SOME OPTICAL AND CATALYTIC PROPERTIES OF METALLIC NANOPARTICLES

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SOME OPTICAL AND CATALYTIC PROPERTIES OF METALLIC NANOPARTICLES

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<tr>
<td>$\alpha$</td>
<td>dipole polarizability</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>vacuum permittivity</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>dielectric permittivity of the material</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>dielectric permittivity of the medium</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>shape factor for dipole polarizability equation</td>
</tr>
<tr>
<td>$\alpha_R$</td>
<td>polarizability of Raman reporter molecule</td>
</tr>
<tr>
<td>$\eta$</td>
<td>refractive index</td>
</tr>
<tr>
<td>$\tau$</td>
<td>decay length of near-exponential decay model for plasmon coupling</td>
</tr>
<tr>
<td>$\mu$</td>
<td>transition dipole moment</td>
</tr>
<tr>
<td>$\nu_0$</td>
<td>incident frequency</td>
</tr>
<tr>
<td>$\nu_R$</td>
<td>Raman scattered frequency</td>
</tr>
<tr>
<td>$I_{\text{SERS}}$</td>
<td>Intensity of the SERS photon</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Activation Energy</td>
</tr>
<tr>
<td>$S$</td>
<td>Interparticle separation measured from surface to surface</td>
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<tr>
<td>$R$</td>
<td>Interparticle separation measured from the centers of mass of the particles</td>
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<tr>
<td>1165 Remover</td>
<td>1-methyl-2-pyrrolidinone</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>CTAB</td>
<td>Cetyl trimethylammonium bromide</td>
</tr>
<tr>
<td>DDA</td>
<td>Discrete Dipole Approximation</td>
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<tr>
<td>EBL</td>
<td>Electron Beam Lithography</td>
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<tr>
<td>EF</td>
<td>Enhancement Factor</td>
</tr>
<tr>
<td>EGFR</td>
<td>Epidermal Growth Factor Receptor</td>
</tr>
<tr>
<td>FDTD</td>
<td>Fourier Difference Time Domain</td>
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<tr>
<td>FRET</td>
<td>Förster Resonance Energy Transfer</td>
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<tr>
<td>HSAB</td>
<td>Hard-Soft Acid Base Theory</td>
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<tr>
<td>LB</td>
<td>Langmuir-Blodgett</td>
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<td>LSPR</td>
<td>Localized Surface Plasmon Resonance</td>
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<td>MECT</td>
<td>Molecular Exciton Coupling Theory</td>
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<tr>
<td>MIBK</td>
<td>Methyl isobutyl ketone</td>
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<td>NIL</td>
<td>Nanoimprint Lithography</td>
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<tr>
<td>NSL</td>
<td>Nanosphere Lithography</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>PMMA</td>
<td>Poly methyl methacrylate</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinyl pyrrolidone</td>
</tr>
<tr>
<td>R / S</td>
<td>Rotations Per Minute per Second (acceleration)</td>
</tr>
<tr>
<td>RPM</td>
<td>Rotations per Minute</td>
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<td>SEF</td>
<td>What it Means</td>
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<td>SEIRA</td>
<td>Surface Enhanced Infrared Absorption</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>SERS</td>
<td>Surface Enhanced Raman Scattering</td>
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<td>SPP</td>
<td>Surface Plasmon Polariton</td>
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<tr>
<td>SPR</td>
<td>Surface Plasmon Resonance</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>TOF</td>
<td>Turn Over Frequency</td>
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SUMMARY

Nanomaterials have been the focus of many previous publications and studies. This fact is due to the wealth of new and tunable properties that exist when a material is confined in size. This thesis discusses some of those properties pertaining to metallic nanoparticles. The primarily focus is on the plasmonic properties of gold nanoparticles with a final chapter discussing nanocatalysis and the nature of nanocatalytic reactions.

The strong electromagnetic field that is induced at the surface of a plasmonic nanoparticle can be utilized for many important applications, including spectroscopic enhancements for molecular sensors and electromagnetic waveguides for sub-wavelength light manipulation. For many of these applications, it is necessary to use two or more nanoparticles in close proximity with overlapping plasmonic fields. Knowledge of how these overlapping fields are affected by the particle orientation, size, and shape is critically important, not only in understanding the fundamental properties of plasmons but also in designing future architectures that employ plasmonic particles.

The field of metallic nanoparticles is introduced from its beginning, with artistic use as early as the 4th century AD through current applications and understanding. The broad spectrum of current methodologies for fabricating nanoparticles is discussed, from top down methods using lithography and from bottom up methods using metal salt reduction in solution. There are several methods used in this thesis, all of which are discussed in great detail, with some details pertaining to the specific instrumentation used here.
The first study is on the transfer of surface supported gold nanoprisms from a substrate into solution using photo-thermal heating with a femtosecond pulse coincident with the plasmon resonance frequency of the nanoprisms. The mechanism of transfer is discovered to be due to super heating of solvent molecules dissolved at the particle-substrate interface. This process is studied as a function of irradiance fluence and solvent. The stability of the unprotected nanoprisms in solution is discussed. This technique has applications for creating a colloidal suspension of nanoparticle without a surfactant layer covering the surface. The particles can be chemically functionalized with any desired moiety for specific solution phase applications.

The second study is on the fundamentals of plasmonic near-field coupling between two plasmonic nanoparticles as a function of the nanoparticle size, shape, and orientation. Experimental results using electron beam lithography fabricated samples are used to better understand the plasmonic coupling between dimers. Previously, the coupling between plasmonic fields around nanoparticles has been described as a near-exponential decay dependence on interparticle separation. This decay was proposed to be consistent among all sizes and shapes of nanoparticles, which was quantitatively measured using the best-fit decay length in units of the nanoparticle size. Experimental proof is presented of the shape dependence of this decay length, which is roughly 50% greater for nanoprisms than for nanodiscs, nanospheres, and nanoellipses. This was shown using simulated and experimental data. Using simulated results, the coupling decay length was shown to be independent of size for all nanoparticle shapes examined.

Additionally, the effect of particle orientation on the coupling of the induced near-fields of the plasmonic particles is intensely investigated. Systematic studies using a
combination of experimental samples and computer simulations are presented that examine the role of one particle’s orientation to another within a plasmonic dimer system. This dependence is compared to the mathematically derived dependence and shown to be in excellent agreement. The plasmon hybridization method is given as a straightforward method to understand and predict the effect of plasmon near-field coupling on orientation. Previous methods used to understand the effect of separation on the plasmon coupling are incorporated into this method.

As an extension, the coupling between plasmonic nanoparticles is shown in a common application, namely surface enhanced Raman scattering. This phenomenon is studied using colloidally prepared silver nanocubes deposited on a substrate using the Langmuir-Blodgett technique. Using various surface pressures during deposition, the surface density of the deposited nanocubes can be controlled, and thus the degree of plasmonic coupling. By controlling the plasmonic coupling, the enhancement of the Raman scattering from the PVP capping layer was altered and a correlation between the enhancement and the plasmon field intensity is reported.

