32
f	22	63	555	0.37
g	25	65	558	0.34

wavelength and becomes broader. The structural and optical parameters are summarized in Table 4.1. In these experiments, the Ag film was chosen to have $d_m = 50$ nm so that the underlying glass surface, with RI = 1.52, would play a role in the plasmon spectra. As the nanowell deepens, the fraction of exposed glass increases (as depicted in Figures 4.7B, 4.7C, and 4.7D). With more glass exposed, the plasmon peak position shifts to longer wavelengths. This is also in agreement with previous studies on the substrate effect on LSPR of Ag nanoparticles.¹³⁰

With regard to the changes in the plasmon peak width, the coupling mechanism must be considered. When more glass is exposed, besides the through-air coupling, there is a greater amount of through-glass coupling. The averaging of these two coupling mechanisms leads to the observed broadening of the plasmon bands. It is worth noting that a uniform refractive index is a

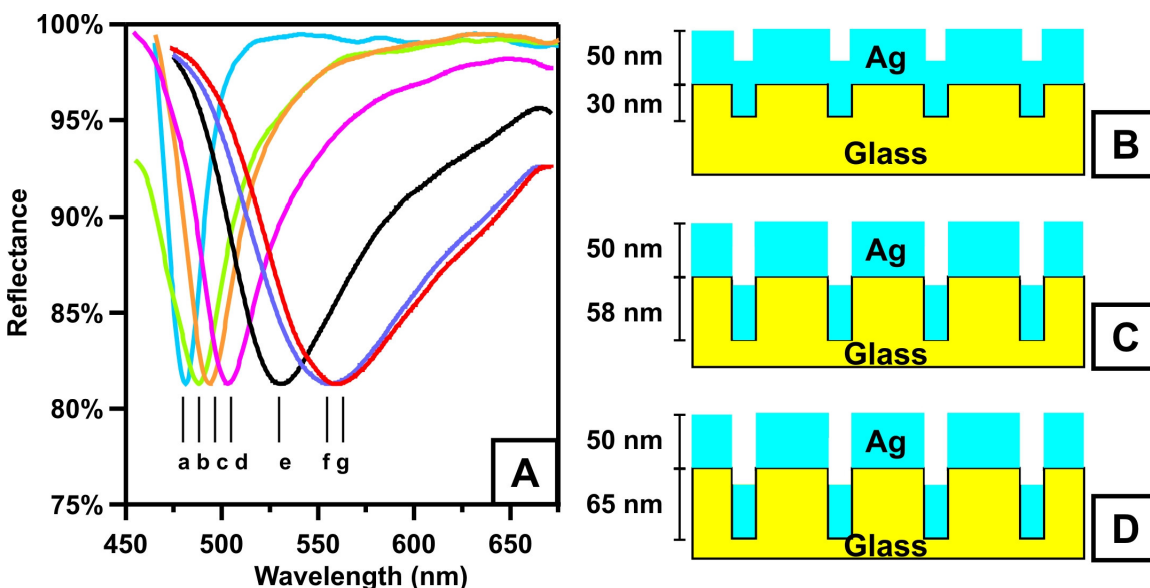


Figure 4.7. Extinction spectra of surface made with varying etch depth (A) A collection of reflectance spectra using a series of surfaces with various nanowell depths but fixed internanowell distance and mass thickness ($D = 510$ nm, $d_m = 50$ nm). (a) $t_e = 7$ min, (b) $t_e = 10$ min, (c) $t_e = 13$ min, (d) $t_e = 16$ min, (e) $t_e = 19$ min, (f) $t_e = 22$ min, and (g) $t_e = 25$ min. (B), (C), and (D) are schematic side views, drawn to scale, of the surfaces corresponding to the spectra b, e, and g in Figure 7A respectively.

critical factor to achieve the narrow plasmons, reported previously for nanoparticle arrays in both theory^{176,177,179} and experiment.¹⁷⁸ In addition, minor shape changes in the nanowell structure, such as the increased in-plane width of nanowells caused by longer etching time (Figure 4.3), can affect the shape and position of the spectra.

4.4.4 Dependence on the External Dielectric Environment

After examining the dependence of the plasmon spectra on the structural parameters of the film over nanowell surfaces, we systematically explored the effect of external dielectric media on the plasmon peak by altering the surrounding solvent. For all of the surfaces used in this study, the metal thickness ($d_m = 50$ nm) and etch time ($t_e = 10$ minutes, nanowell depth = 30 nm) remained constant, while the sphere diameter was varied ($D = 450, 510$ and 590 nm). These sizes of nanospheres were selected so that the plasmon spectra were located within the 400 – 950

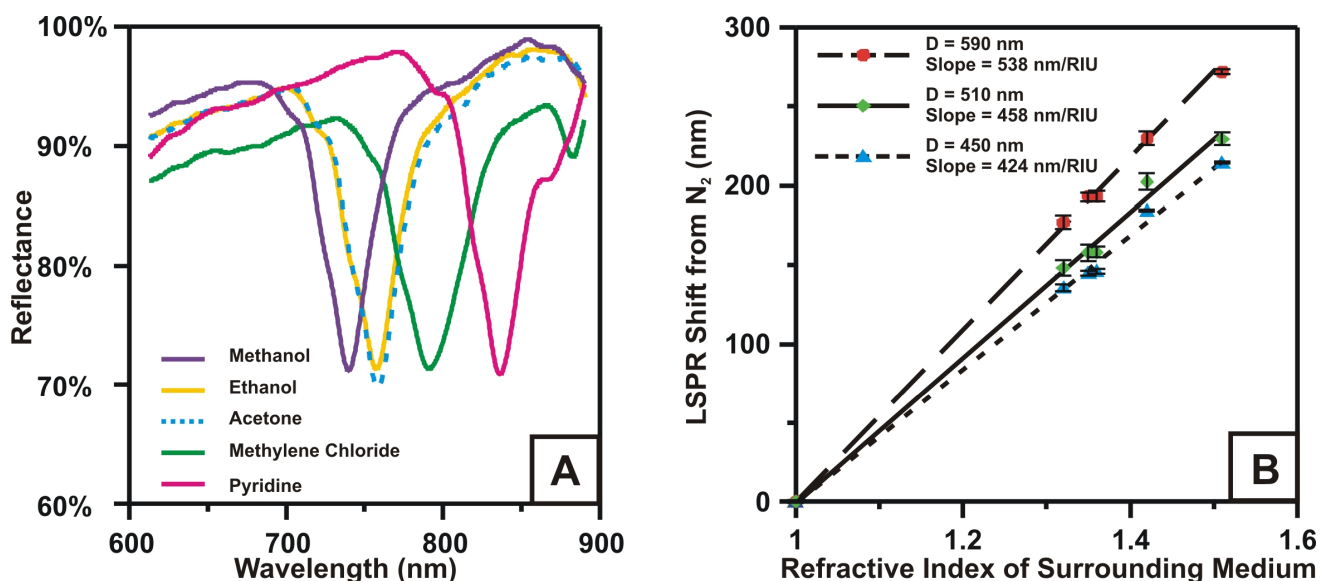


Figure 4.8. spectra of surface made with varying refractive indices. (A) A collection of reflectance spectra of a Ag film over nanowell surface in different solvents ($D = 590$ nm, $d_m = 50$ nm). (B) Plots of the $\lambda_{\min}(\text{solvent}) - \lambda_{\min}(\text{dry nitrogen})$ versus the refractive index of the solvent for three nanosphere sizes: $D = 450, 510$ and 590 nm. Each data point represents the average value obtained from at least three surfaces. Error bars show the standard deviations. For all the surface preparations, $d_m = 50$ nm and $t_e = 10$ min.

nm operating range of our UV-vis spectrometer. Figure 8A shows the reflectance spectra from the surface with $D = 590$ nm that was immersed in various refractive index media. The spectra for the samples with $D = 450$ and 510 nm are not shown, since they demonstrate similar trends as Figure 4.8A.

Figure 4.8B shows plots of $[\lambda_{\min}(\text{solvent}) - \lambda_{\min}(\text{dry nitrogen})]$ for each film over nanowell surface as a function of the refractive index of the surrounding medium. We have plotted the data as a function of peak position shift referenced to the dry nitrogen value in order to normalize the data and better compare the slopes for samples with different Internanowell distances. Each data point in Figure 4.8B represents the average value obtained from at least three surfaces. Error bars show the standard deviations. Within this range of refractive index units, the data points for the surfaces fabricated using the same size polystyrene nanosphere can be fit well to a linear regression. We find that the film over nanowell surface using the largest sphere ($D = 590$ nm) is most sensitive to changes in the surrounding refractive index, followed by $D = 510$ nm, then $D = 450$ nm. For the most sensitive film over nanowell surfaces ($D = 590$ nm), the linear regression analysis yielded a refractive index sensitivity of 538 nm/Refractive Index Unit (RIU), which means that every 0.002 change in the refractive index of the solvent will produce a change in the peak position of approximately 1 nm. To summarize the data above, since we found that $\lambda_{\min} = (\text{RI}) \times (\text{nanosphere diameter})$, then $\Delta\lambda_{\min} = (\text{RI}-1) \times (\text{nanosphere diameter})$. This means that the RI sensitivity is just the nanosphere diameter, and the larger nanospheres will have the largest sensitivity. To place these results in context, it should be noted that previous published sensitivity of both single gold nanoholes and nanohole arrays to refractive index is 100-400 nm/RIU.^{153,170} In addition, the sensitivity of NSL fabricated Ag nanoparticles is 191- 230 nm/RIU^{165,166} and gold nanoshells 328.5 nm/RIU.¹⁸⁰

Furthermore, the overall refractive index sensitivity also depends on the FWHM. A “Figure of Merit” (FOM) is defined in equation 1, in order to quantitatively evaluate the refractive index sensitivity of various sensing platforms.

$$FOM = \frac{m \text{ (eV RIU}^{-1}\text{)}}{FWHM \text{ (eV)}} \quad (1)$$

where m is the linear regression slope for the refractive index dependence. The film over nanowell surfaces exhibit extremely narrow plasmon peaks with the FWHM as little as 0.1 eV and exceedingly large linear regression slopes as steep as 538 nm/RIU, which result in a favorable FOM performance as a refractive index sensor.

4.5 Theoretical Discussions

Previous work by Zou et. al.^{176,177,179} has predicted narrowed plasmon peaks in extinction from one- and two-dimensional arrays of nanoparticles. The narrow peaks are caused by coherent dipolar (photonic) interactions between the particles when the incident wavelength of the light is close in value to the interparticle distance. The mechanism behind the present results is similar to this earlier work, although the theory needed to describe the nanohole structures is different, given that the present experiments refer to suppressed reflectance, rather than enhanced extinction. Thus for an array of nanoholes, the coherent interactions between nanoholes lead to stronger local electric fields around nanoholes, however, the transparency is enhanced instead of extinction.^{9,11,181}

To model the experimental system, a periodic boundary condition version of the discrete dipole approximation (DDA) method¹⁸² was used similar to that described previously by Zou and Schatz.¹⁷⁷ We first modeled exactly the same structures as in the experiments; meaning that the thickness of the film is taken to be the same both in the nanoholes and on the plateau regions that

are produced when the mask is removed. With reference to Fig. 4, this means that the film is composed of flat cylindrical disks of a given thickness of metal on the plateau regions, and then nanowells with the same thickness. We find that as the thickness of the metal in the nanowell is varied, the resonance wavelengths do not change significantly, which is consistent with our earlier conclusion that the reflection dips are determined by the region of the film at the top of the wells rather than the metal in the nanowells. Given this, we simplified the calculations by removing the metal in the wells, and the results that we present will all refer to a structure in which the only metal present is on the plateau regions. We also leave out the glass surface, as

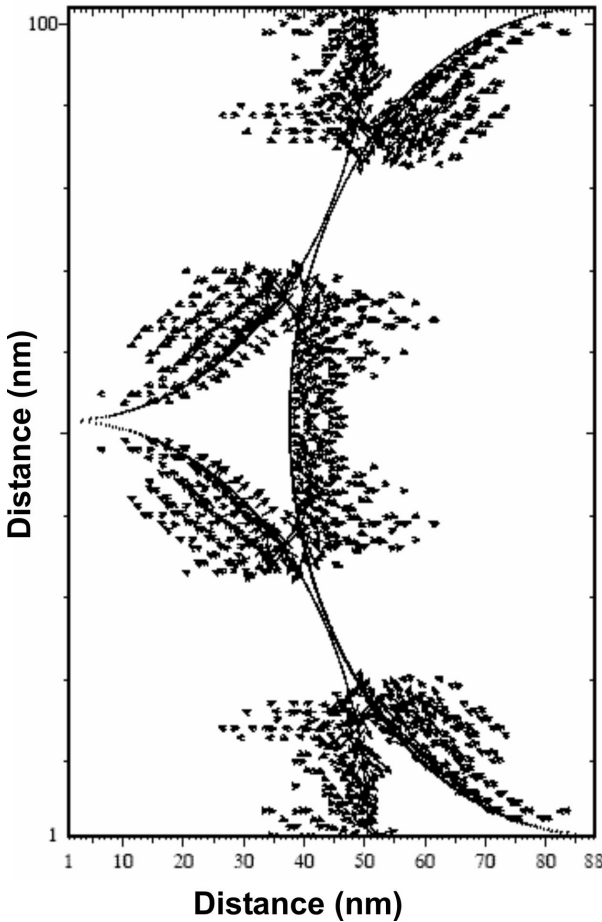


Figure 4.9. Induced polarization plot. Induced polarization corresponding to a wavelength of 475 nm for 450 nm nanoparticles and Z polarization.

this was found to have minimal influence on the resonance wavelength (with exception of the work described in Fig. 4.7).

To understand the nature of the plasmon excitation, a map of the induced dipole field was generated (Figure 4.9) for a wavelength corresponding to the reflection minimum (choosing $D = 450$ nm). In these calculations, the grid spacing in the DDA method is taken to be 5 nm. This large spacing may lead to 10 nm variations in the resonance wavelengths, but this is comparable to the

experimental uncertainty and thus of minor consequence. Figure 4.9 shows results for one unit cell, using polarization along the Z direction. Only the largest induced dipoles are included in the plot. The wave vector is always in the X direction which is perpendicular to the surface.

The plane considered in Figure 4.9

is the top layer of the surface, which is where the polarization is largest (consistent with our earlier conclusions). The results show that the polarization is localized around the nanohole region, with the largest polarizations being associated with “junctions” where the nanoparticles almost touch. Regions where the nanoparticles do touch are “shorted out”, and there is also little polarization in the centers of each plateau region. This means that it is best to think of the plasmon excitation as being “localized to the nanoholes”, rather than “localized to nanoparticles”, as was the case in our earlier studies of coupled nanoparticles. In addition, Figure 4.9 shows an example of what might be termed a “three particle junction” in which the polarization is large all around the triangular hole, rather than just when pairs of particles nearly touch.