The final study investigates the nature of nanocatalysis for several reactions using metal nanoparticles. Arguably, the largest unanswered question currently in nanocatalysis is the nature of the catalytic reaction, namely homogeneous catalysis or heterogeneous catalysis. This question has been very difficult to answer because of the lack of current techniques to completely restrict one form of catalysis. The issue is reviewed in this thesis with new insights discussed while using experiments that show evidence of both sides of the issues, homogeneous and heterogeneous.
CHAPTER 1
INTRODUCTION

Abstract
This chapter is an introduction to metallic nanoparticles. Nanoparticles have been studied for over one and a half centuries, yet only recently in the past few decades have scientists really begun to explore the possibilities of nanomaterials. Firstly, the ability of metallic nanoparticles to couple with electromagnetic radiation is one of their most useful properties—specifically using gold, silver, and copper nanoparticles that couple to visible light. The interaction can be tuned to provide a metallic nanoparticle with desired optical properties. The maximum coupling occurs at the surface plasmon resonance, which is presented and defined here. Several radiative applications are discussed, including photothermal therapy, imaging diagnostics, surface enhanced spectroscopies, and plasmonic waveguides. Secondly, nanocatalysis, a newly defined field that is currently being studied, is introduced and defined. Finally, the organization of the dissertation is presented.
Beginnings of Nanomaterials

Civilizations have always been driven in the direction that current technology and the properties of the available materials have dictated. Such is the case for the malleability of bronze during the Bronze Age, the strength of iron during the Iron Age, the high strength to weight ratio of steel during the Industrial Revolution, and the tunable electronic properties of semiconductors during the computer age. Currently we are living in what some have termed the information age, where information is transferred at the speed of light using fiber optic cables. The ability for 21st century societies to manipulate and control light will thus have an enormous influence on technology development and ultimately the world economy. Similarly, the field of catalysis is one of the most important fields in the last five decades and is a $900 billion a year enterprise. Over 90% of modern day materials utilize a catalyst for more efficient, faster, and more affordable production. Nanocatalysis is a field that is rapidly increasing and has important applications in numerous fields, including chemical production, sustainable energy, and materials chemistry. The reason for such a high level of interest in nanocatalysis is due to the large increase in surface sites available for catalysis when a material is divided into nano-sized particles. Nanomaterials have played and will continue to play a crucial role in the development of new technologies due to the single fact that they have tunable properties. Specifically, changing their size, shape, and environment can vary the electromagnetic and chemical properties of metallic nanomaterials. An example of the tunability of the optical properties of dissolved particles is shown in Figure 1.1.

For the greater part of history, nanomaterials have been extensively used in art. Dating from the 4th century AD, the Lycurgus Cup, shown in Figure 1.2, incorporates silver and gold nanoparticles into the glass to give the cup a dichroric property. When the cup is illuminated from the outside by white light, bluish-green light is scattered by the particles and the cup appears green. When the light is placed inside the cup, the particles inside the glass absorb the green light and the remaining colors of the white light appear...
reddish-orange, which are transmitted and the cup appears ruby red. Similarly, the stain
glass windows of the Gothic cathedrals in France utilize gold and silver nanoparticles
incorporated into the glass to give the panes various hues.

Figure 1.1

Figure 1.1: Changing optical properties of colloidal gold suspensions
with variation in nanoparticle size.

Michael Faraday was the first to scientifically study metallic nanoparticles in
colloidal solutions\(^4\). These colloidal suspensions were synthesized intentionally to study
the optical properties of metallic particles on the nanoscale. These incredibly stable
solutions are still on display in the British Museum in London and their color remains
brilliant after 150 years—as is also true of the Rose window at Notre Dame and the
Lycurgus cup shown in Figure 1.2. The colors are still intense because light scattering
and absorption, not electronic transitions, which occur in organic dyes that photo-bleach after extended exposure to light, produce the color of metallic nanoparticles.

**Figure 1.2**

A.) B.)

Figure 1.2: 4th Century Roman cup (the Lycurgus Cup) appears green (A) when illuminated from the outside and appears red (B) when illuminated from the inside.

**Plasmonic Responses in Metallic Films and Nanoparticles**

Surface plasmons are electronic fluctuations at the interface between two materials in response to an applied electric field and are often referred to as surface plasmon polaritons (SPPs). These fluctuations were first observed in thin metallic films by Ritchie in 1957. The field propagates along the interface and extends into the materials to a certain depth, referred to as the skin depth and is defined as the distance into the material that the field decays to 1/e. This distance is a function of the dielectric permeability of the material. **Figure 1.3.A** depicts the surface plasmon polariton as it propagates along the interface inducing fluctuating charged regions.
When the size of the interface between the metal/dielectric becomes small compared to the wavelength of light incident upon it, a localized surface plasmon resonance (LSPR) occurs that is isolated at the interface (Figure 1.3.B). This occurs either when the metal is reduced in size, such as is the case for metallic nanoparticles\textsuperscript{6,7}, or the dielectric is reduced in size, as is the case for nanoholes\textsuperscript{8,9}. The result of this localized plasmon is an intensely focused electric field that can be used for a wide range of applications, some of which are discussed in the following section. Both nanohole arrays and nanoparticle arrays have their distinct advantages in applications, and will certainly play a major role in new technologies of the future. Since nanoparticles are exclusively studied in this thesis work, the focus here will be centered on phenomenon associated with nanoparticles and applications thereof. However, in principle, the field of plasmonics is broad and the concepts discussed herein for nanoparticles are completely applicable and transferable to all metal-dielectric interfaces.

The plasmonic metal nanoparticle should be first examined from the fundamental equations that describe the interaction of light with the particle. Equation 1 is the dipole polarizability of any particle that is small with respect to the wavelength of light (size $\leq \frac{1}{4}\lambda$).

\[ \alpha = 3\varepsilon_0 \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + \kappa\varepsilon_m} \right) V \]  

Equation 1.1

In Equation 1.1, $\varepsilon$ is the frequency dependent dielectric permittivity of the particle material, $\varepsilon_m$ is the dielectric permittivity of the medium (usually assumed to be independent of the frequency within the range of measurement), $\kappa$ is a variable that depends on the shape of the particle, and $V$ is the volume of the particle. For a sphere, $\kappa$ is equal to 2 and at the wavelength where $\varepsilon = -2\varepsilon_m$, the denominator of Equation 1.1 falls to 0 and the real portion of the dipole polarizability goes to infinity. Metals have the distinct advantage that the dielectric permittivity is negative in most regions of the electromagnetic spectrum, and therefore are able to establish a LSPR. At this frequency
(termed the localized plasmon frequency) the conduction band electrons within the particle are delocalized and oscillating in resonance with the electric field of the light. For certain noble metals, such as gold, silver, and copper, this frequency occurs in the visible or near IR region, and they are therefore very appropriate for optical applications. In addition, the electronic oscillation is not strongly damped and thus the breadth of the resonance energy band is much more narrow than other metals. The strong fields induced by the LSPR and the ability for noble metal nanoparticles to transfer information at optical frequencies has inspired many researchers to investigate the potential of utilizing nanoparticle arrays of different architectures. The ability to design such architectures and study the fundamental rules which govern plasmonic field coupling have become feasible only in the last decade, and have led to an eruption of funding and research in the area of nanoparticle plasmonics.

**Radiative Applications of Noble Metal Nanoparticles**

As mentioned previously, noble metal nanoparticles have historically been used in artwork to give brilliant, enduring color to glass, such as the stain-glass windows of the Notre Dame cathedral or the ancient Roman Lycurgus cup. The tunability and longevity of the nanoparticle optical properties (scattering and absorption) makes them extremely suitable for applications utilizing the visible and near-infrared region of the electromagnetic spectrum. The mechanism of coupling between metal nanoparticles and light, localized surface plasmon resonance, provides plasmonic nanoparticles distinct advantages over fluorescent dyes which have often been used as optical markers in biological and chemical applications but have the downfall of becoming photo-bleached. Additionally, the scattering from plasmonic nanoparticles is an ultra-fast process, occurring in the femtosecond time scale\textsuperscript{10-12} compared with fluorescence which occurs on the time scale of the fluorescence lifetime in the nanosecond time scale\textsuperscript{13,14}. 
Figure 1.3: A) Surface plasmon polariton (SPP) propagates along a thin metal film at the metal / dielectric interface in response to electric field stimulus. The “skin depth”, the distance the field penetrates into the material, is different for the metal and the dielectric. B.) Localized surface plasmon resonance (LSPR) in a metallic nanoparticle where the size of the particle is much smaller than the wavelength of light.

The strong absorption properties of plasmonic metal nanoparticles coupled with their efficient non-radiative relaxation give them powerful photothermal properties. The energy attenuated by the plasmonic nanoparticle upon irradiation of light at the plasmonic resonance is partially absorbed by the particle. The percentage of the light extinction that is absorbed is dependent on the size and shape of the nanoparticle. As the particle size increases, the ratio of scattered light to absorbed light increases. This is an important fact for photothermal therapy using nanoparticles. The scattered light is elastically
scattered from the particle, while the energy from the absorbed light is transferred to the hot electron gas that is oscillating in resonance with the light. At moderate intensities the hot electron gas cools via electron-phonon coupling (~1-10 ps) and transfers the energy to the positive nuclear lattice. The energy is then transferred to the surrounding medium (~100’s ps) as the hot positive lattice cools through phonon-phonon coupling with the environment.\textsuperscript{10,16-19}

As the nanoparticle transfers heat to the environment, it thermally heats up anything in the nearby vicinity. This technique has been used to photo-thermally treat cellular material around the nanoparticle, typically that has become cancerous. Through conjugating anti-EGFR to gold nanoparticles, researchers have been able to preferentially tag cancerous cells with gold nanoparticles. The excitation of the particles with a CW laser at the plasmonic frequency can then lead to photo-thermal death of the cancer cells.\textsuperscript{20,21} The nanoparticle shape can be tuned to shift the frequency to the NIR where a biological window exists and radiation can penetrate deep into tissue in order to irradiate nanoparticle laced cancer cells.\textsuperscript{22}

Another application that has become very important in nanoscience over the past couple decades is surface enhanced spectroscopies such as surface enhanced Raman scattering\textsuperscript{22-28} (SERS), surface enhanced infrared absorption\textsuperscript{23,29,30} (SEIRA), and surface enhanced fluorescence\textsuperscript{27,31-33} (SEF). These techniques have become significant because the strong fields that are induced around the nanoparticle upon irradiation at the plasmon frequency can be used to enhance the intensity of the observed spectroscopic response. Analytical methods such as SERS are truly a nanoscale event, occurring only when nanomaterials are present. Even on continuous metal films, where the phenomenon was first observed, the mechanism behind SERS was later discovered to be due to the roughness of the film which generates countless nanoscale features that focus the incident light into many LSPRs, which are responsible for the enhancement. In particular, SERS is important because of the wealth of information that can be obtained from the Raman
scattering spectra of an analyte, and unlike FTIR absorption, water is not Raman active so measurements can be done in ambient conditions. The drawback to normal Raman spectroscopy is that Raman signals are very weak, with only one out of one million photons undergoing Raman scattering. For SERS, the strong plasmonic near-fields at the surface of the nanoparticle amplify the intensity of the incident and the scattered light, resulting in a surface enhanced Raman scattering signal. The intensity of the Raman signal, or the enhancement factor (EF), is roughly proportional to the enhancement of the field ($g$) to the fourth power. Equation 1.2 shows the functional dependence of the intensity of the SERS signal ($I_{SERS}$) on the polarizability of the molecule ($\alpha_R$), the enhancement of the field ($g$), and the intensity of the incident light ($I_0$).

\[
I_{SERS} \propto \alpha_R^2 g^4 I_0
\]  

Equation 1.2

It is clear in Equation 1.2 that the intensity of the signal is most influenced by the strength of the field. For this reason, the ability to maximize the near-field strength around plasmonic nanoparticles has been a major effort in the past decade\textsuperscript{34,35}. This can be done in two general ways. The first is by changing the shape of the nanoparticle in order to focus the electronic cloud into a small spatial region, which is referred to as the “lightning rod effect”\textsuperscript{36,37}. Figure 1.3 is a simulation of the field around a nanoparticle performed by Kelly et al\textsuperscript{38}. The maximum field strength for the sphere is 50x the incident intensity, whereas the maximum field strength of a nanoprism of comparable size is ~350x the incident intensity. The second way to increase this field is by bringing multiple particles together. When the plasmonic near-fields of two particles couple with one another, there is an enhanced field that is greater than the sum of the two, mainly attributed to coupling of higher order multipoles (quadrupole, octopole, etc…)\textsuperscript{39,40}. Figure 1.4 shows a schematic of two colloidal silver nanoparticles and the junction in
between where localized hot-spots occur. With enhancement factor’s being reported of $10^{13}$-$10^{15}$, the concentration needed to obtain a Raman signal is greatly reduced, sometimes around single molecule detection limits.

**Figure 1.4**

Figure 1.4 Localized hot spot between two colloidal nanoparticles that generates strong fields that enhance Raman scattering.

While surface enhanced IR absorption (SEIRA) has been less studied than SERS, there are some reports discussing the ability of the induced fields at the nanoparticle surface to enhanced IR absorption in nearby molecules$^{23,29,30}$, which provides a very sensitive complimentary technique to SERS. Surface enhanced fluorescence is also an enhanced spectroscopy that benefits from the strong field surrounding the nanoparticle to potentially enhance fluorescence intensities$^{32,41}$. However, SEF does suffer from the possibility of particle quenching if the separation between the fluorophore and the plasmonic particle is small$^{42}$.

Optical waveguides$^{23,43-50}$ have become a major focus of applications utilizing plasmonic materials on the nanoscale level. Particularly, this fact is due to their ability to localize light in a sub-wavelength regime and to transport absorbed energy and the information on a sub-wavelength level. Plasmonic studies originated in studying nanostructures that were nano-sized in only one dimension, such as thin films. As mentioned previously, propagating polaritons were studied as an energy transport
phenomenon. More recently, nanomaterials that are restricted in two and three dimensions (nanowires and nanoparticles, respectively) have been investigated as optical waveguides\textsuperscript{45,48,49}. These devices use less material and direct the energy through two dimensions along a chip surface, as shown in Figure 1.5. It is important for these applications that fundamental and systematic studies are performed to understand the functional dependence of the plasmonic coupling and therefore the energy transport on geometric variables, such as particle separations and particle orientations, and the effect of the external dielectric environment on the field coupling. Studies such as these have become more prevalent in the literature as fabrication techniques have become more sophisticated and better control over nanoparticle positions, sizes, and shapes is available\textsuperscript{25,49,51-55}. Part of the work in this thesis is concerned with this question and will investigate the relationships that govern plasmonic nanoparticle near-field coupling.

**Figure 1.5**

Figure 1.5: Directed propagating plasmon resonance across a 1D nanoparticle array. Time progression goes from A-F sequentially.
Applications of Nanoparticles in Catalysis

Historically, solution-phase heterogeneous catalysis was rarely viewed as being profitable due to the much higher yield (i.e. conversion × selectivity) afforded by homogeneous catalysts. This paradigm has recently begun to change due to increased research in nanoparticle synthesis. Colloidal nanocatalysts combine the advantages of heterogeneous and homogeneous catalysts while circumventing many of their individual drawbacks. Drawbacks of homogeneous catalysts include poor recycling potential and contamination of the products by the catalyst (with sometimes significant loss of catalyst). Heterogeneous catalysis in solution alleviates these drawbacks because the contamination of the products is low and the catalysts can be phase separated from the reaction media and reused. However, the turnover frequency (TOF), or the reaction rate normalized to some indicator of the number of sites (reported in units of reactions per site per unit time), of these catalysts are highly inferior to their homogeneous counterparts. The inferior catalytic ability of conventional heterogeneous catalysts is attributed to the low number of active sites per volume of catalytic material because only surface atoms directly participate in catalysis. The use of colloidal nanoparticles alleviates the dimensional limitations of traditional heterogeneous catalysts because they have high surface-to-volume ratios and expose a greater number of surface atoms per unit volume compared to supported heterogeneous catalysts.

A heterogeneous catalyst exists in a physical state different from that of the reactant(s), while homogeneous catalysts are in the same physical state as the reactant(s). It is important to recognize the subjective nature of this definition when applied to nanocatalysis. The traditional definition of a heterogeneous catalyst may have evolved in 1985 in a paper by Schwarz, in which the nature of the catalyst was classified based on the number of different catalytically-active sites available on a single catalyst. A catalyst with only one type of active site was termed homogeneous, while a catalyst with various types of active sites was termed heterogeneous. This definition was proposed by
Schwartz and further utilized by others\textsuperscript{57-59} in order to classify nanoparticles as heterogeneous and distinguish them from homogeneous counterparts since colloidal nanoparticles possess both solution-phase properties, such as mobility in solution, as well as solid-phase properties, such as a liquid-solid interface. Nanoparticles inherently have multiple catalytically active sites (corners, edges, and different exposed crystal facets) and were categorized as heterogeneous. However, confusion has arisen from this definition. The work on “single-site” heterogeneous catalysts is one example. Metallic complexes bound to a macroscopic solid support that can be easily separated from the reaction solution are inherently contradictory to Schwartz’s definition. Schwartz’s definition lacks applicability throughout the nanocatalytic field; therefore, we shall adopt the traditional definition of heterogeneous catalysis with a few clarifications related to catalysis by nanomaterials. If catalysis takes place on the surface of the nanoparticle it is defined herein as heterogeneous, regardless of the catalytic species (i.e. active site on the nanoparticle surface or a metallic complex bound to the nanoparticle surface). If the nanoparticle supplies the solution with a complex that subsequently conducts the catalysis at a distance from the nanoparticle surface, the catalysis is classified as homogeneous. This definition is consistent with the International Union of Pure and Applied Chemistry (IUPAC) definition of heterogeneous/homogeneous catalysis\textsuperscript{60}.