To further study the experiments, we have performed calculations in which the sphere diameter was varied for fixed film thickness. Figure 4.10 presents results for four choices of the diameter. This shows that when the diameter is 450 nm, a spectral dip at 424 nm wavelength is calculated, this theoretical $\lambda_{\min}$ is 8 percent away from the experimentally obtained $\lambda_{\min}$ of 459

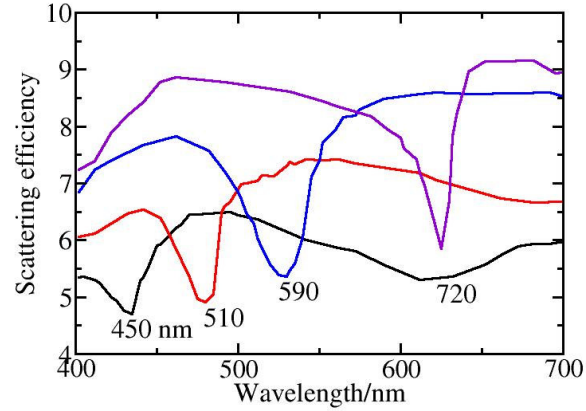


Figure 4.10. Theoretical calculations of the scattering spectra of the nanowell surfaces fabricated using different nanosphere sizes.

nm. The calculated $\lambda_{\min}$ for other nanosphere sizes (510, 590 and 720 nm) are found to be 480, 527 and 625 nm respectively. All of these values all about 8 percent smaller than the experiments, which is probably a measure of the error in our idealized model of the film structure (i.e., leaving out the glass surface and metal in the nanowells). Also, in the model, all the polystyrene nanospheres are

assumed to be in direct contact, while it is clear from Figure 4.4 that there is space between the nanospheres. Therefore, the calculated $\lambda_{\min}$ is smaller than that in the experimental

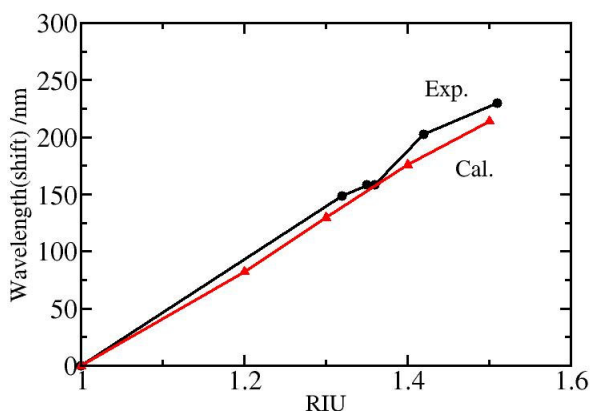


Figure 4.12. Comparison of the shifts from theoretical calculations in vacuum of the resonances wavelengths and experimental results in N_2 for film over nanowell surfaces in different media vs the indices of refraction of the media.

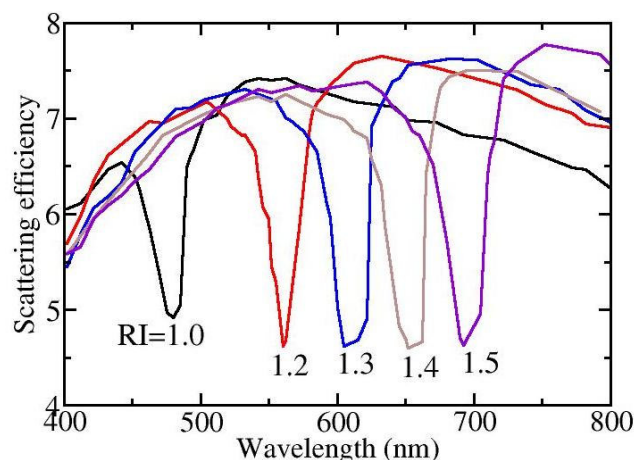


Figure 4.11. Theoretical calculations of scattering spectra of the nanowell surface fabricated with 510 nm nanospheres surrounded by different media.

measurements.

Another aspect of our modeling was concerned with the effect of varying the external dielectric constant. Here we take the diameter of the polystyrene nanospheres to be 510 nm, the metal thickness is taken to be 50 nm, and the nanowell depth is 50 nm. Figure 4.11 shows that the resonance wavelengths red shift when the index of refraction of the

medium increases. In the calculations, the resonance wavelength is at 480 nm when the film is in vacuum; it red shifts to 693 nm when the index of refraction is 1.5. In the experiment, the resonance wavelength is at 483 nm when the film is in vacuum; and it red shifts to 713 nm when the medium refractive index is changed to 1.51. The variation in resonance wavelength with index of refraction of the medium is presented in Figure 4.12. This shows excellent agreement between theory and experiment. In the experiment, the slope of the straight line is 450 nm/RIU while the calculations give 426 nm/RIU (Figure 4.8). This slope grows linearly with increasing diameter of the polystyrene nanospheres, which is consistent with our earlier discussion that the slope is simply given by the diameter.

4.6 Conclusions

The results presented herein show the unique plasmonic characteristics of film over nanowell surfaces. These nanostructures were fabricated using the combination of NSL and RIE, then characterized by AFM, SEM and LSPR reflectance spectroscopy. The Ag film over well-ordered, triangular cross-section nanowells exhibits narrow plasmon peaks, the position and shape of which can be tuned by varying the structural parameters during fabrication. By increasing the diameter of the nanosphere used as the etch mask, the plasmon peak shifts to longer wavelength. The relationship between the peak position and the nanosphere diameter has been solved as $\lambda_{min} = 0.959D$. As the nanowells deepen, a systematic red shift and peak broadening were observed due to the exposure of the underlying glass surface.

The plasmon peaks are not only controlled by the structural parameters, but are extremely sensitive to the surrounding dielectric environment as well. As the refractive index of the surrounding medium increases, the plasmon peak shifts to longer wavelengths. There is a linear relationship between λ_{min} and the refractive index of the external dielectric medium. The

sensitivity increases with larger nanosphere diameter. For example, the most sensitive surfaces among those evaluated were fabricated using polystyrene nanospheres with a diameter of 590 nm, which shows the linear regression slope as large as 538 nm/RIU, i.e., approximately 1 nm shift in the plasmon peak with the change of 0.002 RIU in the refractive index.

The theoretical results modeled the system as a two-dimensional hexagonal array of touching circular disks, and we found that this model provided a semi-quantitative description of the narrow resonance structures. Plots of the induced polarization show that the plasmon excitation is localized to the top portion of Ag films, and to regions around the three particle junction where the disks nearly touch. This means that the film over nanowell structure is best thought of as consisting of coupled nanoholes, rather than as coupled nanoparticles, although there is clearly a continuous transition between one limit and the other as the disk diameter is varied relative to the disk spacing. We also find that diffractive coupling between nanowells causes the plasmons to be remarkably narrow (~ 0.15 eV FWHM). Our experimental results showed that if the nanowell is deep enough compared to the metal film thickness, the disks can couple through glass as well as through air, therefore red-shifting and broadening the peaks (~ 0.33 eV FWHM).

The experimental and theoretical results show the first example of a two-dimensional array that has been specifically fabricated to take advantage of diffractively coupled plasmon resonances. This has yielded array structures with narrow plasmon bands and greater sensitivity to external dielectric constant than has been seen in other nanostructures. Future studies will allow these surfaces to be used in a wide variety of applications, including developing novel refractive index based platforms and fabricating innovative nanostructured catalysts.

Chapter 5

1-Dimensional Chains of Nanoparticles

5.1 Introduction

The unique size-dependent properties of nanomaterials have driven research in a multitude of fields, often leading to materials with important catalytic,¹⁸³ electronic,¹⁸⁴ and magnetic¹⁸⁵ properties. One of the most active areas of nanomaterials research is in applying the distinctive optical properties of noble metal nanoparticles for various applications such as chemo- and bio-sensors.^{71,186,187} The reason for the use of noble metal nanoparticles lies in their localized surface plasmon resonance (LSPR). The LSPR involves a collective oscillation of the conduction band electrons that arises in the metal nanoparticle when excited by a specific wavelength of electromagnetic radiation.¹⁸⁸ The position of this plasmon peak is determined by the shape, size, and composition of the particles as well as the interparticle distance and the external dielectric environment.^{65,104,125}

Assemblies of nanoparticles often can be used to provide special functionalities that are important in sensing,¹⁸⁷ optical waveguides,⁴⁷ and filters¹⁸⁹. The use of assemblies, rather than single particles, offers the ability to average a signal over several similar particles, thus increasing intensity and reducing discrepancies caused by defects. Since the design of a practical plasmonic nanodevice relies heavily on arrays of noble metal nanoparticles, the interactions between these nanoparticles is a crucial, and often overlooked, design parameter. These interactions, which include both short or long range contributions, are important for a variety of structure types, including both highly dense array structures^{117,190} and individual pairs of nanoparticles⁷. The interactions can be measured and studied by observing changes in the LSPR peak shape and position. Theoretical calculations also show these unique interactions. For example, previous work by Schatz et al. has predicted narrowed plasmon peaks in two-dimensional¹⁷⁹ and one dimensional arrays¹⁷⁶ as a result of diffractive interactions between the

particles. For one-dimensional chains of particles above a critical size and with polarization and wave vectors taken to be perpendicular to the array axis, narrow peaks with widths less than 1 nm were predicted. The narrow peaks are caused by the coherent dipolar interactions between the particles when the incident wavelength is close in value to the interparticle distance.^{176,191,192} Details of this mechanism, which involves rapid variation in the dipole sum as the wavelength is varied close to the interparticle separation, are described in reference 191. Because of radiative dipolar coupling between the particles (which varies as e^{ikr}/r), this interaction can be very long range, and the larger the array, the narrower the peak. By taking advantage of these coherent interactions, it is possible to create nanodevices with narrow lines that could lead to better sensing capabilities than are possible with isolated metal particles or aggregates of particles.

Methods for preparing nanoparticle arrays vary as widely as their uses. Standard lithographic techniques can be broken into two major categories, direct-write methods and natural lithographies. Natural lithographies, including nanosphere lithography^{193,194} and colloidal lithography¹⁹⁵ are massively parallel and offer an inexpensive and rapid method for fabricating a large array of nanostructured materials. They, however, are limited by restricted lattice/inter-particle spacings, shapes, and sizes that can be produced, as well as a large range of defects that occur in the structure. On the other hand, direct write methods, such as photolithography,¹⁹⁶ dip-pen lithography,²⁰ and electron beam lithography (EBL),⁶¹ offer fine control of size, shape, and lattice spacing, as well as few defects. Of the major problems associated with direct write methods are the serial nature of the process and the higher cost associated with production of arrays. EBL was chosen for this project because fine control over sample morphology was crucial (based on theoretical modeling) to whether or not the coherent diffractive coupling was going to be observed.

This chapter presents experimental evidence for the effects of diffraction on plasmon lineshapes predicted by theory, using lines of silver particles fabricated with EBL. A critical factor in producing this effect is the uniformity of the all the particles and the straightness of the linear array. EBL readily lends itself to precision control of nanoparticle features and particle spacing, which is ideal for studying the plasmon narrowing. Because different experimental parameters were used than in the original theoretical study,¹⁷⁶ an extension of the theoretical work is also presented.

5.2 Experimental Methods

5.2.1 Nanoparticle Fabrication

Nanoparticle arrays were prepared by EBL on number 2 cover glass slips (Fisher Scientific, Pittsburgh, PA). The resolution of the EBL system used (JEOL JBX5D-II, JEOL, Japan) is approximately 20 nm, employing an accelerating voltage of 50 kV. The rest of the preparation follows a published procedure.⁶¹ ZEP 520 (dilute 1:2 anisole, Nippon Ltd, Japan) was spun onto the glass cover slips and 10 nm of Au was deposited prior to exposure in the EBL. After exposure, the Au film was removed by etching and the patterns were then developed in hexylacetate. Ag was thermally deposited (AVAC HVC600) over both the pattern and resist and subsequently removed leaving patterned nanoparticles behind. This was accomplished by slightly over-developing the resist. In this work each array contained columns of 500 particles and, because of this, the sizes of the arrays varied depending on the interparticle spacing.

5.2.2 Experimental Geometry

The theoretical predictions involved particles in a homogeneous medium rather than on a substrate. To reproduce this environment, the particles were sandwiched between two glass cover slips with Nikon oil in between ($RI = 1.5$). All optical measurements were made using an

inverted microscope (Eclipse TE300, Nikon Instruments) with a fiber coupled to a miniature grating spectrometer (AvaSpec 2048, Avantes). The scattering measurements reported here were recorded over the range 350-850 nm. White light from the TE300 lamp was polarized before being passed through a dark-field condenser (NA = 0.7-0.85) that was used to excite the nanoparticle arrays. The scattered light was collected with a 60× (NA = 0.7) objective. A color video camera was also attached to the front port to collect optical images of the particle columns.

5.2.3 Structural Characterization

Characterization of the morphology of the samples was conducted with both Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). AFM images were collected using a Digital Instruments Nanoscope III microscope (Digital Instruments, Santa Barbara, CA) operated in tapping mode with asymmetric phosphorous n-doped Si nanoprobe tips (Veeco, Santa Barbara, CA). These tips have resonance frequencies between 305 and 370 kHz and are conical shape with an effective radius of curvature at the tip of 10 nm. SEM images were obtained using a Gemini LEO Ultra 55 (Carl Zeiss SMT AG, Germany), with an accelerating voltage of 1 keV and an average working distance of 4 mm.

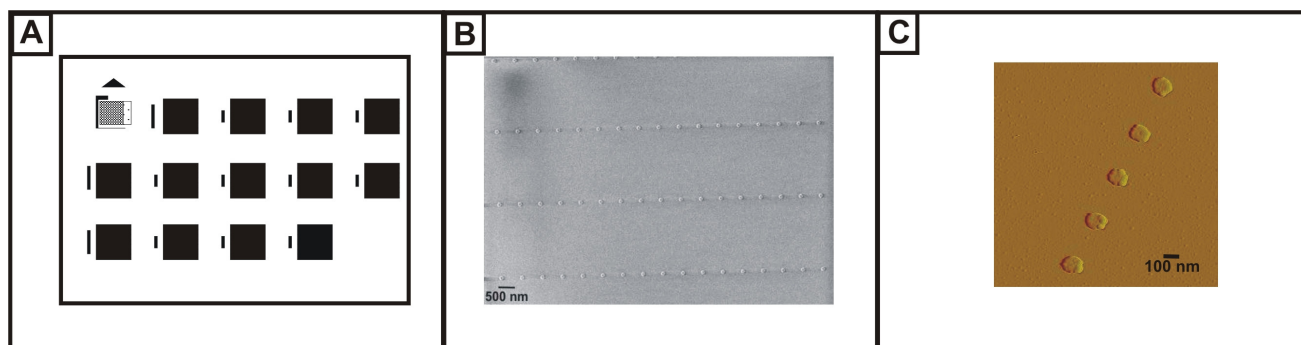


Figure 5.1. Physical Characterization and sample layout. (A) Schematic of overall sample layout. Multiple lines of the same spacing were combined to create pads of particles (orange squares). The pads were arranged in increasing spacing and the last pad was also a single particle pad. (B) An SEM image taken of a pad of particles on glass with a spacing of 632 nm, diameter = 130 nm, height = 30 nm. (C) AFM image of a few Ag nanoparticles on glass. Height = 31.33 ± 1.3 nm, width = 133 ± 4.3 nm.

5.3 Structural Characterization

Sample preparation is a critical step in being able to observe the “diffractively narrowed plasmon”. Using EBL was a logical choice because samples could be easily made with multiple spacings on a single substrate (Figure 5.1A). EBL also produces minimal defect arrays (Figures 5.1B and 5.1C). Figure 5.1A shows a general layout for the overall substrate design. To make finding the particles on the substrate easier, several markers were created far enough away to eliminate any interactions, but close enough to find the particles (triangle and vertical rectangles in Figure 5.1A). Each substrate is made up of pads consisting of columns of particles of various spacing. Large areas of each spacing were fabricated to increase the signal from a specific spacing. The distance between columns was varied from 2 μm to 10 μm to minimize coupling, and take advantage of the predicted narrower lineshapes for one dimensional compared to two dimensional arrays. Each pad was separated by 2 mm, optically isolating each pad. Included on each substrate is also a pattern of particles spaced 5 μm to obtain a single particle spectrum for

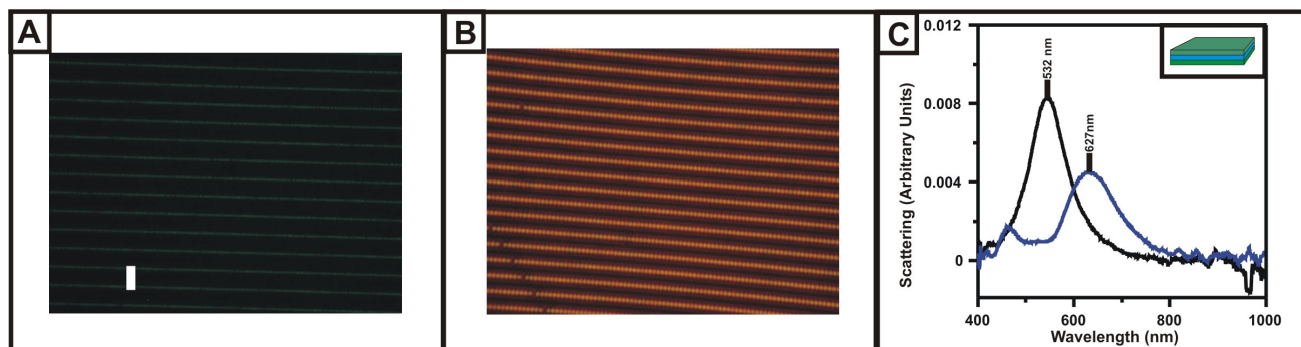


Figure 5.2. Optical characterization and single particle plasmon resonance. (A) is the dark-field image of lines of particles before the uniform refractive index structure is placed around the particles. The line spacing is 5 μm and the particle diameter is 100 nm. (B) is the dark-field image of lines of particles after index matching is applied causing the red-shift in color. Line spacing is 2 μm and particle diameter is 130 nm. (C) The single particle plasmon taken from the sample both with (blue solid line) and without (black solid line) index matching. The particle dimensions are as follows: height = 30 nm, diameter = 100 nm. Inset is a depiction of how uniform RI was achieved with the nanoparticles surrounded by two layers of glass (green) and an index matched oil (blue).

each sample. In Figures 5.1B and 5.1C, the particle uniformity can be seen. The cylindrical nanoparticles have an average height of 30 nm, and width of either 100 or 130 nm depending on the sample type. Also, in Figure 5.1B the straightness of the columns can be seen. In larger field views (data not shown) the columns are continuous over long distances with few defects making them ideal for studying diffractive coupling effects.

5.4 Optical Characterization

Figure 5.2A and 5.2B show the optical uniformity of the samples produced by EBL. Each of the particles is the same color, blue-green, before refractive index (RI) matching, and red-orange afterwards. The red shift seen in the two images is due to the greater RI of the matched sample glass/oil/glass, RI = 1.5/1.5/1.5, (Figure 5.2B) versus the unmatched glass/air

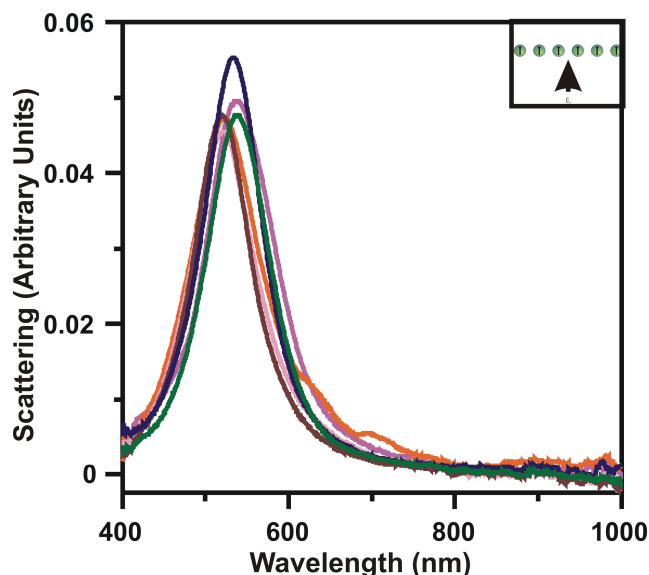


Figure 5.3. Scattering spectra in air for lines of Ag nanocylinders. Plasmon spectra for the linear arrays before any uniform refractive index was made around the particles. This selected set of spectra are spacings from 300 to 800 nm. A limited number of spacings is shown for clarity of the spectra. No sharp plasmonic shoulder is seen. Inset is the excitation direction on the particles.

sample, RI = 1.5/1.0, (Figure 5.2A). The optical micrograph also shows that the separation between columns of particles eliminates any major coupling, as evidenced by the void space between the fields that surround each column. The inset in Figure 5.2A illustrates the excitation geometry of the particles. Figure 5.2C shows representative single particle plasmon spectra for the samples used in this study. The single particle spectrum was obtained using EBL

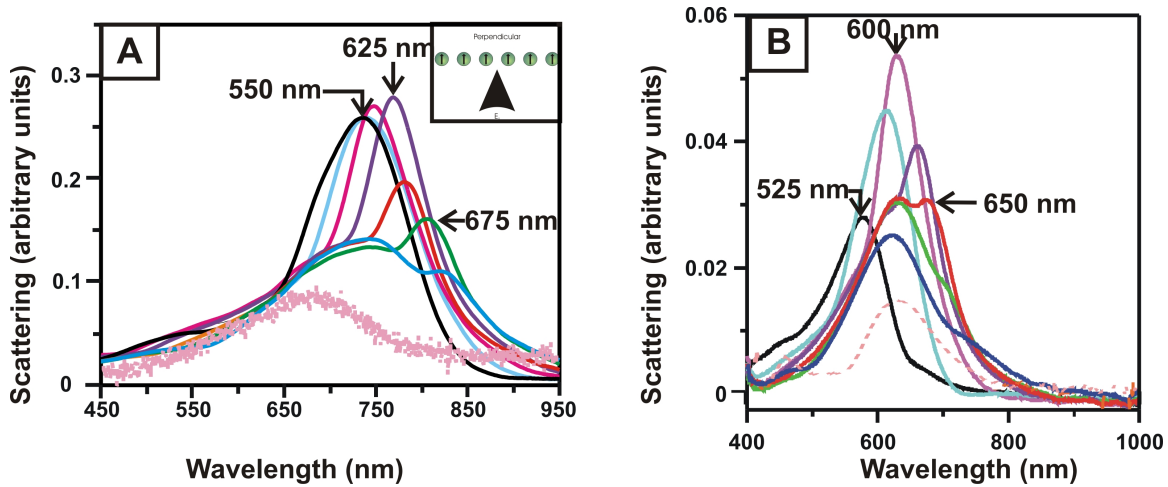


Figure 5.4. Scattering spectra in oil for lines of Ag nanocylinders. (A) and (B) show the darkfield measurements for samples with 2 μm , diameter = 130 nm and 5 μm , diameter = 100 nm spacing between lines respectively taken of arrays varying in spacing from 400 to 700 nm with a uniform refractive index ($\text{RI} = 1.5$) around the particles. Both (A) and (B) were collected with a 60x objective. The inset in (A) is the excitation geometry of the particles for both sets of measurements.

produced cylindrical particles spaced 5 μm apart from each other in both air and oil with another cover slip on top.

5.5 Diffractive Coupling

After preliminary optical and physical characterizations of the samples were conducted, to ensure high sample quality, the non-indexed matched plasmon was investigated for each interparticle distance (Figure 5.3). The λ_{max} for the spacings tested all vary around a peak position of 525 nm and have a full width half maximum (FWHM) of 90 nm. Thus the spectra have narrow uniform peaks, but without the dependence on interparticle spacing that would be a signature of diffractive coupling. The reason for this is simply that the speed of light is different above (air) and below (glass) the particles, preventing an effective coherent coupling between adjacent particles.

Figure 5.4 shows that for the index matched samples, there is a shoulder on the red side of the single particle plasmon, whose wavelength varies with particle spacing. The particles in

Figure 5.4A have a diameter of 130 nm and a height of 30 nm, and for a separation of 550 nm, the peak has low intensity and FWHM of approximately 125 nm. As the interparticle distance increases towards the single particle resonance wavelength, the shoulder on the red portion of the lineshape narrows and becomes more intense, with a maximum intensity occurring at a spacing of 625 nm (FWHM = 60 nm). For still larger spacings, the peak remains narrow, but decreases in intensity until it is no longer observed in the spectrum. The narrow shoulder also occurs in arrays with larger column spacings (5 μm) and slightly smaller particles (100 nm), as seen in Figure 5.4B. The progression of plasmon peaks is the same as above: below the optimal spacing the plasmon peak is low in intensity and broad (FWHM = 100 nm, 525 nm spacing), at the optimal spacing of 600 nm there is a shoulder whose FWHM is 50 nm, and above the optimal spacing the shoulder decreases in intensity and eventually disappears altogether. The spectra in 5.4B are blue shifted from those in 5.4A due to the smaller particle size. When collecting with other objectives (ie 10 $\times$), the property can still be seen. (data not shown)

5.6 Theoretical Modeling

In the earlier theory study¹⁷⁶ only the extinction spectra were calculated. Because of the weak signals produced by the arrays it was necessary to use Rayleigh scattering spectroscopy rather than extinction, so in the present studies we have calculated the scattering spectra for one and two-dimensional arrays of silver nanoparticles to simulate the measurements. First, the periodic discrete dipole approximation DDA method described previously¹⁹⁷⁻²⁰⁰ was used to generate results for two-dimensional rectangular arrays of 130 nm diameter particles each with height 30 nm and with a 2 μm distance between each column. The results for a spacing of 600 nm (not shown) were compared with one-dimensional chain results, and only small differences were found, so additional calculations only considered the one-dimensional chains. The

additional calculations involve varying the interparticle distance from 500 nm to 800 nm, with a cylinder height of 30 nm and particle diameter of either 100 or 130 nm. The calculations considered 500 particles in which both polarization and wave vectors are perpendicular to the array axis. The index of refraction of the medium is taken to be 1.5. We first carried out calculations with normal incident light. The results for the 130 nm particles are presented in Figure 5.5A, along with the corresponding single particle spectrum. The figure shows resonance

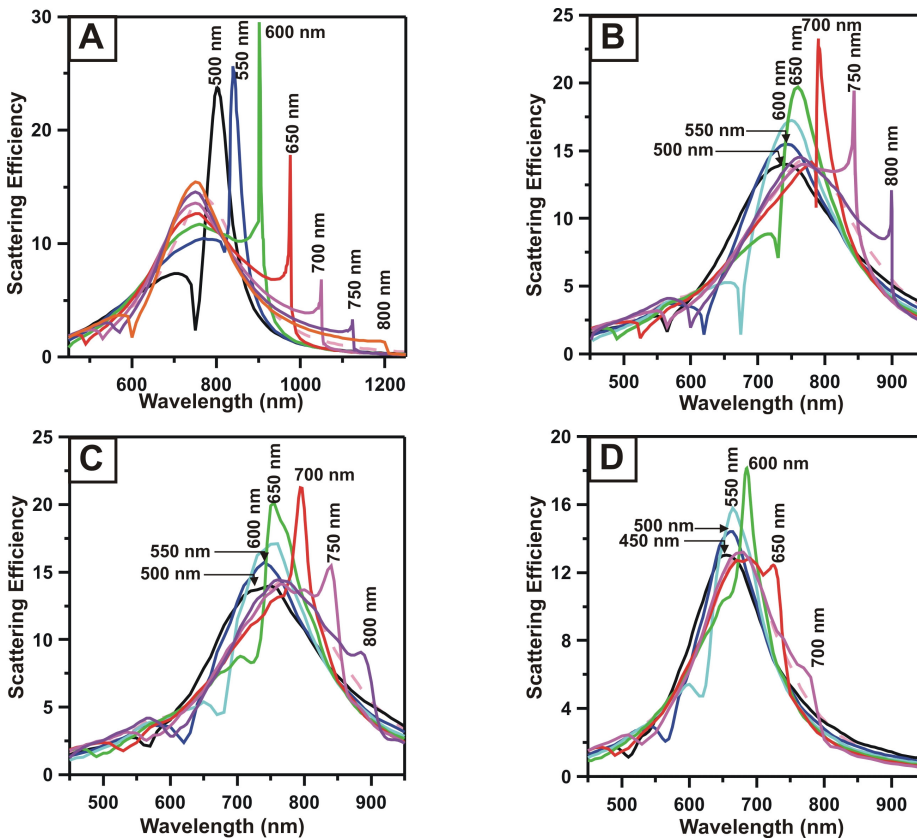


Figure 5.5. Theoretical modeling for the dark-field excitation geometry. (A) Scattering efficiencies for a chain of 500 cylinders with height of 30 nm and diameter of 130 nm with the normal incident light. (B) Scattering efficiencies for a chain of 500 cylinders with height of 30 nm and diameter of 130 nm with an incident angle of 30 degrees . (C) Scattering efficiencies for a chain of 20 cylinders with height of 30 nm and diameter of 130 nm with a 30 degrees incident angle. (D) Scattering efficiencies for a chain of 20 cylinders with height of 30 nm and diameter of 100 nm with a 30 degrees incident angle. Corresponding single particle spectra for each case are included (dashed line).

wavelengths at longer wavelengths comparing with the experimental results. We then carried out the same calculations with an incident angle of 30 degrees. The results for the 130 nm particles are presented in Figure

5.5B, along with the corresponding single particle spectrum. The

figure show resonance wavelengths and variation with spacing that are in qualitative agreement with the observations. However the shoulder on the red portion of the plasmon band is much narrower than in the experiments, with widths as small as 2 nm when the interparticle spacing is 750 nm. Figure 5.5C shows that if only adjacent groups of 20 particles in the 500 particle chain are allowed to couple, the widths are in reasonable agreement with the measured results in Figure 5.4A. Figure 5.5D shows analogous results for the 100 nm diameter particle, and again we see that the results when only 20 adjacent particles are allowed to couple match the experiments in Figure 5.4B reasonably. The good agreement for reduced coherent coupling between the particles likely mimics the influence of the spread in illumination and collection angles in the experiment, which smear the strict scattering configuration assumed in the theoretical simulation. It is also possible that defects, lattice imperfections, the incoherent light source and local variations in the index of refraction contribute to the broadening.

5.7 Conclusions

In summary, this chapter demonstrates that it is possible to significantly affect plasmon line shapes in linear arrays of cylindrical particles through diffractive coupling, following up the earlier predictions of theory¹⁷⁶ Critical factors to the success of this experiment are the use of a dark field configuration, a uniform refractive index and high sample quality. By varying the interparticle spacing from 350-800 nm, the diffractively induced peak grows into the plasmon spectrum, reaches a maximum and then decreases in intensity and eventually disappears. Also presented are theoretical calculations that support the experimental data. EBL has provided the ideal tool to make multiple sample areas on a substrate with precise control over particle size and spacing. By showing experimental evidence for diffractive control of plasmon line shapes, the design of new schemes to further improve the diffractive response should be possible.