Determination of the catalytic nature (i.e. heterogeneous or homogeneous) of a reaction is not trivial in solution-phase catalysis by nanomaterials. The interfacial region at the nanoparticle surface is not clearly understood and prompts the question as to whether the catalysis is heterogeneous in nature and takes place on a well-defined surface or homogeneous due to an unstable surface. Nearly every experiment that has been performed has been unable to fully eliminate the possibility of one catalytic nature. Some reports have suggested that metal salts such as palladium (II) chloride or tetrachloroplatinate\textsuperscript{61,62} rather than nanoparticles\textsuperscript{63,64} are the true active catalysts – acceptance of such conclusions is not widespread.
Dissertation Focus and Organization

The work discussed in this thesis is possible due to recent advances in nanoparticle fabrication technology and methodology. Chapter 2 discusses these recent advances, particularly pertaining to lithography and the advantages and disadvantages that lithography has over colloidal synthetic techniques. The experimental work done with the electron beam lithography (EBL) and nanosphere lithography (NSL) is discussed in detail. Also discussed are the analytical techniques used to image the samples spectroscopically and using electron microscopy.

Using a relatively simple nanolithography technique, Chapter 3 discusses photo-induced transfer of nanoprisms from a substrate to solution. In this work, it is shown that the photo-induced “jumping” of a gold prismatic nanoparticle in air can be achieved in solution so as to successfully transfer the gold nanoparticle from a bound state on a substrate to a colloidally suspended solution medium while maintaining the shape and size of the nanoparticle. This process is carried out by using a femtosecond pulse coincident with the dipole plasmonic resonance energy of the nanoprism to transfer energy to the particles and induce separation from the substrate. The mechanism of particle ejection was investigated and it was concluded that a different mechanism is responsible for particle lift-off from the substrate when the bound array is submerged in solution. UV-Vis spectroscopy, SEM, TEM, AFM, and Raman spectroscopy are used to characterize the particles before and after particle ejection.

It has been shown by numerous groups that plasmonic field coupling between two particles is near exponentially dependent on particle separation. When this separation is measured in units of the particle size, the exponential decay of the plasmonic coupling was postulated to be independent of particle size, shape, material, and environment. This was previously shown experimentally for nanodiscs and nanospheres and theoretically for nanospheres, nanodiscs, nanoellipses, and nanoshells. However, Chapter 4 discusses the non-universality of the plasmonic ruler equation, specifically the decay...
length in units of the particle size that governs the near-exponential decay of the coupling. Nanoprisms were systematically fabricated via electron beam lithography with decreasing interparticle separations when they are oriented tip-to-tip. These arrays were investigated using UV-Vis microspectrometry, and the decay length of the plasmonic coupling was measured to be approximately 50% greater. Simulations were also performed that matched this value. Physically this is discussed as a comparative measure between nanoparticle shapes, and the effect of changing the shape on the range of coupling between nanoparticles. This has significance in plasmonic ruler applications, where the smallest nanoparticle is desired to serve as the optical marker. I also systematically report in this chapter on the insensitivity of the decay length on the size of the nanoparticles using DDA simulation methods.

Due to the report in Chapter 4 on the increased range of anisotropic nanoparticles in the plasmonic ruler application, it becomes clear that it is essential to also understand how orientation affects plasmonic coupling. This is investigated in Chapter 5 by systematically studying the plasmonic coupling between two nanorods as one rod is rotated through 90°. The mathematical model that is used to describe the coupling is the plasmon hybridization model, often utilized in the literature. This model is analogous to molecular exciton coupling theory that utilizes a mathematical equation to predict the shift in an excited state energy level. This equation is used as a starting point to develop a general relationship between the degree of plasmonic coupling and 1) relative orientation of the particles, 2) separation between particles, 3) inherent strength of the induced plasmonic dipole field (which is a function of nanoparticle shape), and 4.) the dielectric medium in which the particle pair is embedded in.

The fundamental studies of plasmonic coupling have thus far been discussed. In Chapter 6, I will describe work that was performed with Dr. Mahmoud Mahmoud on the relationship between the plasmonic resonance energy and surface enhanced Raman scattering (SERS). Dr. Mahmoud synthesized silver nanocubes and deposited them onto a
quartz substrate at various surface pressures. We investigated the intensity of surface enhanced Raman scattering from these substrates as a function of particle density. A significant correlation between the broad plasmonic resonance band of the coupled nanoparticles and the Raman enhancement is made. The electromagnetic and chemical enhancement mechanisms are separated and independently investigated.

Chapter 7 is a critical examination of the field of solution phase nanocatalysis, which has been studied extensively in recent years because of the enhanced surface to volume ratio provided by colloidal nanoparticles. This chapter discusses the nature of catalysis that is taking place with nanocatalysts, being homogeneous or heterogeneous. While colloidal nanoparticles provide a surface for reactions to take place at lower activation energies, which is a heterogeneous catalysis property, this surface is innately unstable and therefore potentially reactive. If the surface is reactive, whereby metallic atoms or ions are able to leach into solution to perform the reaction, the nature of the reaction is homogeneous. Previous results from our group and from other groups are reviewed with the goal to elucidate the catalytic nature (homogeneous or heterogeneous) of nanocatalysis. This chapter was included as an invited chapter of a book on ideal heterogeneous catalysts to investigatively discuss the nature of nanocatalysis.
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CHAPTER 2
SYNTHESIS AND FABRICATION OF PLASMONIC
NANOMATERIALS: LITHOGRAPHY AND COLLOIDAL
PREPARATION

Abstract
Nanomaterials have been a major area of interest in scientific research over the previous few decades. Two approaches have been used to synthesize nanoparticles, 1) bottom up – consisting of building up a nanoparticle atom-by-atom and is often performed in solution to produce a colloidal suspension. 2) top down – where one starts with a bulk material and removes all the bulk except the material that makes up the nanoparticle and is typically executed lithographically. In this chapter, the techniques for colloidal synthesis (bottom-up) and lithographic fabrication (top-down) are discussed and the advantages and disadvantages of each approach are compared. Specific details of the synthetic and fabrication techniques and of the instrumentation that was used in this dissertation are elucidated.
**Introduction**

**Directed Metal Nanoparticle Synthesis in Solution**

Historically, metallic nanoparticles have been used in art long before they were intentionally synthesized and studied. From the ancient Roman Lycurgus Cup to the Rose windows of the Gothic cathedrals in northern France, these artists used the scattering and absorptive properties of nano-sized metals to give everlasting color to their work. They were discovered, identified, and determined to originate from colloidal suspensions synthesized via metal salt reduction. Since first performed by Faraday in the 1850’s, the technique has been well-studied and modified to produce nanoparticles of a wealth of metals such as gold, copper, silver, palladium, platinum, and other metals with various sizes and shapes, such as rods, shells, cubes, and cages, to name a few.

Colloidal metal nanoparticles are nearly all synthesized using the same general three-step method:

1.) First, a metallic salt is dissolved in solution.

2.) The metal salt is reduced using a reducing agent, resulting in ground state metal atoms in solution that begin to bond and form a solid particle.

3.) The particle grows in size as time progresses until a capping agent restricts the growth at a specific size and or shape.