Chapter 6

2-Dimensional Arrays of Nanoparticles

6.1 Hexagonal Arrays of Cylinders

6.1.1 Introduction

There is an ever-increasing demand for smaller device feature sizes and better device performance. It is therefore imperative to explore the size-dependent chemical and physical properties of current and new materials. The magnetic,^{185,201,202} catalytic,³ thermodynamic,^{203,204} electrical transport,^{45,205,206} and electrochemical^{108,111,112} properties of nanoscale materials differ significantly from the properties found in their bulk, molecular, or atomic counterparts. Of particular interest are the optical properties of single metal nanoparticles and nanoparticle arrays. Studies of nanoscale noble metal materials are especially important because these materials have potential as plasmonic waveguides,²⁰⁷ bio/chemosensors,^{38-40,90,92-95} and substrates for surface-enhanced spectroscopies.^{55,208,209} Because of interest in nanoparticle-based devices, many research groups are currently fabricating and studying nanoparticle arrays. Chumanov and coworkers have studied nanoparticle coupling effects by dispersing nanoparticles onto polymer-coated quartz substrates.^{210,211} However, the varying lattice spacing between the randomly dispersed nanoparticles prohibits a thorough understanding of the relation between nanoparticle arrangement and the optical properties of the array. Aussenegg and coworkers studied the extinction spectra of Ag and Au nanowire gratings of various dimensions, and square arrays of Au.⁶⁶ The work presented in this Chapter examines two-dimensional noble metal nanoparticle arrays fabricated using electron beam lithography (EBL) that systematically probe the effect of plasmonic/photonic coupling on the localized surface plasmon resonance (LSPR). LSPR occurs when light at a specific wavelength impinges onto the surface, inducing a collective oscillation of the conduction band electrons. This oscillation can be localized on a single nanoparticle, or it

may involve many nanoparticles in an array. This selective photon adsorption is very dependent on the effective size, shape, arrangement and separation of the nanoparticles on the surface. Gold and silver typically support these resonances in the visible and near-infrared regions of the electromagnetic spectrum, making them the best choices for use in optical systems, as the LSPR can be measured by UV-visible-IR extinction spectroscopy.

Nanoscale devices are likely to require assemblies of nanoparticles for a variety of applications that include sensors and waveguides. The design of plasmonic nanodevices relies heavily on the nature of the electromagnetic interactions between nanoparticles in the device elements. These interactions, which include both short^{190,212} and long^{117,212} range contributions, are important for a variety of structure types, including both highly dense array structures⁸ and individual pairs of nanoparticles.⁷ These interactions can be measured and studied by observing changes in the LSPR peak shape and position. Some aspects of these electromagnetic interactions are well understood.^{176,213,214} Other aspects have just begun to be explored, both experimentally and theoretically. For example, previous work by Schatz and coworkers predicted narrowed plasmon peaks in two-dimensional and one dimensional arrays as a result of diffractive/plasmonic interactions between the nanoparticles.²¹³ The particles were far enough apart that the coupled dipole approximation could be used to describe the interparticle interactions, and for infinite lattices we were able to develop a semi-analytical solution to the electrodynamics, providing considerable insight as to the origin of the narrow bands. We found that one dimensional arrays of spherical silver particles having at least 50 particles can generate extremely narrow plasmon resonances under certain conditions. These narrow resonances occur when the incident wave and polarization vectors are both perpendicular to the chain (leading to coherent excitation of all the particles in phase), and the particles are above a critical size ($r = 30$

nm). In this case, narrow plasmon peaks with widths less than 1 nm (less than few meV) can be obtained for spacings larger than the isolated particle plasmon resonance wavelength. The narrow bands arise from the interaction between the localized plasmons in the particles and photonic states associated with the array. This leads to a mixed state whose wavelength is slightly longer than the photonic state i.e., slightly larger than the particle spacing and whose intensity is tied to the isolated particle plasmon intensity and to the difference in wavelength between the photonic and isolated particle plasmon wavelengths. One can also describe these states as arising from coherent dipolar interactions among the particles wherein the imaginary part of the retarded dipole field cancels the damping that is associated with the single particle resonance due to radiative damping and scattering of the conduction electrons by phonons, electrons, defects and other factors. Of course, one cannot eliminate all damping effects, so the overall extinction spectrum of the particle array still contains broad features in addition to the sharp plasmonic/photonic line. Also, the effect disappears if the particles or the array size is too small, as the dipole sums in either case are too small to cancel the single particle relaxation effects.¹⁷⁹ This also explains why one dimensional arrays, with polarization perpendicular to the array axis, produce the narrowest lines, as there is less destructive interference in the dipole sums in one dimensional (1D) than in two dimensional (2D) arrays.^{176,179,214} In addition to giving sharp lines in the extinction spectrum, the narrowing effect is also evident in the scattering and absorption spectra of the particle arrays. Furthermore, the diffractive coupling effect leads to remarkably high electric fields near the particle surfaces, so it is possible that it may provide a mechanism for producing single molecule surface-enhanced Raman scattering with certain morphologies. Experimentally, we used electron beam lithographically prepared structures to study the influence of electromagnetic interactions in the 1D chains. Using a dark field

configuration we were able to see evidence of the narrow plasmon predicted by theory.

Chumanov and coworkers also identified a narrow plasmon in disordered 2D arrays, but a detailed study has yet to be conducted.²¹⁰

A variety of methods have been implemented to fabricate all of these arrays above. Herein, we systematically study the plasmonic properties of two different two-dimensional nanoparticle architectures, hexagonal arrays of cylinders and the NSL structure produced by EBL. The effects of interparticle distance, external dielectric environment, and materials properties have been studied in detail. Structures have been identified that exhibit a narrowing of the plasmon resonances and photonic/plasmonic coupling within the array. Also, a non-plasmonic material was investigated to help understand the interactions between diffraction and plasmonic effects.

6.1.2 Experimental Methods

6.1.2.1 Sample Preparation.

Microscope optical glass; No. 1 25-mm circle coverslips were purchased from Göteborgs Termometerfabrik (Goteborg, Sweden), surfaces were cleaned in a piranha solution (1:3 30 % $\text{H}_2\text{O}_2\text{:H}_2\text{SO}_4$) at 80°C for 30 minutes (CAUTION: piranha solution should be handled with great care). Once cooled, the glass surfaces were rinsed with copious amounts of DI water and stored in the final rinse until use. The clean glass substrate was spin-coated with a 70 nm thin film of an electron-sensitive resist; ZEP 520 (Nippon ZEON Ltd., Japan) diluted 1:2 in anisole. The resist film was coated with a 10 nm thin film of gold to make the surface conductive before the pattern was exposed. During patterning, the electron beam passes straight through this thin metal coating and exposes the resist as desired. After exposure, the Au film was removed by etching in an aqueous solution of 4 g of KI and 1 g of I_2 in 150 mL of deionized water. The patterns

were then developed in hexylacetate (used for the high contrast development), creating a patterned resist film on top of which the Ag was deposited in a high-vacuum thin film vapor deposition system (AVAC HVC 600). The deposited thickness and deposition rate were measured by a quartz crystal microbalance. The deposition rate was maintained at $\sim 1 \text{ \AA/s}$ to create a smooth film. In the last step of the sample preparation, the lift-off step, the resist was dissolved in a strong solvent (Shipley Remover 1165), which also removes the metal deposited on top of the resist. Samples were prepared with an “undercut” in the resist film to ensure that the metal film on top of the resist does not have any physical contact with the metal deposited directly on the substrate. This is accomplished by slightly overdeveloping the resist. In this work, both cylinder and triangular nanoparticle arrays of Ag were prepared in two shapes and arrangements. Keeping all of the other parameters in the array constant, we varied the lattice spacing of the array from near contact to several hundreds of nanometer separation. The arrays fabricated for this study are summarized in Table 1.

6.1.2.2 Dark-field Microscopy.

The theoretical predictions involved particles in a homogeneous medium rather than on a substrate. To reproduce this environment, the particles were sandwiched between two glass cover slips with Nikon oil in between ($RI = 1.5$). All optical measurements were made using an inverted microscope (Eclipse TE300, Nikon Instruments) with a fiber coupled to a miniature grating spectrometer (AvaSpec 2048, Avantes). The scattering measurements reported here were recorded over the range 350-850 nm. White light from the TE300 lamp was polarized before being passed through a dark-field condenser ($NA = 0.7\text{-}0.85$) that was used to excite the nanoparticle arrays. The scattered light was collected with a $60\times$ ($NA = 0.7$) objective. A color

digital camera was also attached to the front port to collect optical images of the particle columns.

6.1.2.3 Extinction Spectroscopy.

Extinction spectra were collected using an Ocean Optics USB2000 fiber-coupled spectrometer for the 400-1000 nm region and a fiber-coupled near-infrared (NIR) spectrometer (NIR 128L-1.7T1-USB, Control Development) for the 900-1700 nm region. The spectra over this wide region have a slight mismatch near 900 nm signifying where one spectrometer ends and the other begins. White light from a tungsten-halogen lamp light source was fiber-coupled

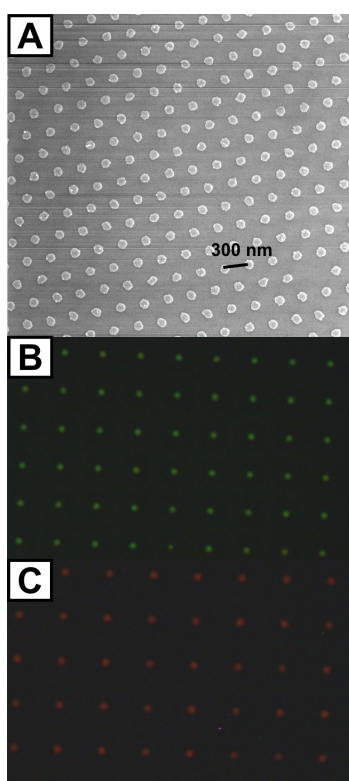


Figure 6.1. Physical and Optical characterization of Ag cylinders. Physical characterization of the samples done by (A) SEM and (B) and (C) Dark-field LSPR imaging. For the SEM images the accelerating voltage was 1 kV with a working distance of 7 mm. The cylinder diameter was 130 nm, with a spacing of 300 nm in this image. The difference in figures (B) and (C) are they are in air and oil respectively.

with a 100 μm fiber to a +40 mm focal length achromatic collimating lens. The collimated beam was then polarized by a Glan-Taylor calcite polarizer with 5 mm aperture and focused onto the sample by a +12.7 mm focal length achromatic lens with the optic axis normal to the sample surface. Transmitted light was collected by an infinity corrected 10x Nikon microscope objective (NA=0.30) at a working distance of 16.0 mm and focused into a 600 μm fiber that couples into the spectrometer. The white light spot size on the sample was scanned with a straight edge and was close to Gaussian with a 20 μm diameter at FWHM.

The sample was mounted on two computer controlled micro translational stages (M-111.1DG, Physik Instrumente) to form a x-y system with a 50 nm step size. The x-y stage system is fixed on the manual vertical linear stage (MVN50, Newport Corporation) and manual rotational stage (M-UTR120A, Newport Corporation). All the samples were studied under a stream of dry nitrogen with some additional samples being tested in index matched oil as well.

6.1.2.4 Scanning Electron Microscopy (SEM).

SEM images were obtained using a FEI Quanta 200 ESEM FEG. All samples were imaged in the ESEM mode with an accelerating voltage of 15 kV.

6.1.3 Physical Characterization

Physical characterization was performed by both SEM and dark-field LSPR image.

Figure 6.1 shows the results from both techniques. Figure 6.1A shows the SEM image on glass of the cylinders made to match the previous work done on 1 dimensional chains of cylinders of a 130 nm radius. Center to center spacings were varied from 300 nm to 800 nm, as well as including an isolated nanoparticle array to obtain the single particle plasmon resonance.

Figures 6.1B and 6.1C show dark-field LSPR images

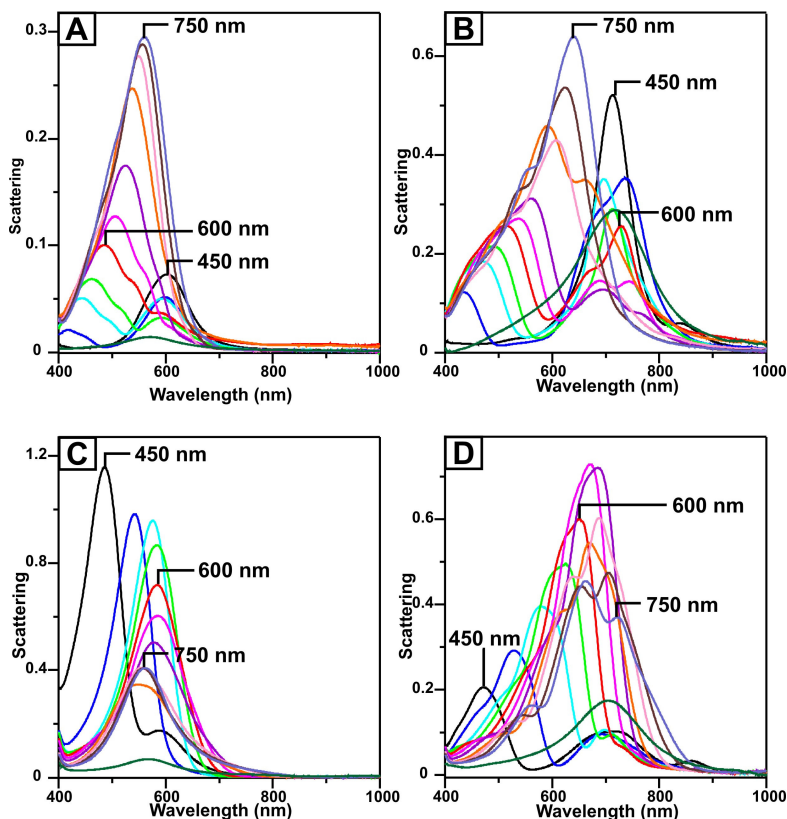


Figure 6.2. Scattering spectra in air and oil for two different objectives. (A) and (B) are the air and oil spectra for a 10x objective. (C) and (D) are the air and oil spectra for a 60 x objective. Both were obtained on

of the same nanoparticle size as in Figure 6.1B, but with a center to center spacing of 5 μm . This spacing allows us to isolate the particles and see them individually in the LSPR image. In Figure 6.1B the image was taken in air, and in Figure 6.1C the image was taken in index matched

oil with a coverslip on top.

The nanoparticle plasmon resonance red-shifts, as evidenced by the change in color from green to red. The SEM image verifies that the nanoparticles are highly uniform, with less than a 2 nm variation in size, and is corroborated by the LSPR image by a uniform color in all the nanoparticles.

6.1.4 Photonic/Plasmonic Coupling

Using both dark-field microscopy and UV-vis spectroscopy the complete pictures of diffractive coupling in 1 and 2 dimensional arrays of cylinders was observed. Figure 6.2 shows the dark-field microscopy results obtained for the 2D hexagonal array of cylinders. Figures 6.2A and 6.2B for the results for a 10 $\times$ objective and Figures 2 C and 2D are the results for a 60 $\times$ objective. As can be seen in the results, there is a difference between index matched and non-index matched systems for both the 10 $\times$ and 60 $\times$ objectives. Most notably, a shoulder appears

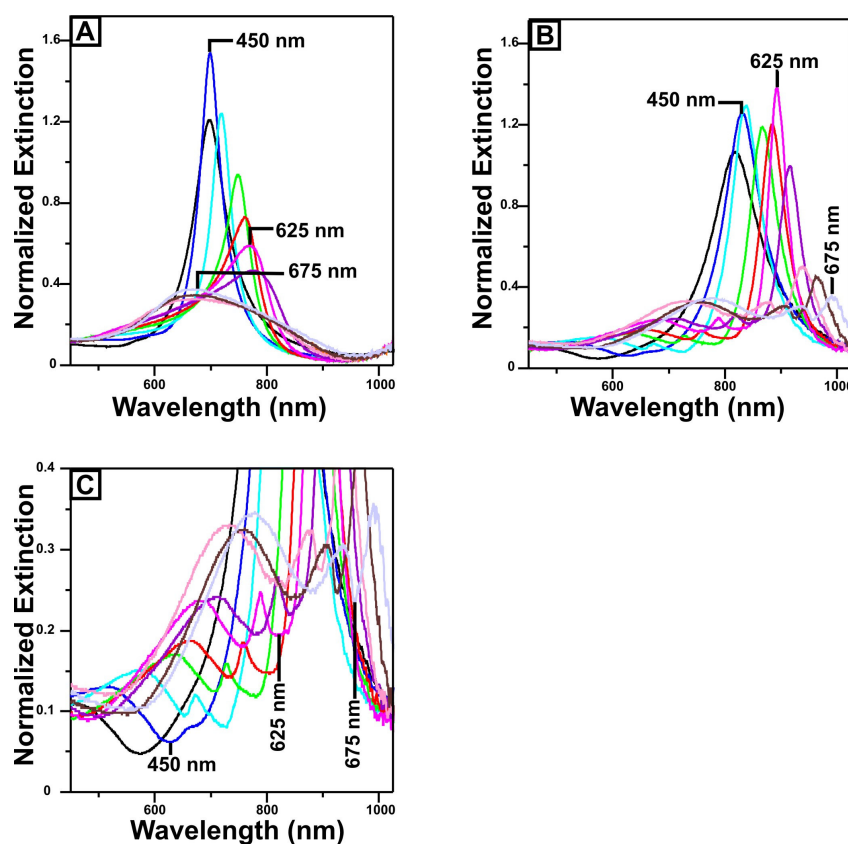


Figure 6.3. Extinction spectra in air and oil for Ag cylinders. Extinction spectra in air, (A), and oil (B) for varying the interparticle distance in a hexagonal array of cylinders. (A) and (B) both used the visible detector, while (C) also used the NIR detector since the extinction spectra extended

in the index matched data for both objectives that grows in and dies off as expects for a diffractive coupling peak. This matches what was observed in the 1 dimensional case, but with less intensity and sharpness. An ultimate sharpness (FWHM) of 75 nm was observed for the 2 dimensional arrays versus a FWHM of 50 nm for the 1 dimensional case. However, there are also evident diffraction effects, as illustrated by the difference in the results for the 10 × and 60 × objectives.

Because of the complications in collecting the scattering spectra, due to the collection of extraneous diffraction effects, normal incidence UV-visible spectroscopy was also used. Figure 6.3 details the extinction data obtained for a hexagonal array of cylinders. In the non-index matched case the peak position loses intensity as the particle density decreases in each pad. There is also evident a slight red shift before reaching the single particle limit. In the index matched case, the optimal spacing as already been reached, and no smaller spacings were tested. The trend still follows that after the optimal spacing, the peak continues to red shift and decrease in intensity. One noticeable difference is the lack of interference from higher order diffraction peaks, however, both techniques to show the cooperative coupling between the plasmon and diffraction to create the narrow peak.

6.1.5 Non-Plasmonic Materials

To help elucidate the effects of diffraction on the results, fabrication and testing of a Ti array was performed. The results for a 10 × objective are seen in Figures 6.4A and 6.4B. At close spacings, there are strong diffraction effects, but as the spacing is increased, the peak broadens out and becomes more like a background. This effect in the longer interparticle spacings is due to two possible effects: (1) the diffractions orders that are sharp are no longer being collected by the selected objective and (2) the diffraction effects are not that strong for

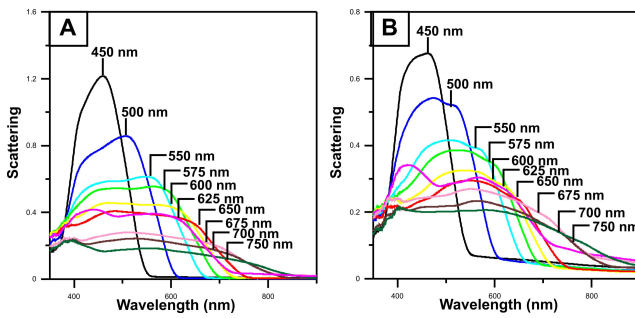


Figure 6.4. Scattering spectra for a non-plasmonic material. Scattering spectra for a Ti hexagonal array of cylinders using a 10x objective in (A) air and (B) oil.

those spacings. Another missing feature from Figures 6.4A and 6.4B is the sharp shoulder that should be evident in Figure 6.4B, the index matched system.

Instead of having a sharp shoulder, the air and index matched systems are identical.

These results show that in order to see the cooperative coupling there needs to be an intimate interplay between the plasmon and diffraction, with only one or the other the very narrow resonances cannot be observed.

6.1.6 Conclusions

In summary, the 2 dimensional arrays of Ag cylinders do show the diffractive coupling phenomena, just as in the 1 dimensional analog. Similar results were observed in the scattering and extinction spectra. With the spacings tested, the scattering spectra showed more diffraction effects, but increase in intensity to a maximum and then drop after the optimum spacing is reached. These effects could be higher order interactions. This is also seen in the extinction spectra, which show the plasmon peak position starting out at the optimal spacing where the peak is at its most intense point, and then dropping off. Smaller spacings to be able to observe the full range of coupling will also need to be done in order to create a fuller picture of the coupling in the systems and comparison of scattering and extinction spectra. Testing of a non-plasmonic material, Ti, has shown that having both diffraction and plasmonic properties present is critical to observing this phenomena.

6.2 Nanosphere Lithography Pattern (Kagome Lattice)

6.2.1 Introduction

There is an ever increasing demand for smaller, faster, and more sensitive devices in industry today. Because of this, there is a huge push in developing and comparing varying fabrication techniques. The comparison of these techniques is important to optimize speed, reliability, and of the techniques. There are three main categories of nanostructures fabrication: (1) chemical synthesis, (2) direct-write lithography, and (3) natural lithography. Both direct-write and natural lithographic methods are used to produce surface-bound structures utilized in many device applications. Two popular methods are electron beam lithography and nanosphere lithography.

In electron beam lithography (EBL), the desired pattern is serially produced by exposing a thin layer a photoresist to high-energy electrons altering the photoresist that has been exposed. This exposed resist is then developed in a solvent to remove it from the surface. After development, the samples are placed in a deposition system and used a mask to deposit the material of choice on the surface. The leftover resist is subsequently removed from the surface, usually with a strong base, leaving the nanostructures behind.

Nanosphere lithography (NSL) is another technique that offers a versatile platform to examine the properties and explore the applications of such nanoparticle structures. NSL is a parallel, inexpensive fabrication method that produces, with a high degree of reproducibility and control, periodic nanoparticle arrays with adjustable size, shape, and material properties.^{22,34,123} NSL uses ordered arrays of hexagonally close-packed nanospheres as lithographic masks on silica, mica, silicon, and other solid surfaces. Typically, a thin layer of metal is deposited over the nanosphere mask. An ordered array of metal nanoparticles, in the Kagome lattice, remains on the surface after removal of the nanosphere mask.

The reason both of these methods are of interest for studying noble metal nanoparticle systems, is because of a unique optical property called the localized surface plasmon resonance (LSPR). The LSPR is excited when a specific wavelength of light impinges on a noble metallic nanoparticle and causes the plasma of conduction electrons to oscillate collectively.⁸⁵ This collective oscillation of electrons occurs only for light within a certain bandwidth, therefore, noble metal nanoparticles exhibit selective photon absorption and resonant Rayleigh scattering which can easily be monitored using UV-visible extinction spectroscopy. It is well established that the maximum extinction wavelength, λ_{max} , of the LSPR is strongly and systematically dependent upon the composition, size, shape, and interparticle spacing of nanoparticles.¹⁰⁴

In traditional NSL, while the in-plane width and out of plane height can be varied by changing the nanosphere size used, the interparticle distance is fixed for a given in-plane width. Also, with NSL, typical defect-free domain sizes are in the 10 nm range. Electron beam lithography (EBL) allows the study of not only the coupling within the NSL structure, but also the effects of defects within the structure.

This section describes work that was performed using both scattering and extinction spectroscopies to examine the coupling regimes within the Kagome lattice as well as initial comparisons of the perfect EBL structure to the traditional NSL structure to analyze the effects of defects on the LSPR peak position and shape. Theoretical modeling using the coupled dipole approximation was also performed for the EBL structure as the interparticle spacing is varied.

6.2.2 Experimental Methods

6.2.2.1 Sample Preparation

Microscope optical glass; No. 1 25-mm circle coverslips were purchased from Göteborgs Termometerfabrik (Goteborg, Sweden), surfaces were cleaned in a piranha solution (1:3 30 %

H₂O₂:H₂SO₄) at 80° C for 30 minutes (CAUTION: piranha solution should be handled with great care). Once cooled, the glass surfaces were rinsed with copious amounts of DI water and stored in the final rinse until use. The clean glass substrate was spin-coated with a 70 nm thin film of an electron-sensitive resist, ZEP 520 (Nippon ZEON Ltd., Japan) diluted 1:2 in anisole. Before the pattern was exposed, the resist film was coated with a 10 nm thin film of gold to make the surface conductive. During patterning, the electron beam passes straight through this thin metal coating and exposes the resist as desired. After exposure, the Au film was removed by etching in an aqueous solution of 4 g of KI and 1 g of I₂ in 150 mL of deionized water. The patterns were then developed in hexylacetate (used for the high contrast development), creating a patterned resist film on top of which the Ag was deposited in a high-vacuum thin film vapor deposition system (AVAC HVC 600). The deposited thickness and deposition rate were measured by a quartz crystal microbalance. The deposition rate was maintained at ~1 Å/s to create a smooth film. In the last step of the sample preparation, the lift-off step, the resist was dissolved in a strong solvent (Shipley remover 1165), which also removes the metal deposited on top of the resist. To ensure that the metal film on top of the resist does not have any physical contact with the metal deposited directly on the substrate, samples were prepared with an “undercut” in the resist film. This is accomplished by overdeveloping the resist slightly. In this work, both cylinder and triangular nanoparticle arrays of Ag were prepared in two shapes and arrangements. Keeping all of the other parameters in the array constant, we varied the lattice spacing of the array from near contact to several hundreds of nanometers separation. The arrays fabricated for this study are summarized in Table 1.

6.2.2.2 Dark-field Microscopy.

The theoretical predictions involved particles in a homogeneous medium rather than on a substrate. To reproduce this environment, the particles were sandwiched between two glass cover slips with Nikon oil in between ($RI = 1.5$). All optical measurements were made using an inverted microscope (Eclipse TE300, Nikon Instruments) with a fiber coupled to a miniature grating spectrometer (AvaSpec 2048, Avantes). The scattering measurements reported here were recorded over the range 350-850 nm. White light from the TE300 lamp was polarized before being passed through a dark-field condenser ($NA = 0.7-0.85$) that was used to excite the nanoparticle arrays. The scattered light was collected with a 60 $\times$ ($NA = 0.7$) objective. A color video camera was also attached to the front port to collect optical images of the particle columns.

6.2.2.3 Extinction Spectroscopy.

Extinction Measurements were carried out using two systems. Both macro- and micro-extinction measurements were recorded using an Ocean Optics model S2000 spectrometer over the range 350-850 nm. For macro-extinction measurements, the spectrometer was coupled to a fiber probe (Ocean Optics, Dunedin, FL) and a halogen lamp (F-O-Lite H, World Precision Instruments, Sarasota, FL). The light was focused into the 400 μm core diameter fiber coupled to the spectrometer. The probed spot size was approximately 1 mm in diameter at the sample. For micro-extinction measurements the spectrometer was fiber-optically coupled to a Nikon TE300 inverted microscope. White light from the TE300 lamp was collimated before being passed through the sample. The transmitted light was collected with a 20 $\times$ ($NA = 0.5$) objective. The light was then spatially filtered at the image plane on the side port of the microscope before being focused into the 400 μm core diameter fiber coupled to the spectrometer. Because of the spatial filtering, the probed spot size was approximately 50 μm in

diameter at the sample. Data processing included boxcar smoothing and identification of the extinction maximum ($\lambda_{\max}$) using a derivative routine.

6.2.2.4 Scanning Electron Microscopy (SEM).

SEM images were obtained using a FEI Quanta 200 ESEM FEG. All samples were imaged in the ESEM mode with an accelerating voltage of 15kV.

6.2.3 Physical Characterization

Physical characterization by both SEM and dark-field LSPR imaging was done. Figure 6.5 shows the results from both techniques. Figure 6.5A shows the SEM image on glass of the triangles made to match the perpendicular bisector of the tetrahedron produces using a 390 nm diameter nanosphere, our most commonly made NSL sample. Spacings as close as 20 nm tip to tip were also achieved. Few to no defects were also observed in an entire 100 μm area (data not

shown).

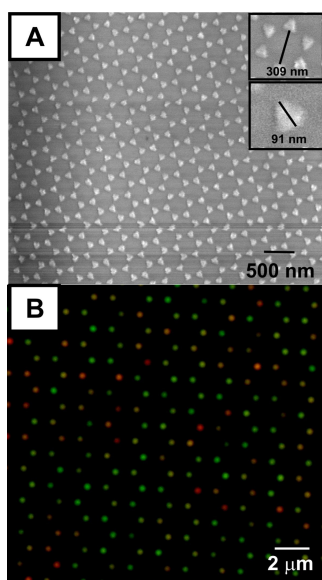


Figure 6.5. Physical characterization of the Kagome lattice. Physical characterization of the samples done by (A) SEM and (B) Dark-field LSPR imaging. For the SEM images the accelerating voltage was 1 kV with a working distance of 7 mm. The average perpendicular bisector of the triangles was 90 nm. (B) Was taken in air.

Figure 6.5B show a dark-field LSPR image of the same nanoparticle size as in figure 6.5B, but with a tip to tip spacing of 2 μm . This spacing allows us to isolate the particles and see them individually in the LSPR image. The image was taken in air which is why there are multiple colors shown in the image. The SEM image verifies that there is high uniformity of the nanoparticle with less than a 2 nm variation in size, in an LSPR image this should show up as a uniform nanoparticle color across the surface. This is not so, however, with the majority being a green color with a few red dots. These

can be caused by selective condensation of water on the surface and the sensitivity of the triangle is high enough to cause a color change/shift in the plasmon resonance of these selective nanoparticles.

6.2.4 Coupling in the Kagome Lattice

In traditional NSL, while the in-plane width and out of plane height can be varied, the interparticle distance is fixed for a given in-plane width. By using electron beam lithography (EBL) this can

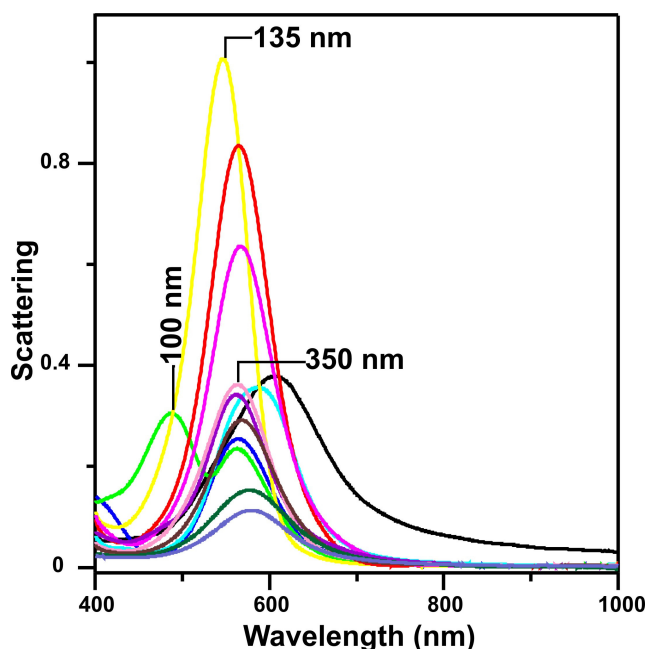


Figure 6.6. Scattering spectra in air for different interparticle spacings while the perpendicular bisector of the triangles remained constant ($b = 90$ nm)

be overcome, allowing for the study of the coupling distance in the NSL structure. Results for the dark field scattering can be seen in Figure 6.6. At close spacings there are interesting effects on the plasmon resonance. Once a spacing of 500 nm is reached, the plasmon stays very stable in position and shape - therefore showing little to no coupling in the array. Still utilizing an inverted microscope for ease of moving the sample around and pad alignment, the LSPR extinction spectra were collected. In both systems, one observes an initial red-shift in the peak position and a unique double peak structure at close spacings. The resonance position then blue-shifts and decreases in intensity as the single nanoparticle limit is neared. At 135 nm, the spacing produced by a 390 nm diameter sphere, shows a different interaction as it red-shifts whereas the rest continue to follow a blue-shifting pattern. Unlike the scattering spectrum, the extinction spectrum at 135 nm tip to tip distance does not increase in intensity or narrow.