While these three steps are generally used for most colloidal syntheses, there are many varieties that can be implemented to produce a variety of shapes and sizes. For instance, the reducing agent can be a dissolved molecular agent, such as NaBH₄ or sodium citrate, or a previously nucleated metal core. Often times a metallic seed solution of small (<2 nm) nanoparticles are used as a surface that reduces a metal salt in solution without the need of an additional chemical agent. The use of tiny seed precursors can lead to desired characteristics such as crystallinity. Another variant of the above three-step method is to utilize one molecular agent to serve as both the reducing agent and the...
capping agent. A very common method used is citrate reduction for gold nanoparticles\textsuperscript{34,35}, where the citrate anion both reduces the gold salt and electro-statically isolates the gold particles from one another in solution. For gold nanorods\textsuperscript{30,36}, cetyl trimethylammonium bromide (CTAB) is used to preferentially protect one crystal facet, which facilitates atomic growth along one direction and leads to the elongated nanorod shape.

**Surface-Bound Metal Nanoparticle Fabrication**

There are several drawbacks to using a colloidal synthesis method. The first drawback is the necessity of a protecting layer, which suspends the particles in solution and restricts aggregation. This molecular surfactant can utilize either steric hindrance, as in a polymer coating, or electrostatics to isolate the particles. These surface capping agents are necessary during the formation of the particles to restrict their growth to a desired size and shape. However, after the formation steps are complete, the particle surface sites are occupied by the surfactants, which influence the properties of the nanoparticles, such as the catalytic activity and optical extinction. Although some reports have discussed methods for controlling the surfactant layer\textsuperscript{37-39}, completely removing the ligand shell around the particle requires that the particles be suspended on a substrate\textsuperscript{40}.

To avoid these issues, lithographic methods have been increasingly utilized to fabricate arrays of nanoparticles to systematically study the effect that nanoparticle shape, size, and medium have on the properties of the particle. Several different lithographic techniques are currently available. The first type of lithography discussed here is photolithography\textsuperscript{41-45}, often referred to as conventional lithography. This technique selectively irradiates predetermined areas of a light sensitive polymer resist and utilizes photochemistry to chemical modify the exposed polymer. The exposed areas are removed using a solvent that does not affect the unexposed regions, leaving behind a polymer mask supported on a substrate that is a negative image of the desired structure. The
material of choice, typically a metal, is evaporated onto the polymer mask. The material adheres to the underlying substrate only at the areas that were exposed to light and removed. Subsequent removal of the unexposed polymer layer by a strong solvent such as acetone leaves only the material that was evaporated onto the substrate through the mask. This technique has served the semiconductor industry well since the 1950’s in mass-producing integrated silicon chips. However, Moore’s law has created a current need to push the physical limits of resolution.

The structural resolution or minimum feature size that is possible using conventional lithography is dictated by the diffraction limit of light. The smallest resolvable feature size is proportional to,

\[ D = \frac{\lambda}{NA} \]  

Equation 2.1

where \( \lambda \) is the wavelength of the light used to irradiate the polymer resist and \( NA \) is the numerical aperture of the lens, which is defined as \( NA = \eta \sin \theta \), where \( \eta \) is the refractive index of the medium and \( \theta \) is the half angle of the maximum cone of light that can enter or exit the lens. As the wavelength of light used to irradiate the sample is reduced, the minimum resolution of the lithography system is decreased, and is why UV light is commonly used. By using the 193nm line of an ArF excimer laser\(^{46-48} \) and a recent technique termed “immersion lithography”\(^{49,50} \) where exposure is performed in a higher index medium that increases the NA, the current minimum feature size of photolithography is 30nm\(^{51} \).

To meet the need for better resolution capability, researchers have developed new lithographic fabrication methods. Several of these techniques are used in this work, such as nanosphere lithography and electron beam lithography, which are described in detail in the following sections. Additional methods that will not be used in this work include nanoimprint lithography\(^{52,53} \), focused ion beam\(^{54-57} \) fabrication, and scanning probe lithography\(^{58-60} \).
Comparison Between Colloidal Synthesis and Nano-Lithography

Both the bottom-up and top-down techniques have their associated advantages and disadvantages. The bottom-up method is capable of producing high quantities of nanoparticles in solution at a relatively low cost compared with lithographic samples. There are also many applications, particularly in biological and medicinal areas, that require nanoparticles to be dissolved in aqueous solutions. Most colloidal metal nanoparticle suspensions are compatible with water, and are therefore nearly ready to use in most biological applications.

The disadvantage of the colloidal suspensions is that the ligands that are required to protect the nanoparticles in solution from aggregation are also often time hindrances to the applications in which they are being used. For example, nanocatalysis is a promising field because of the large surface area provided by colloidal metal nanoparticle suspensions, however the chemical reactions that occur on the surface of the particle are restricted by the presence of the ligands. Additionally, some of the ligands used to synthesize interesting nanoparticle shapes in solution, such as CTAB in the synthesis of nanorods, are toxic in humans\textsuperscript{61,62} and extremely difficult to fully remove after chemical synthesis\textsuperscript{62}.

Although nanolithography is generally expensive and time consuming compared with colloidal synthesis, there are distinct advantages associated with such methods. One advantage is that there is much more control over the particle size, shape, and orientation. This is very useful when performing systematic studies of nanoparticle properties as a function of geometry. Additionally, the nanoparticle surfaces are bare and do not need to be covered by capping ligands since aggregation is not an issue. This is extremely useful for applications in sensors and catalysis, where the surface needs to be free to react with chemical agents. There are some drawbacks with top-down techniques, which should be taken into account, such as the low yield and lack of 3-dimensional control of the
nanoparticle shape. Often times, the adhesion of the particles to the substrate must be increased using an adhesion layer of Ti or Cr, which affects the electronic properties of the nanomaterial.

**Supported Nanoparticle Fabrication Used in this Work**

**Nanosphere Lithography (NSL)**

Nanosphere lithography (NSL) is a technique that utilizes the self-assembly process of nanospheres to produce a polymer lithographic mask with homogeneous pores that serves as a lithographic polymer mask\textsuperscript{63,64}. It is often referred to as “poor man’s lithography” due to the relative lower expense of the samples compared with other types of lithography\textsuperscript{64,65}. The technique has been expanded upon in recent years\textsuperscript{66,67} by tilting the sample upon deposition of the metal, which results in a variation in the shape. In addition, two depositions can be performed consecutively to produce two particles side-by-side by tilting the sample to a different angle during the second deposition. Nevertheless, NSL does have inherent limitations, such as no independent control over nanoparticle size and separations and the shape is limited only a few selected geometries. In this work it is used to study the interaction between an NSL fabricated nanoprism and a femtosecond pulse coincident with the nanoprism’s plasmonic frequency (@ 800nm) while submerged in a liquid medium.

In this work, NSL was performed on quartz microscope slides from Technical Glass Products, which were cut into 1 x 1.5 cm pieces. Polystyrene spheres 450 nm were purchased from Duke Scientific with a size distribution less than 3%. All other chemicals were used as received. NSL was used here to fabricate gold nanoprisms. A nanosphere (NS)-mask was created by drop coating a 1:1 solution of aqueous polystyrene spheres ($D = 450$ nm) and absolute ethanol onto a glass cover slide, which was suspended on the surface of DDI water. A diluted drop of sodium dodecyl sulfate was used to alter the surface tension of the water and arrange the spheres into a well-ordered, closely packed
array on the water’s surface. This array was then transferred to a quartz substrate and allowed to dry. Deposition of gold through the interstitial spaces in the PS mask was done with a PVD75 filament evaporator at a chamber pressure no greater than 5.0 E-6 Torr. Mask removal was accomplished by sonicating the sample (<5 min) in absolute EtOH. **Figure 2.1** shows false color SEM images of the three steps in the process.

**Figure 2.1**

Figure 2.1: SEM images showing the three steps in nanosphere lithography (NSL). A. Polystyrene (PS) spheres are deposited onto a hydrophilic substrate in a hexagonally close-packed array. B. Metal is deposited over the PS spheres. The metal is only deposited onto the substrate at the interstitial spaces between the spheres. C. The PS spheres are removed in EtOH via ultra-sonication leaving behind only the particles fabricated in between nanospheres. *Figure adopted from Dr. Wenyu Huang’s dissertation.