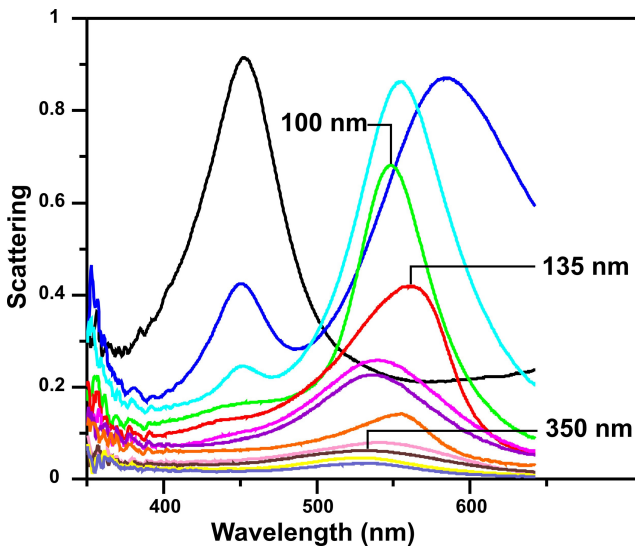


Figure 6.7. Extinction spectra in air for different interparticle spacings while the perpendicular bisector of the triangles remained constant ($b = 90$ nm)

6.2.5 Defect Effects

One important feature, other than the coupling regime in the Kagome lattice is how defects interact with the triangles. This is evident by comparing the exact same structure produced by the natural lithographic technique NSL and the direct write method EBL. Figure 6.8 depicts the results of the samples made by these two fabrication techniques. EBL can produce an essentially perfect $100\ \mu\text{m} \times 100\ \mu\text{m}$ area of tetrahedron, whereas a NSL

produced sample has at best a perfect area of $10\ \mu\text{m} \times 10\ \mu\text{m}$ on a very good sample. Defects in the NSL structure vary in concentration and type from bow tie like structures to large point defects. All of these structures themselves should have resonances far into the infrared, but they cause a difference in the smaller particle plasmon by coupling, or by interrupting the coupling in the system. In Figure 6.8, there are some stark differences between the two systems. At first glance, there is already evident a peak position difference with the EBL produced sample being blue shifted by 76 nm. Another very noticeable difference is the peak widths are different with the more perfect structure having a much smaller FWHM of 0.27 eV versus a 0.35 eV FWHM for the NSL produced structure. These results show strong evidence that there are defects within the NSL structure. Further studies to look more closely at what types of defects are affecting the plasmon more.

Other than defect effects the blue shift can also be attributed to the difference in the radius of curvature of the traditionally produced NSL structure and the EBL produced NSL. EBL, because it uses a circular beam has a limit to the sharpness of the features produced. This rounding causes a slight narrowing and a blue shift in the plasmon resonance. Inset in Figure 6.5 shows SEM images illustrating the roundedness of the EBL produced samples.

6.2.6 Theoretical Modeling

Using the discrete dipole approximation (DDA) method, we modeled the extinction spectra of truncated silver nanoparticle arrays with varied interparticle distance. The unit length (length of the polarizable cubes) in the simulation is 5 nm. The index of the refraction of the medium is chosen to be 1.5. The height of the silver particle is 30 nm with a 90 nm bisector. The size of the silver particles is fixed while the interparticle distances are varied in the simulations.

In Figure 6.9, the center to center distances of the particles in a dimer are varied from 140

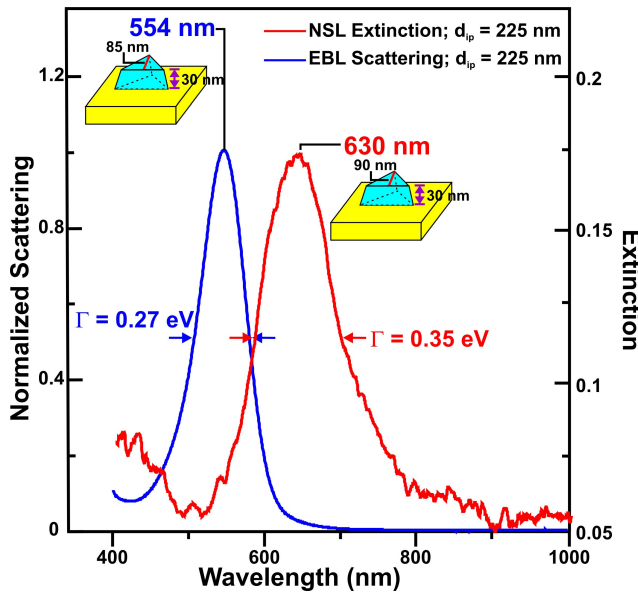


Figure 6.8. Comparison of the Kagome lattice generated by both EBL (blue line) and NSL (red line). The sample conditions mimicked each other as closely as possible to obtain a proper comparison. For both samples $b = 90$ nm; $d_{ip} = 225$ nm ($D = 390$ nm).

nm which corresponds to a 20 nm ($140 - 2 \times 60$) tip to tip distance and a 242 nm $\sqrt{3} \times 140$ in diameter of the sphere if the nanosphere lithograph to 1120 nm. The incident light is perpendicular to the particle plane. The simulations show that when the distance between particles is 120 nm, a broad peak is observed with a resonance wavelength at 820 nm. When the particle distance is increased to 255 nm, the resonance wavelength blue shifts.

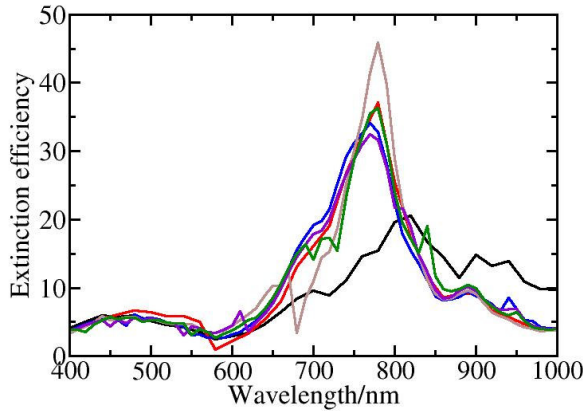


Figure 6.9. Theoretical extinction spectra of silver dimer arrays with different interparticle distances. The incident light is perpendicular to the particle plane. (Center to center particle distance: Black: 140 nm; Red: 255nm; Blue: 420 nm; Brown: 520 nm; Violet: 720; Green: 1120nm)

The resonance peaks narrow with the increase of interparticle distance, and the highest intensity is observed when the particle distance is increased to 520 nm. The resonance wavelengths slightly shifts to shorter wavelengths when the particle distances are further increased.

We also simulate the extinction spectra of the particle arrays with angle between the incident light and the particle

plane of 60 degrees (Figure 6.10). The size of the particles is kept the same and the particle distance is changed from 620 to 720 and 820 nm. The simulations show that a narrow peak can be observed at 780 nm when the particle distance is 620 nm. The narrow peak is shifted to 820 nm when the particle distance is expanded to 720 nm.

More simulations with smaller unit length and particles on a substrate are expected.

6.2.7 Conclusions

Both theoretical and experimental data showed unique coupling as the spacing in the Kagome lattice was

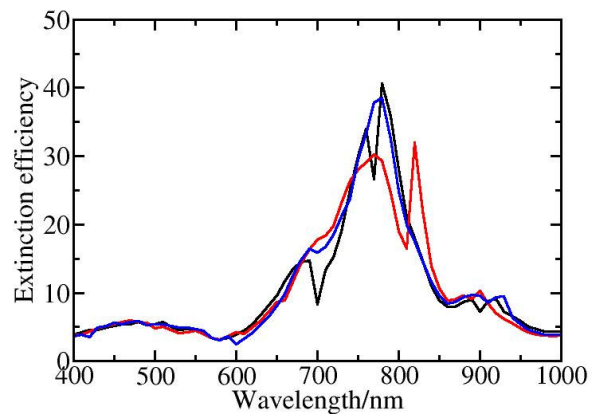


Figure 6.10. Theoretical modeling with 60 degree incidence excitation light. Extinction spectra of silver dimer arrays with different interparticle distances. The incident light is 60 degrees relative to the particle plane. (Center to center particle distance: Black: 620 nm; Red: 720nm; Blue:820 nm)

increased as the perpendicular bisector remained constant. Initial results were also able to look at defect effects within the NSL lattice. These results will allow for the logical design of future sensors based on the NSL system for both diagnostic and research applications.

Chapter 7

Evaluation of Commercially available SERS Substrates

7.1 Introduction

The utilization of once difficult spectroscopic techniques in everyday analysis is coming ever closer to realization as technology advances. For many of these techniques, there is a need to create a miniature and robust hardware system as well as a robust and sensitive sensing surfaces and media. Surface-enhanced Raman spectroscopy is one of these emerging techniques. As the name implies, the surface used for this technique is critical to being able to reproducibly obtain the same results. There have been several companies (Mesophotonics, Oxana, and Nanotecture) that have begun to explore commercial uses of SERS substrates that they have developed for specific biological and chemical sensing applications.

As these companies progress with designing SERS surfaces, standards need to be established for the logical design of the optimal systems. A deep understanding of the SERS mechanism is required to set these standards. There are two main SERS mechanisms; chemical enhancement and electromagnetic enhancement. Most in the SERS community believe the electromagnetic enhancement to be the more dominant mechanism. It will be discussed below. One must consider nanostructure optics to understand the electromagnetic mechanism. Excitation of the LSPR (see chapter 1 section 1.2 and 1.3) results in the generation of large electromagnetic fields at the surface of the roughness feature. The electromagnetic mechanism is based on these amplified electromagnetic fields (E) generated by the LSPR of nanoscale features.²¹⁵ The LSPR is intricately tied to the shape, size, and material composition of these structures. Thus, there is a complex relationship between the surface structure and the structurally dependent optical characteristics that determines the magnitude of the electromagnetic portion of SERS enhancement.²¹⁵ This mechanism has several experimental signatures, such as long-range (i.e. a few nanometers) distance dependence,^{117,157,190,216,217} the

weak dependence of the enhancement factor (EF) on the chemical identity of the adsorbate,²¹⁸ and the existence of surface-enhanced second harmonic generation (SESHG) and single molecule SERS.²¹⁹⁻²²¹ Recent improvements in understanding of the nature of the EM enhancements has created a renewed interest in the use of SERS as an analytical technique. Many groups continue to generate new insights as new mathematical models are coupled to more accurate characterization in the nanoscale regime.^{6,222}

This chapter critically compares one of the commercially available SERS substrates, Klarite from Mesophotonics, Ltd., and the film over nanosphere substrate, a commonly used surface in the Van Duyne group. This comparison will be conducted in three ways, by looking at the stability of the LSPR across the surface, the stability of the SERS signal across the surface, and the enhancement factors of benzenethiol for each surface.

7.2 Experimental Methods

7.2.1 Materials

Absolute ethanol was purchased from Pharmco (Brookfield, CT). Benzenethiol was purchased from Sigma-Aldrich (Milwaukee, WI). Ag pellets (99.99%, 0.125 inch diameter) and Au pellets (99.99%, 0.125 inch diameter) were obtained from Kurt J. Lesker (Pittsburgh, PA). Borosilicate glass surfaces, No. 2 Fisherbrand 18-mm circle coverslips were purchased from Fisher Scientific (Pittsburgh, PA). Polystyrene nanospheres with diameters (D) of 510 ± 7.65 nm and 590 ± 12.98 nm were received as a suspension in water from Interfacial Dynamics Corporation (Portland, OR). Millipore cartridges (Marlborough, MA) were used to purify water to a resistivity of $18 \text{ M}\Omega\text{cm}^{-1}$. All materials were used without further purification. All chemicals were used as received.

7.2.2 Surface Fabrication

Glass coverslips were cleaned in a piranha solution (1:3 30 % H_2O_2 : H_2SO_4) at 80°C for 30 minutes (*CAUTION: piranha solution should be handled with great care*). Once cooled, the glass surfaces were rinsed with copious amounts of water and then sonicated for 60 minutes in 5:1:1 H_2O : NH_4OH :30% H_2O_2 . Lastly, the glass was rinsed repeatedly with water and was stored in water until used.

To prepare the film over nanosphere substrates, clean glass coverslips were prepared with both mono- and multi- layers of nanospheres by drop-coating different amounts of nanosphere solution onto the glass and allowing it to dry. Once the nanosphere masks were dry, the surfaces were mounted in an electron beam deposition system (Axxis Thin Film Electron Beam Evaporator, Kurt J. Lesker, Pittsburgh, PA) and 200 nm of either Ag or Au were deposited onto the surface.

Klarite surfaces were received from Mesophotonics, Ltd. (Southampton, UK) and rinsed in ethanol for several minutes prior to use.

Both Klarite and FON samples were incubated in an ethanolic 1 mM benzenethiol solution for 3 hours, and then rinsed with copious amounts of ethanol to remove any excess electrostatically bound molecules.

7.2.3 Scanning Electron Microscopy

SEM images were obtained using a Hitachi S-4500. An accelerating voltage of 10kV and a working distance of 7 mm was used for both normal and side view SEM images.

7.2.4 Scanning Localized Surface Plasmon Resonance Spectroscopy

Measurements were carried out using a SD2000 spectrometer coupled to a reflection probe (Ocean Optics, Dunedin, FL) and a halogen lamp (F-O-Lite H, World Precision

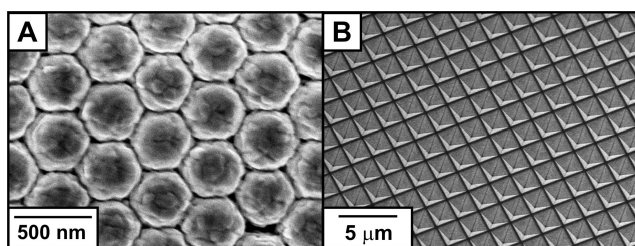


Figure 7.1. SEM images of (A) AgFON with 390 nm diameter spheres and (B) the Klarite surface. The accelerating voltage used was 10 kV with a working distance of 7 mm.

Instruments, Sarasota, FL). The reflection probe consists of a tight bundle of 13 optical fibers (12 illumination fibers around a collection fiber) with a useable wavelength range of 400–900 nm. All reflectance spectra were collected against

a mirror-like Ag film over glass surface as a reference. The flow cell was held in place by micrometer stages that allowed movement in both the x and y directions (15 mm in x and 15 mm in y, with 0.1 μm step).

7.2.5 Scanning Surface-Enhanced Raman Spectroscopy

A Spectra-Physics model Millennia Vs laser (λ_{ex} 532 nm) was used to excite a Spectra-Physics model 3900 Ti-sapphire laser to produce the 785-nm excitation wavelength (λ_{ex}); the laser spot size on the sample was less than 0.5 mm in diameter. This excitation wavelength was chosen to minimize autofluorescence of proteins.^{22,23} The SERS measurement system includes an interference filter, an edge filter (Semrock, Rochester, NY), a model VM-505 single-grating monochromator with the entrance slit set at $100 \lambda_{\text{ex}}$ (Acton Research Corp., Acton, MA), and a LN₂-cooled CCD detector (Roper Scientific, Trenton, NJ). A collection lens with magnification 5 was used to collect the scattered light.