Nanosphere lithography can be performed reliably and in a cost effective manner to produce large arrays of homogeneous nanoprisms. The nanoprism bisector (b) and the tip-to-tip separation (s) between nanoparticles are dependent functions on the size of the polystyrene nanosphere used to fabricate the polymer mask. These dimensions are...
given below in Equations 2.2 and 2.3. The nanoprism shape created using this technique has very sharp tips that generate intensely focused fields. The drawback is that there is no independent control over the size of the nanoprism and the separation between two nanoparticles. It is also difficult to study only two or three nanoparticles in a system as they radiatively couple with one another, which is apparent from Equations 2.2 and 2.3. For this independent control and systematic variation in particle geometries, a more sensitive method is necessary, such as electron beam lithography.

\[ b = \frac{3}{2} \left( \sqrt[3]{3} - 1 - \frac{1}{\sqrt[3]{3}} \right) D \]  

Equation 2.2

\[ s = \frac{1}{\sqrt[3]{3}} D \]  

Equation 2.3

**Electron Beam Lithography (EBL)**

Electron beam lithography (EBL) offers an advantage over conventional lithography in that the feature size that can be fabricated is much smaller. This is because the electrons, which serve as the exposing medium instead of photons, have a de Broglie wavelength < 0.005 nm when they are accelerated to 100kV. The resolution is then limited not by the diffraction limit, but by the instrumentation itself. This limitation in the resolution comes from the magnetic focusing lenses that compress the negatively charged electrons together into a coherent beam. The tighter the beam is at the exposure spot the smaller the minimum feature size becomes. While other steps in the fabrication process, such as solvent washes and substrate selection, introduce further limitations in feature size, the ultimate resolution surpasses that of conventional lithography, even under the extremely complicated systems of immersion lithography coupled to excimer laser generation. There are also advantages over NSL such as independent control over nanoparticle size and separation, as well as much better control over the nanoparticle shape.
The electron beam lithography instrument used in this dissertation work is located in the microelectronics facility at the Georgia Institute of Technology. The instrument is a JEOL JBX-9300FS and has a minimum beam size of 4nm with a 50-100kV acceleration and a 50pA-2nA current range. For all experiments done here, the acceleration was 100kV and the current used was 2nA. Unless otherwise noted, the substrates used were pre-fabricated Si$_3$N$_4$/Si membrane wafers fabricated by graduate students in Dr. Henderson’s lab. This was done in the following manner;

A prime grade double-side polished silicon wafer with a <100> face, 5-25 ohm-cm resistivity, and 380 25um thickness was purchased and cleaned in a CMOS cleaning station inside a Cleanroom. The wafers were placed in a Tystar Furnace and a nitride layer (Si$_3$N$_4$) was deposited onto the wafer surface using a low-pressure chemical vapor deposition process at a deposition rate of 5 nm / min to a final thickness of 50 ± 3 nm. A combination of optical photolithography and dry etching with CF$_4$ removed selected areas of the membrane from one side of the wafer. These areas were exposed to KOH to anisotropically etch the silicon wafer through to the other side, exposing the other silicon nitride membrane. This produced an array of silicon nitride membrane windows freely supported that were ~ 250 x 250 µm$^2$. Each window was used for a single design pattern.

The necessity of these membrane samples compared with typical silicon wafers is because of the proximity effect in electron beam lithography. Only a portion of the electrons that pass through the resist are involved in exposing the resist. Some of the electrons that do not energetically react with the resist during the first pass through the polymer layer are backscattered by the substrate,
resulting in some undesired areas of the resist being expose. Figure 2.2.A shows this using a Monte Carlo simulation at an acceleration voltage of 20kV. Since the fabrication was done at 100kV, the effects from backscattering in the experiment would even greater than what is simulated. Figure 2.2.B demonstrates the same Monte Carlo simulation with a 50nm thick substrate at the exposure spot.

**Figure 2.2**

A.) B.)

Figure 2.2: A) Monte Carlo simulation of the scattering (both back scattering and forward scattering) of the substrate as the electrons expose a thin PMMA resist layer and that is supported on a silicon wafer. B.) Same simulation as in (A) with the assumption that the substrate is only 50 nm thick at the spot of exposure, as is the case with the Si₃N₄ substrates used in this work.

The EBL polymer masks were generally fabricated in the following manner. (Any divergences in the method are noted in the specific chapters below.) Figure 2.3 is a cartoon representation of the processing steps for fabricating nanoparticles on a support using EBL.
1.) Spin-Coat Resist 

2.) Exposure of focused electrons

3.) Develop the Sample

4.) Evaporate Metal

5.) Remove Resist

Figure 2.3: Schematic of the general electron beam lithography fabrication process. 1.) Spin-coat a thin layer (~100s of nm) of an electron sensitive resist (e.g. PMMA) onto a conductive substrate (typically silicon). 2.) Exposure of the PMMA resist with a focused beam of electrons. 3.) Develop the exposed areas of the PMMA resist in order to remove all exposed areas. 4.) Evaporate a metal onto the substrate and into exposed areas of the PMMA resist. 5.) Remove all polymer resist to leave only the fabricated nanoparticles.

The Si$_3$N$_4$ / Si membrane substrate was first cleaned in acetone for several minutes to remove any residual organics left by the membrane fabrication process. The substrate was the dried and spin-coated with a thin layer of PMMA dissolved in anisole (2%) at a speed of 4000 RPM and a rate of 500 R/s for 60 seconds. Prior to spin coating the substrate, a piece of single side tape was applied to the bottom surface of the substrate to protect the Si$_3$N$_4$ windows from being shattered by the vacuum applied to the substrate during the spinning process. This tape was removed immediately after the spin coating process and the substrate was baked on a hot plate for 2 minutes at 180°C. This produced a PMMA layer of approximately 80 ± 5 nm as determined by contact profilometry.
The polymer-coated substrate was then loaded into the EBL cassette and inserted into the EBL autoloader, which was then automatically loaded into the EBL instrument. The JBX-9300FS is equipped with an SEM function in addition to the standard EBL function, which was used to align the Si$_3$N$_4$ membranes to overlap with the pattern writing. This resulted in a sacrifice of several of the windows due to over-exposure of the polymer resist to the electrons used in imaging.

The exposure patterns were written using either AutoCAD or Cadence and were converted to the appropriate .v30 files. These files are arranged by two separate files (job and schedule) and complied into one “magazine” file that is read by the instrument. The dose used for the exposures was between 2500-3500 uC/cm$^2$. Following the exposure, the sample was removed from the cassette and developed in a 3:1 IPA:MIBK solution for 10 seconds and then rinsed in an IPA bath for 30-60 seconds. The sample was gently blown dry with a stream of N$_2$.

The developed EBL sample was then inverted in a CVC electron beam deposition chamber. A thin layer of Cr (0.5-1.5 nm) was deposited onto the sample at a rate of 0.1 Å/s to serve as an adhesion layer followed by a layer of gold (18-20 nm) at a rate of 0.5 Å/s. After deposition, the remaining PMMA was removed in 1165 remover, leaving only the gold nanostructures.

**Langmuir-Blodgett (LB) Deposition**

An Langmuir-Blodgett (LB) film is one or more monolayers composed of an organic molecule that is transferred from the surface of a water bath to a solid substrate via dipping the substrate into or removing the substrate from the water phase. Langmuir-Blodgett films are named for Drs. Irving Langmuir and Katherine Blodgett who were the first to discover and characterize these films in the late 1920’s. Their work in surface science led to a Noble Prize in chemistry in 1932. Figure 2.4.A is a schematic of the
Langmuir-Blodgett trough used in this work. The aqueous phase is divided into two sections by a mobile scanning arm. The films self-assemble into a monolayer on the surface of an aqueous phase due to opposing interactions between the amphiphilic molecule and the polar water phase (attractive interactions with the polar heads of the molecule and water and repulsive interactions between the non-polar tails of the molecule and water). Figure 2.4.B depicts this balance as the amphiphilic molecules align on the surface of the water. The amphiphilic molecules, dissolved in an organic solvent, are dispersed onto the surface of the water sub-phase. The scanning arm reduces the surface area of the section that the molecules are dispersed and increases the density of the molecular monolayer. The surface density of the monolayer is monitored using the Wilhelmy plate. Figure 2.4.C shows how the plate is used to measure the force of the water and the monolayer. This force is used to calculate a pressure / area graph that describes the density of the monolayer on the surface of the water.

The Langmuir-Blodgett deposition technique has recently been applied to nanoparticles in order to create single monolayers of colloidally synthesized nanoparticles. The Yang group has pioneered this technique in order to fabricate monolayers and sub-monolayers of non-polar ligand protected nanoparticles by controlling the surface pressure of the nanoparticles when dispersed onto an aqueous sub-layer. The particles are typically colloidally suspended in a volatile organic solvent such as chloroform or toluene and then dispersed onto the surface of an aqueous sub-layer. As the volatile solvent evaporates, the nanoparticles are left stranded at the air-water interface at a sub-monolayer density. When the area of the deposited nanoparticle layer is reduced, the particles are forced together until they form a close packed monolayer. The layer can be transferred to a substrate at any intermediate particle density, which allows for some control over the average separation between nanoparticles on the substrate.
Figure 2.4: A) The Langmuir-Blodgett trough used to make and transfer monolayers of molecules or nanoparticles from an air-water interface to a substrate. B) Cartoon of amphiphilic molecules deposited from an organic phase onto the surface of an aqueous sub-phase after the organic solvent has evaporated. The non-polar tails are hydrophobic while the polar heads are hydroscopic. These two interactions at the air-water interface cause all the molecules to align homogeneously in a monolayer or sub-monolayer. C) Illustration of a Wilhelmy plate used to measure the pressure of the monolayer deposited on the aqueous sub-phase. The force down (F) is zeroed prior to particle deposition on the sub-phase and is monitored as the monolayer surface area is reduced.
There are a couple of advantages to using the LB deposition method to prepare substrate supported nanoparticle samples. The first is the low cost of sample preparation compared to many types of nano-lithography such as EBL and NIL. For example, the expense of an LB film of colloidal particles includes the cost of chemicals (metal salt, reducing agent, and capping agent), use of the LB trough, and the substrate. The EBL samples cost much more because of the expensive equipment used (metal deposition, the EBL tool, and spin coating) and the wide range of specific solvents needed to develop the sample. This results in the lithography samples costing roughly 10x more than an LB film of colloidally prepared nanoparticles. A second advantage of LB deposition is that one can utilize the advantages of colloidal synthesis, such as high particle yield\textsuperscript{72-74} and single crystallinity\textsuperscript{33,75,76} and apply them to a surface supported architectures and applications. Additionally, the disadvantage of a surfactant layer on the nanoparticles can be corrected for by exposing the deposited monolayer of particles to an O\textsubscript{2} plasma that oxidizes the organic ligands on the particle surface\textsuperscript{40}.

*The LB model used in this work was purchased from Nima Technologies and was model 611D.

**Other Instrumentation used in this Dissertation**

**Electron Microscopes and Surface Probe Microscopes**

The samples were imaged using several microscopy methods. Scanning electron microscopy (SEM) was used to image the particles that were fabricated by EBL and NSL. Two instruments were used; the first a LEO 1530 FE-SEM located in the electron microscopy center at Georgia Tech and the second a Zeiss Ultra 60 FE-SEM located in Microelectronics Research Center at Georgia Tech. All images were taken using a secondary electron detector and an accelerating voltage from 1-10kV.
Colloidal solutions of synthesized nanoparticles were imaged using a JEOL 100CX-2 transmission electron microscope (TEM). The TEM grids used for imaging were formvar coated copper grids purchased from Ted Pella. The JEOL 100CX-2 was located in the electron microscopy center at Georgia Tech.

Height measurements of surface supported nanoparticles were obtained using atomic force microscopy (AFM). Both contact and non-contact modes were used, depending on the sample stiffness (contact for metals; non-contact for polymers). The AFM used was located in the Microelectronics Research Center at Georgia Tech.

**Spectroscopic Characterization**

The UV-vis extinction spectroscopy of the EBL fabricated nanoparticle arrays was performed using an Olympus microscope. The software used to collect and analyze the spectra was from Craic. The typical magnification used was 20x which presented a collection area roughly of a diameter 8.0 um. In some instances (where specified) the magnification was 5x or 50x with respective collection areas of 20um and 4um. The signal was averaged over 1000 scans whenever possible to minimize noise.

The Raman experiments performed in this dissertation were completed on a Kaiser Optical System coupled to an Olympus microscope. The excitation wavelength was 785nm and the power was tunable from 10-350mW. The signal collection was taken at 180° through a chilled CCD camera.

**Electromagnetic Simulations using Discrete Dipole Approximation**

To obtain more information about the fabricated plasmonic nanoparticle dimers, the discrete dipole approximation (DDA) method was used to simulate optical properties of the metallic nanoparticles. This technique divides the simulated material into an array of discrete polarizable points with assigned optical properties and environments, given as a separate file that models the experimental optical properties of the material. These
discrete polarizable dipole points can be arranged in any orientation to simulate an endless variety of particle shapes (Figure 2.5.A). These polarizable points are excited by an electric field and the optical extinction for each point is self-consistently calculated in response to the incident field and all neighboring dipole points to produce a net optical extinction response (Figure 2.5.B). This net response is generated from the 1000’s of dipole points in each particle with a radiative reaction correction that accounts for electromagnetic retardation, radiative damping, and other finite-size effects. The code that was used was DDSCAT 6.1 and is publicly provided by Draine and Flatau\textsuperscript{77,78}. In addition to the original code from Draine and Flatau, we also utilized modified code from the Schatz group\textsuperscript{79,80} that allows for the calculation of the surface field intensities around the particles and the individual dipole vectors (Figures 2.5.C & 2.5.D, respectively).

While the dominant work in this dissertation is experimental in nature, using nanosphere lithography, electron beam lithography, and colloidal synthesis, DDA is able to provide new insights that are not accessible using experiment alone. Many of the size dependent studies performed here would take a great deal of resources and time that DDA is able to condense. There are also electromagnetic responses that can be observed in the calculations, such as dipolar / higher order multi-pole excitations and surface field distributions. The validity of such calculations has been experimentally confirmed in many cases by several investigators\textsuperscript{31,81-83}.

The DDA method has some limitations that were appropriately taken into consideration. The first is the occurrence of localized hot spots on the surface of the particle that are generated from the discreteness of the dipoles that make up the particle shape, especially on edges or corners. This can result in unrealistic electric fields values that do not naturally occur on a smooth continuous surface. However, in the limit of small discrete dipole separations with respect to the size of the particle and the separation distance between particles, the extinction spectra have shown consistent agreement with experimental results\textsuperscript{84,85}. A second limitation is that it only approximates a small number
of particles, usually one or two at a time. This does not allow for calculations of many particle systems. For this reason, the simulations in this dissertation are limited to one or two particle systems.

**Figure 2.5**

**A.) Shape Simulation**

**B.) Extinction Spectra**

**C.) Surface Field Simulation**

**D.) Particle Polarization**

Figure 2.5 A) DDA simulation of two nanospheres. B.) Simulated extinction spectra of two nanospheres in (A) with various separations. C.) Surface fields surrounding a nanoprism dimer with prisms oriented tip-to-tip excited parallel to the interparticle axis. D.) Particle polarization for nanoprism excited with light polarized in the x-direction.
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CHAPTER 3

DEPENDENCE OF THE THRESHOLD ENERGY OF FEMTOSECOND LASER EJECTION OF GOLD NANOPRISMS FROM QUARTZ SUBSTRATES ON THE NANOPARTICLE ENVIRONMENT

Abstract

It has been reported that gold nanoprisms in a monolayer array on a quartz substrate were ejected in air when irradiated with femtosecond laser pulses near their surface plasmon absorption maximum. It was deduced from the measured reduction in particle thickness upon irradiation that the mechanism involved ablation of surface atoms from the gold particle, which creates a sudden large pressure at the particle-substrate interface. The present study reports on this phenomenon when the nanoparticle-substrate is immersed in a liquid environment. In this system, it is found that the nanoparticle ejection requires one tenth the energy required if the system was irradiated in air. The ejected nanoparticle is found to increase in thickness, instead of the decrease observed in air. These results suggest another photo-initiated ejection mechanism, different from surface ablation, when the particles are surrounded by a liquid environment. From this and other spectroscopic and microscopic results on the ejected nanoprisms, we suggest a mechanism which involves energy transfer from the photo-excited nanoprisms to the solvent within the cavities and defects at the particle-substrate interface. The hot solvent molecules result in an intense pressure at the particle-substrate interface, resulting in particle ejection. Ejection is proposed to consist of two processes, namely nanoparticle-substrate dissociation and nanoparticle solvation and diffusion away from the substrate. These two processes have independently been studied as a function of solvent property.
Introduction