7.3 Klarite versus Film Over Nanosphere Surfaces

7.3.1 Structural Characterization

SEM micrographs of both the Klarite and AgFON surfaces were obtained to further elucidate any differences in morphology and fabrication between the two SERS substrates. Figure 7.1 shows the results obtained for these two surfaces. The standard FON surface has both nanoscale periodic roughening from the nanospheres used in fabrication, and an innate surface

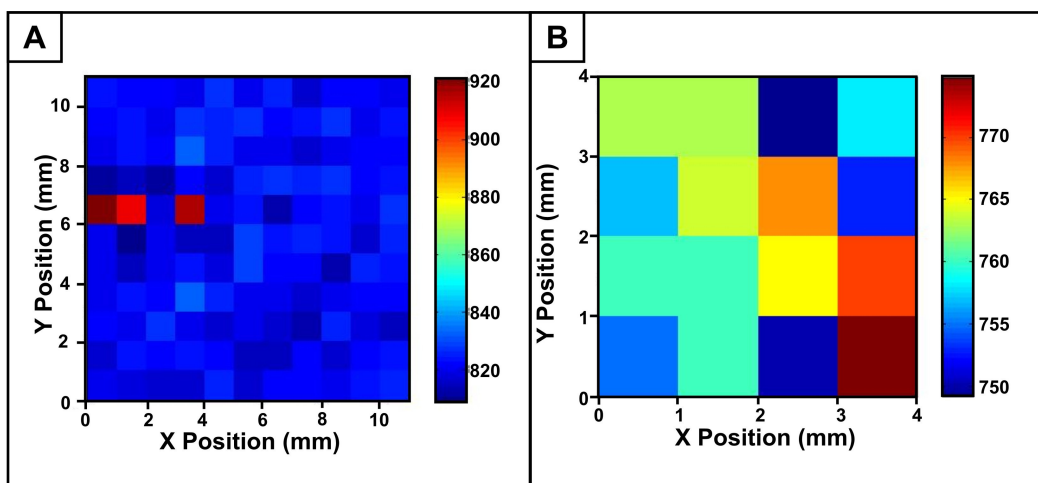


Figure 7.2. Scanning LSPR experiments for (A) an AgFON and (B) Klarite surfaces. Statistics for (A) are as follows: average = 824.1 ± 18.6 nm, high = 810.5 nm, low = 810.5 nm, $\Delta\lambda = 111.7$ nm. Statistics for (B) are as follows: average = 766.1 ± 9.2 nm, high = 799.2 nm, low = 756.1 nm, $\Delta\lambda = 43.1$ nm. All spectra were obtained in a nitrogen environment. The spot size and step size were 1 mm.

roughness from the deposition of the metal onto the surface. The native metal roughness on a flat film of silver is around 50 nm. (see figure 7.1) The features on the Klarite surface are created via the lithographic process, and are on the micron scale ($\sim 2 \mu\text{m}$ edge length on the square base), with a nanoscale roughness of ~ 50 nm over the entire surface.

7.3.2 Scanning LSPR

Once the physical parameters for both surfaces were measured, the next step was to examine the consistency of the plasmon resonance across each of the nanostructured surfaces. Figure 7.2 displays the results for scanning across both an AgFON (Figure 7.2A) and a Klarite surface (Figure 7.2B). These surfaces were bare and kept in a nitrogen environment by the use of a flow cell. The spectrometer's sampling area is 1 mm^2 , and the step size was therefore set at 1 mm for both samples. The AgFON scanned area is much larger due to the sample covering the whole surface. The active SERS area on the Klarite substrate is 3 mm by 5 mm, and therefore the scanning area was much smaller. The 1 mm step size on the surface allows for non-overlap of the sampling area. For the AgFON surface the average plasmon peak position occurred at 823 ± 14 nm with a total spread in the plasmon of 30 nm. The Klarite's average plasmon peak

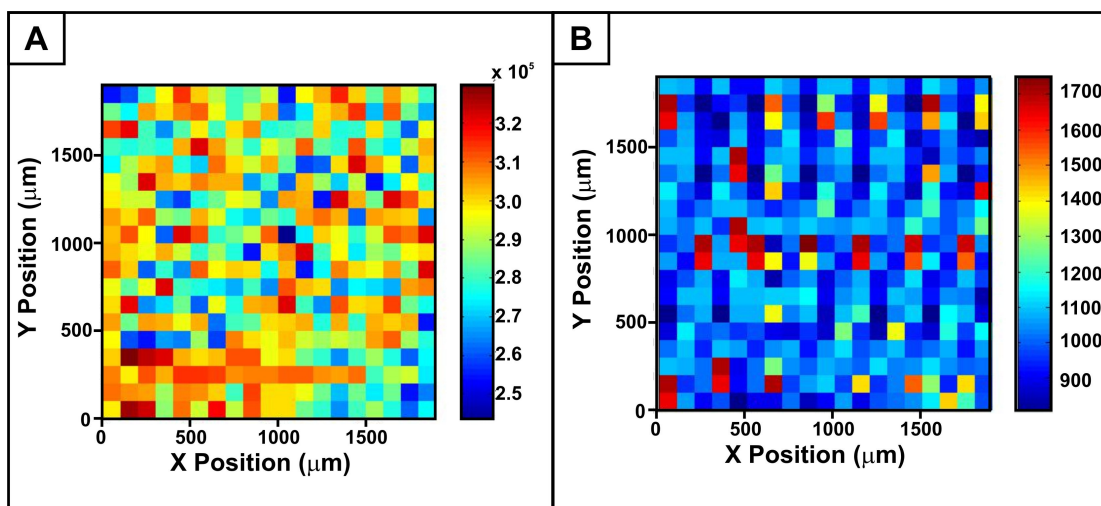


Figure 7.3. Scanning SERS data for the 1081 cm^{-1} peak of benzenethiol for both (A) a AgFON and (B) klarite. Statistics for (A) area as follows: average = $2.9 \times 10^5 \pm 2.4 \times 10^4$, high = 3.3×10^5 , low = 2.5×10^5 , $I_H/I_L = 1.3$. Statistics for (B) area as follows: average = 1060 ± 205 , high = 1696, low = 802, $I_H/I_L = 2.1$. $\lambda_{\text{ex}} = 785\text{ nm}$; power = 47.6 mW; acquisition time = 60 sec; Both scans covered a 2 mm x 2 mm size of the sample with a spot size of $100\text{ }\mu\text{m}$ and a step size of $100\text{ }\mu\text{m}$. The scale bar the right of each map is the SERS intensity in counts of the 1081 cm^{-1} peak and given a respective color.

position was $763 \pm 5\text{ nm}$. The Klarite surface offers a more stable plasmon, but the FON surface is much cheaper and faster for the fabrication of a variety of surfaces with the ability to move the peak position around to maximize the SERS signal from the surface. So, although these initial results favor the Klarite surface due to the higher reproducibility of the surface, the lack of flexibility does could hamper its usage.

7.3.3 Scanning SERS

The next step in evaluating the potential of the Klarite surface for SERS applications is the comparison of the reproducibility of the SERS signal across the surface. Benzenethiol was chosen as the probe molecule due to its high affinity to Ag and Au surfaces, and its large Raman cross section. Figure 7.3 shows the results for scanning across both surfaces. The laser power, collection time, incubation time, and laser wavelength remained constant for both surfaces, therefore counts were compared between the two surfaces in the two figures. Counts were used to compare the gross signal intensity response of the two systems. As the analysis shows, the

Klarite surface has more uniformity in signal across its surface. Although the AgFON surface has slightly higher variability, the overall signal is much larger than the Klarite signal. This will be further illustrated in Section 7.3.4 in calculating the enhancement factors of the two surfaces. For the AgFON surface there is an average observed intensity of $2.9 \times 10^5 \pm 2.1 \times 10^4$ counts. For the Klarite surface an average intensity of $1.1 \times 10^3 \pm 2.0 \times 10^2$ counts. Again, the Klarite surface offered a more uniform signal across the surface. However, the overall signal of the benzenethiol was 4 orders of magnitude weaker than that from the FON surface, with the same surface coverage of the benzenethiol. The weaker SERS signals from the Klarite are primarily attributable to two factors: (1) non-optimal plasmon peak position and (2) enhancing surface area. In the first case, the peak position of the Klarite is not in the best position for the highest enhancement. It has been shown that for the largest enhancement it is necessary for the plasmon peak position to be to the red of the excitation wavelength.^{86,147} For a 785 nm λ_{ex} , the Klarite plasmon resonance at 763 nm clearly is non-optimal, while the AgFON LSPR is tuned to 823 nm. Another influence in the relative enhancement of the benzenethiol signal is the overall molecular coverage. For the Klarite surface, due to it being covered by gold, the assumption was made that there is full coverage, but the actual SERS active area of the Klarite surface could be much smaller therefore decreasing the overall signal, whereas for the AgFON surface, everywhere there are nanospheres is a SERS active site. This, the areas where the electromagnetic fields are high enough to create this enhancement are much smaller and/or weaker than the AgFON surface.

7.3.4 SERS Enhancement Factors

The ultimate test of a potential SERS surface is to compare their enhancement factor of probed molecules. The method outlined by McFarland, et al. was used to calculate the

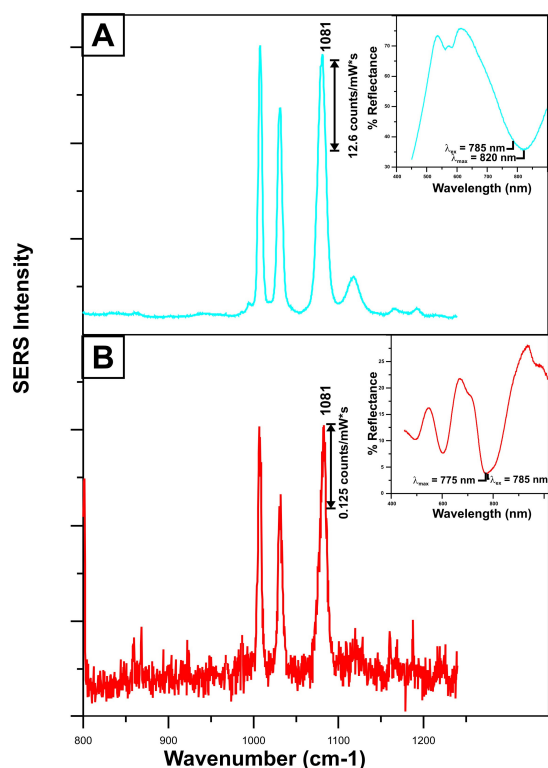


Figure 7.4. The SERS spectra of Benzenethiol on (A) a AgFON and (B) kalrite surfaces. Inset in each spectrum is the reflectance spectrum for the sample taken at that spot. Labeled are both the extinction and excitation maximum. $\lambda_{ex} = 785$ nm; power = 47.6 mW; acquisition time = 60 sec.

enhancement factors for each surface.⁸⁶ SERS EF values were calculated by comparing the intensity of the 1081 cm^{-1} benzenethiol peak measured in the SERS experiments to the peak measured from liquid benzenethiol at a laser excitation wavelength of 785 nm. The SERS enhancement factor is given by:

$$EF = N_{vol}I_{surf}/N_{surf}I_{vol}$$

where N_{vol} and N_{surf} are the number of molecules probed in the liquid sample and on the SERS substrates, respectively, and I_{vol} and I_{surf} are the corresponding normal Raman and SERS

intensities. Figure 7.4 shows the SERS spectra for (A) an AgFON and (B) a Klarite surface (liquid

benzenethiol not shown). The inset of each figure shows the plasmon resonance spectrum for each sample, with the excitation wavelength and peak position labeled. The EF of the AgFON was calculated to be on average 2.8×10^7 , while the klarite surface only had an EF on average of 1.0×10^5 , a difference of 2 orders of magnitude.

7.4 Conclusions

Klarite surfaces are more structurally uniform than AgFON surfaces, and therefore yield better reproducibility in SERS experiments. Also, the elimination of possible delamination problems, caused by the peeling of the latex nanospheres used in the FONs, offers a great alternative. The use of the nanospheres, even with delamination issues, broaden the tunability

of the FON surfaces allowing for precise control of the plasmon peak position, whereas the klarite surface has shown limited tunability, as evidence by the fact that the surface tested in not optimized for the excitation wavelength of 785 nm. These nanospheres can also be used to create a more stabile periodic surface of truncated tetrahedron in the Kagome lattice. This surface was not tested in this study, however, in other work performed by Van Duyne and coworkers, have shown that these surfaces show remarkable enhancements and can be tuned for the specific target system.^{90-96,99,100} But, in the fight for higher sensitivity to compete with other techniques, the overall enhancement and even raw signal needs to be improved. While the FON surfaces still offer the best surface on which to get large enhancements of the molecular signal, high sensitivity, high selectivity, and respectable reproducibility.

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Appendix 1

Geometric changes of Electrochemically modified NSL nanoparticles

A1.1 Volume of a NSL-Produced Nanoparticle:

We describe the particle as a truncated tetrahedron as Figure A1.1. V_{bot} is the volume of a truncated tetrahedron to mimic a NSL-produced nanoparticle, V_{tetra} is the volume of the untruncated tetrahedron (constructed using the particle as the base), and V_{top} is the volume of the tetrahedron that is on top of the particle. These volumes are related to the structural parameters of the particle using the following equations:

$$(1) \quad V_{bot} = V_{tetra} - V_{top}$$

$$(2) \quad V_{tetra} = \frac{2}{27} \sqrt{6} a_{bot}^3$$

$$(3) \quad a_{top} = a_{bot} - \frac{3\sqrt{2}}{4} h_{bot}$$

$$(4) \quad h_{op} = \frac{2\sqrt{2}}{3} a_{bot} - h_{bot}$$

$$(5) \quad V_{top} = \frac{1}{3\sqrt{3}} a_{top}^2 h_{top}$$

$$(6) \quad V_{top} = \frac{2\sqrt{6}}{27} \left(a_{bot} - \frac{3\sqrt{2}}{4} h_{bot} \right)^3$$

$$(7) \quad V_{bot} = \frac{2\sqrt{6}}{27} \left[a_{bot}^3 - \left(a_{bot} - \frac{3\sqrt{2}}{4} h_{bot} \right)^3 \right]$$

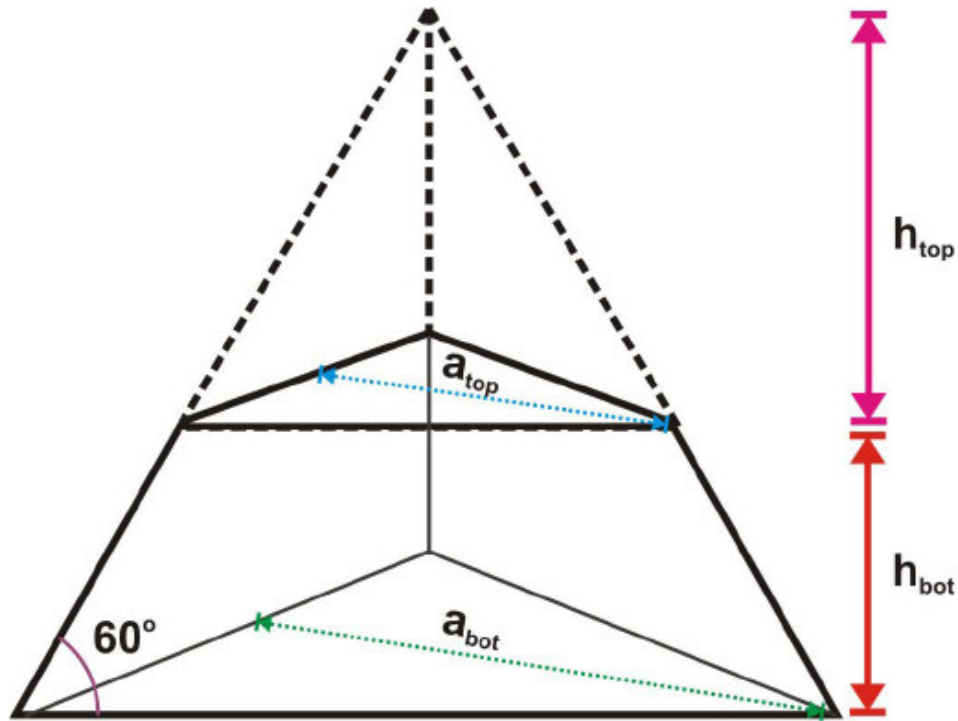


Figure A1.1 Schematic illustration of the theoretical model of a NSL-produced nanoparticle. a_{bot} is the in-plane width of the nanoparticle, h_{bot} is the out-of-plane height of the nanoparticle, h_{top} is the height of the top of the tetrahedron not including the volume taken up by the particle, a_{top} is the in-plane width of the top volume of the tetrahedron.

The parameters are defined as follows (shown in Figure A1.1): a_{bot} is the in-plane width of the nanoparticle, h_{bot} is the out-of-plane height of the nanoparticle, h_{top} is the height of the top of the tetrahedron not including the volume taken up by the particle, a_{top} is the inplane width of the top volume of the tetrahedron. In deriving these expressions we have assumed that the tetrahedron is a regular tetrahedron in which each face is an equilateral triangle.

A1.2 Volume of an Electrochemically Modified Nanoparticle:

We assume that the oxidized nanoparticle (Figure A1.2) consists of a trigonal prism on the bottom, and the unmodified truncated tetrahedron on the top, with the height and width of the trigonal prism determined by the volume change associated with the oxidation process such that the top of the prism and the bottom of the unmodified truncated tetrahedron coincide.

Since the top triangular face of the original particle and the out-of plane height of the particle remain constant, we have $a'_{top} = a_{top}$, $h'_{top} = h_{top}$, $h'_{bot} = h_{bot}$. With these assumptions, the volume of the oxidized particles is the sum of the trigonal prism volume V_1 , and the volume V_2 of the remaining portion of the truncated tetrahedron.

$$(1) \quad V'_{bot} = V_1 + V_2$$

$$(2) \quad V_1 = \frac{H a_{bot}'^2}{\sqrt{3}}$$

$$(3) \quad V_2 = \frac{2\sqrt{6}}{27} (a_{bot}'^3 - a_{top}'^3)$$

$$(4) \quad H = \frac{2\sqrt{2}}{3} (a_{bot} - a_{bot}')$$

$$(5) \quad V'_{bot} = -\frac{4\sqrt{6}}{27} a_{bot}'^3 + \frac{2\sqrt{6}}{9} a_{bot} a_{bot}'^2 - \frac{2\sqrt{6}}{27} (a_{top}')^3$$

The parameters in these expressions are defined as follows (shown in Figure A1.2): a'_{bot} is the in-plane width of the nanoparticle (also the width of the trigonal prism), h'_{bot} is the out-of-plane height of the nanoparticle, h'_{top} is the height of the top of the tetrahedron not including the volume taken up by the particle, a'_{top} is the in-plane width of the top volume of the tetrahedron, and H is height of the trigonal prism.

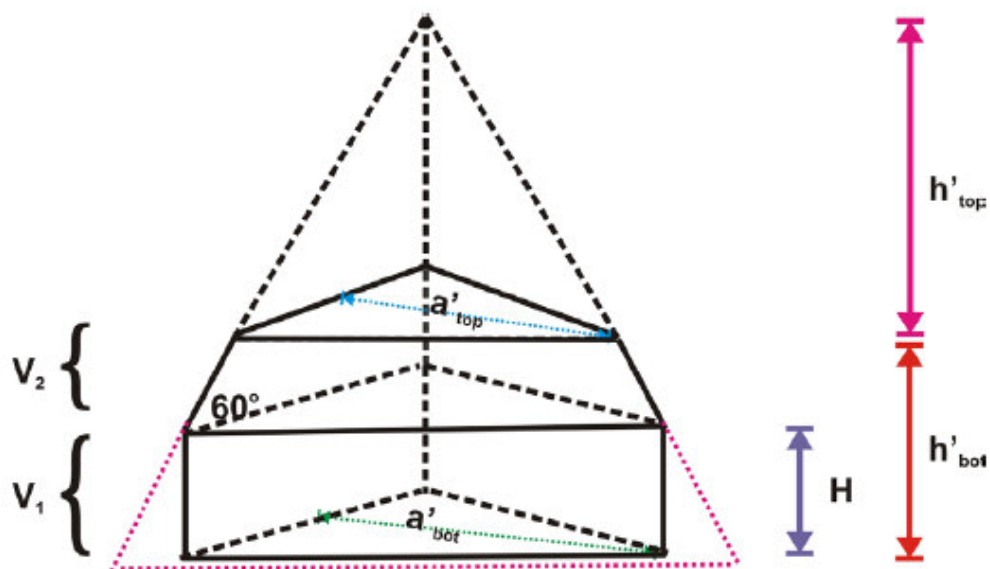


Figure A1.2 Schematic illustration of the theoretical model of an electrochemically oxidized NSL-produced nanoparticle. a'_{bot} is the in-plane width of the nanoparticle (also the width of the trigonal prism), h'_{bot} is the out-of-plane height of the nanoparticle, h'_{top} is the height of the top of the tetrahedron not including the volume taken up by the particle, a'_{top} is the in-plane width of the top volume of the tetrahedron, and H is height of the trigonal prism.

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Objective

To obtain a challenging and enlightening postdoctoral position to

Education

2007(expected)	Ph.D., Chemistry Northwestern University, Evanston, IL Thesis: "Plasmonic Properties of Nanoparticles and Nanostructured Surfaces"	GPA: 3.64/4.0
2002	B.S., Chemistry Rensselaer Polytechnic Institute, NY Focus: Materials Science and Materials Chemistry Graduation Honors: Magna Cum Laude	GPA: 3.76/4.0

Research Experience (USA)

2006-present	Nanoparticle optical coupling, Argonne National Laboratory - Fabrication and optical testing of nanoparticle arrays for type and strength of interparticle coupling - Design and Fabrication of optical "chip" designs for multiple analyte and nanoparticle testing
2002-present	Plasmonics Studies of Nanoparticle and Nanostructured Surface, Northwestern University - Fabrication and optical testing of nanoparticle arrays produced by various lithographic techniques. - Incorporation of microfluidics in multiplex localized surface plasmon resonance sensor. - Fabrication and testing of various substrates for surface-enhanced raman spectroscopy applications
2005-2006	Non-linear Nanoparticle Arrays, University of Michigan -EBL fabrication of nanoparticle arrays for non-linear spectroscopic studies.
2002	Electropolishing Copper for the Microelectronics Industry, Rensselaer Polytechnic Institute -Design and testing of an electropolishing system for the microelectronics industry.
2001-2002	Investigation of Copper Diffusion Barriers, Rensselaer Polytechnic Institute - Design and Testing of novel Self-Assembled Monolayers as Copper Diffusion Barriers in MOS devices.
2000-2001	Polymer/nanotube composites, Rensselaer Polytechnic Institute - Synthesis and testing of polymer/single-walled carbon nanotube composites.
1999-2000	Iron and Manganese Acyl Compounds, Rensselaer Polytechnic Institute - Synthesis and characterization of Fe and Mn organometallic compounds.

Research Experience (International)

2006	Effects of Nanoparticle Coupling on the Localized Surface Plasmon Resonance, Chalmers University of Technology, Göteborg, Sweden - Fabrication and testing of 2D arrays of nanoparticles for coupling effects in the localized surface plasmon resonance.
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- 2004 Diffractive Coupling in 1D chains of Nanoparticles, Chalmers University of Technology, Göteborg, Sweden
 - Fabrication and testing of 1D chains of nanoparticles for evidence of diffractive coupling by observing narrow plasmon resonances.

Related Experience

- 2002-2003 Teaching assistant, Department of Chemistry, Northwestern University
 - Taught general chemistry lab, graded exams, graded lab reports
- 1999-2002 Teaching assistant, Department of Chemistry, Rensselaer Polytechnic Institute
 - General chemistry, inorganic chemistry 1, classroom assistant, graded exams, held review sessions, taught class when professor was absent

Skills

- Spectroscopy:* Raman, UV-visible extinction, Infra-red, Reflectance, PMIRRAS, XPS
- Laser techniques:* Home built Raman system with continuous wave and solid state Ti:Sapphire and dye lasers
- Microscopy:* Atomic force microscopy, scanning electron microscopy, transmission electron microscopy, optical microscopy, TEM solid and solution sample preparation
- Vacuum science:* Thermal vapor deposition, electron-beam assisted deposition
- Nanostructure Formation:* Nanosphere Lithography, Colloidal Lithography, Photolithography, Electron Beam Lithography (JEOL 9300FS and 5DII, Raith 150), chemical synthesis, Convective Self Assembly, Spin Coating
- Cleanroom Skills:* Reactive Ion Etching, Photolithography, Electron Beam Lithography, Focused Ion Beam Milling, Spin Coating Polymers, Plasma Cleaning
- Electrochemical Skills:* Cyclic Voltametry, Double Step Chronocoulometry
- Computer/Programming:* Microsoft Office, Golden Software Grapher 4, CorelDraw, Adobe Photoshop, MathCAD, MatLAB 6.5, Labview 7.1

Volunteer Activities

- 2005-2006 PLU Elementary School Outreach Program
- 2005-2006 Mentor NSEC RET/REU Program
- 2005-2006 Stevenson High School SPARK program (mentoring high school students)
- 2005 Northshore Habitat for Humanity
- 2005 Stevenson High School Engineering Day
- 2003-2005 Chicago Public School Science Fair Judge
- 2003-2005 NSEC All Scout Nanoscience Event

Peer-reviewed Publications

1. "Investigation Plasmonic and Photonic Coupling in Two-dimensional Arrays," Erin M. Hicks, Tomas Rindzevicius, Linda Gunarrson, Shengli Zou, Mikael Kall, George C. Schatz, Richard P. Van Duyne, MRS Proceedings, MRS Symposium E in preparation (2006)

2. "Optical Properties of L shaped Nanoparticle Arrays," Jiha Sung, **Erin M. Hicks**, Richard P. Van Duyne, Kenneth G. Spears, *Journal of Physical Chemistry B*, in preparation.
3. "Coffee Cup Atomic Force Microscopy," David E. Ashkenaz, W. Paige Hall, Christy L. Haynes, **Erin M. Hicks**, Adam D. McFarland, Leif J. Sherry, Douglas A. Stuart, Korin E. Wheeler, Chanda R. Yonzon, Jing Zhao, Hilary A. Godwin, and Richard P. Van Duyne, *Journal of Chemical Education*, submitted October 2006.
4. "Mechanical Stability and Optical Properties of Anchored Nanoparticles Fabricated using Nanosphere Lithography and Reactive Ion Etching," **Erin M. Hicks**, Olga Lyandres, Matthew Glucksberg, Richard P. Van Duyne, *Journal of Physical Chemistry B*, submitted June 2006.
5. "Advances in Contemporary Nanosphere Lithographic Techniques," Xiaoyu Zhang, Alyson V. Whitney, Jing Zhao, **Erin M. Hicks**, and Richard P. Van Duyne, *Journal of Nanoscience and Nanotechnology*, 6, 115 (2006).
6. "Alkanethiol Mediated Release of Surface Bound Nanoparticles Fabricated by Nanosphere Lithography," Jing Zhao, Amanda Haes, Xiaoyu Zhang, **Erin M. Hicks**, George C. Schatz, Richard P. Van Duyne, MRS Proceedings (2005).
7. "Plasmonic Properties of Film Over Nanowell Surfaces," **Erin M. Hicks**, Xiaoyu Zhang, Shengli Zou, Olga Lyandres, Kenneth G. Spears, George C. Schatz, Richard P. Van Duyne, *Journal of Physical Chemistry B*, 109, 22351-22358 (2005).
8. "Electrochemical Tuning of Silver Nanoparticles Fabricated by Nanosphere Lithography," Xiaoyu Zhang, **Erin M. Hicks**, Jing Zhao, Richard P. Van Duyne, *Nano Letters*, 5, 1503-1507 (2005).
9. "Controlling Plasmon Line-shapes through Diffractive Coupling in Linear Arrays of Cylindrical Nanoparticles Fabricated by Electron Beam Lithography," **Erin M. Hicks**, Linda Gunnarsson, Shengli Zou, Tomas Rindzevicius, Bengt Kasemo, Mikael Käll, George C. Schatz, Kenneth G. Spears, Richard P. Van Duyne, *Nano Letters*, 5, 1065-1070 (2005).
10. "Biological Applications of Localized Surface Plasmon Resonance Phenomena," Douglas Stuart, Amanda J. Haes, Chanda R. Yonzon, **Erin M. Hicks**, *IEEE Proc.-Nanobiotechnology*, 152, 13-32 (2005).
11. "Second Harmonic Excitation Spectroscopy of Silver Nanoparticle Arrays," Andrew M. Moran, Jiha Sung, **Erin M. Hicks**, Richard P. Van Duyne, Kenneth G. Spears, *Journal of Physical Chemistry B*, 109, 4501-4506 (2005).
12. "Investigating Narrow Plasmons in Nanoparticle Arrays Fabricated using Electron Beam Lithography," **Erin M. Hicks**, Linda Gunnarsson, Tomas Rindzevicius, Mikael Käll, Bengt Kasemo, Richard P. Van Duyne, MRS Proceedings, MRS Symposium P 872, 317-322 (2005).
13. "Nanosphere Lithography: Fabrication of Large Area Ag Nanoparticle Arrays by Convective Self-Assembly and their Characterization by Scanning UV-vis Extinction Spectroscopy," Anjeanette D. Ormonde, **Erin C. M. Hicks**, Jimmy Castillo, and Richard P. Van Duyne, *Langmuir*, 20, 6927-6931 (2004).

Invention Disclosure

2005 "Electrochemical Tuning of Silver Nanoparticles Produced by Nanosphere Lithography"
 NU 25070

Presentations

2007	“”, Pittcon, Chicago, IL(Oral) “” American Chemical Society National Meeting, Chicago, IL(Poster)
2006	“” Materials Research Society Spring Meeting, Boston, MA (Poster) “Nanostructured Surfaces for Sensing Technologies”, Imego, Göteborg, Sweden (Oral) “Nanostructured Surfaces for Plasmonics and SERS”, Mesophotonics, Ltd., Southampton, England(Oral)
2005	“Diffractive Coupling in One and Two Dimensional Arrays of Nanoparticles and Nanoholes”, Materials Research Society Fall Meeting, Boston, MA (Oral) “Controlling Plasmon Line Shapes through Diffractive Coupling”, Materials Research Society Spring Meeting, San Francisco, CA (Oral)
2004	“Nanooptics”, iNano Ebbeltoft, Denmark (Poster) “Fabrication of Functional AFM and STM tips with Convective-self Assembly and Reactive Ion Etching”, Pittcon, Chicago, Illinois (Poster)
2003	“Nanoplasmonics and SERS”, Great Lakes Regional Meeting, Chicago, Illinois (Poster)

Awards and Recognition

2005	PLU Chapter Travel Grants
2005	Office of Vice President for Research Conference Travel Grants
2005	NSEC International Travel Grant, \$4,500
2004	NSEC International Travel Grant, \$4,500
1998-2002	Dean’s List, Rensselaer Polytechnic Institute
1998	Rensselaer Math and Science Award, \$40,000 scholarship

Memberships

2004-present	Society for Applied Spectroscopy- Chicago division
2004-present	Materials Research Society
2001-present	Phi Lambda Upsilon Chemistry Honor Society
1999-present	American Chemical Society
1998-2002	Rensselaer Chemistry Society