Directed colloidal nanoparticle synthesis was reported in the early 1950’s, where metallic ions are reduced in order to form small clusters of metal particles. Particle growth is controlled by use of a capping agent that binds to the particle surface. Investigation of this process continued over the past 50 years to produce a wealth of particles by varying the identity and concentration of the metal salt, reducing agent, and/or surfactant. These studies produced an increasingly large amount of nanomaterials with a range of shapes and sizes, such as cubes, prisms, rods, and shells. One of the most useful and intriguing properties of plasmonic nanoparticles (gold and silver) is their ability to strongly absorb and scatter light at a frequency that is resonant with their surface plasmon oscillation. This ability stems from a coupling of the particle’s conduction band electrons with the electric field of the incident light that oscillate in resonance with one another, termed the particle’s Localized Surface Plasmon Resonance (LSPR). This resonance frequency is determined by the shape, size, and density of the particle’s electron distribution and the surrounding dielectric environment. The LSPR frequency can selectively be tuned by changing one or both of these parameters. These plasmonic colloidal particles can be used in a wide range of applications such as imaging and biomedical therapy, optical enhancing, nanorulers, and catalysis.

One unfortunate disadvantage of the colloidal method is that it produces nanoparticles with large particle size distribution. Lithographic techniques are known to produce nanoparticles with very narrow size distributions (highly monodisperse) on substrates. While nanoparticles supported on substrates are useful in material nanoscience studies, nanoparticles in solution are useful in broader applications in the fields of chemistry, nanobiology, and nanomedicine. For this reason, it is advantageous to explore the possibility of making nanoparticles by lithographic techniques and then releasing the particles from the substrates into solution. Some of the nano-lithographic techniques used
today are Electron Beam Lithography (EBL), Extreme UV Photolithography (EUV-PL), Nanosphere Lithography (NSL), and more recently Nanoimprint Lithography (NIL). The lithographic scheme is composed of designing a mask overlaying a substrate that is coated with a vaporized metal. The metal adheres to the underlying substrate through interstitial holes in the mask, and once the mask is removed, leaves a “metallic negative” of the mask image bound to the substrate surface. This technique affords the designer opportunity to create highly uniform nano-systems of nearly any shape, size, and/or pattern while eliminating the need for a stabilizing surfactant agent. Similar plasmonic properties exist with lithographically fabricated particles as they do in colloidal solutions. They offer superior ability over colloids to study fundamental attributes of particles as well as offering a wealth of applications for plasmonic devices, optical waveguides, and enhanced spectroscopy platforms. However, for other applications, such as solution based chemistry, biological, and medicinal, nanoparticles in solution are most useful.

The undertaking to combine the advantages of both techniques in order to simultaneously afford the range of monodispersed shapes that lithography offers and the solution specific applications that synthetic techniques display has, to date, not been fully investigated. Van Duyne et al have successfully transferred silver nanoprisms fabricated by NSL into solution by utilizing the weak interaction between Ag nanoparticles and the fabrication substrate. By first capping the surface of the silver prisms with an alkanethiol surfactant and sonicating them in a solution of ethanol, they were able to achieve the first TEM micrograph images of NSL particles in solution as well as absorption spectra of the particles in situ. While this technique is useful, it is restricted to particles that poorly adhere to their substrate and it is advantageous to possess multiple transfer techniques in order to choose the appropriate method for the desired application.
Previously, nanoparticle ejection of NSL fabricated nanoprism from a substrate into air was reported to occur with a nanosecond pulse at $532\text{nm}^{68}$. This “jump” was initiated by melting the particle to its most thermodynamically stable spherical shape, proposed to be mechanistically required for the particle to leave the surface. The fast change in shape generates a rapid change in the particles center of mass as the tips retracted inward, thrusting the particle away from the substrate and rendering a solution of fully melted, spherical particles. In more recent studies our group has discovered that nanoparticle ejection can be initiated in air by exposing the sample to an ultra-fast femtosecond pulse at or near the nanoparticle’s LSPR that results in a decrease in the particle bisector and thickness but with no loss in nanoparticle prismatic shape$^{69}$. The mechanism for ultrafast ejection was proposed to result from fast evaporation of gold atoms from the prism’s surface as a pathway to cool the particle in a time domain much faster than external thermalization (e-ph coupling) of the nanoparticle occurs. The ablation process cools the particle prior to melting and generates an intense pressure gradient at the particle-substrate interface. This intense pressure is believed to result in a particle-substrate separation and a nanoparticle ejection. However, the alternative mechanism of heating the quartz area under the nanoparticle, causing water evaporation was not eliminated.

The present study examines the process of NSL-fabricated Au nanoprism ejection into various liquid media. This femtosecond pumped nanoparticle ejection is compared with the results in air at lower laser fluencies. Various solvents are used with different intrinsic properties in order to understand the nature of the nanoparticle coupling with the solvent and its influence on the ejection process. The solvents used span a wide range and have various intrinsic properties; namely: water, a group of 4 alkane nitriles, and a group of 4 alkane alcohols.
**Experimental**

Quartz microscope slides from Technical Glass Products were cut into 1x1.5cm pieces. Polystyrene spheres (D=450nm) were purchased from Duke Scientific with a size distribution less than 3%. All other chemicals were used as received. Nanosphere Lithography (NSL) was used to fabricate gold nano-prisms on a quartz substrate. A NS-mask was created by drop coating a 1:1 solution of aqueous polystyrene spheres (D=450nm) and absolute ethanol onto a glass cover slide, which was suspended on the surface of DDI water. A diluted drop of sodium dodecyl sulfate was used to alter the surface tension of the water and arrange the spheres into a well-ordered, closely packed array on the water’s surface. This array was then transferred to a quartz substrate and allowed to dry. Deposition of gold through the interstitial spaces in the PS mask was done with a PVD75 Filament Evaporator at a chamber pressure no greater than 5.0e\(^{-6}\) torr. Mask removal was accomplished by sonicating the sample (<5 minutes) in absolute EtOH. Scanning Electron Microscope (SEM) images were taken using a LEO 1530 (T-FE) and all absorption measurements were done with a Beckman DU650 spectrophotometer. Atomic Force Microscopy (AFM) images were taken using a Veeco SPM in tapping mode to analyze particle dimensions on the substrate.

The amplified Ti-Sapphire femtosecond laser system (Clark-MXR CPA 1000) used in the experiments has been described elsewhere\(^70\). Briefly, the Ti:Sapphire Oscillator (Clark-MXR NJA-5) was pumped by a frequency-doubled Nd:Vanadate laser (Coherent Verdi) with an output power of 3.5 W at 532 nm, generating laser pulses of 100 femtosecond duration with a 90 MHz repetition rate at 800 nm. The initial seed pulse coming out from the oscillator with a pulse energy of about 4 nJ was amplified in a regenerative amplifier, which was pumped by a 1 KHz Q-Switched Nd:YAG laser with a 7.5 W output at 532 nm. Before sending the seed pulses to the regenerative amplifier, they were stretched up to 100 ps for the amplifier safety. After amplifying, the pulses were recompressed and typically laser pulses of 100 fs duration at 800 nm with 1 mJ
pulse energy and 1 KHz repetition rate were generated for the experiment. The gaussian beam of 7.0 mm diameter was cut down to 4.0 mm ± 0.1mm using an optical iris in order to obtain a more uniform energy distribution within the irradiation area. Irradiation was done in a raster scan method across the back of a substrate containing the prismatic particle array while submerged into a cuvette with the appropriate solvent. A scan rate of ~1 mm/s and a pitch of ~2 mm were used. All solution suspended particles were imaged with a JEOL 100C TEM.

**Results and Discussion**

**Particle Ejection in Water**

Figure 3.1 shows the results of irradiating substrate bound nanoprisms at 800nm in air and in water. Absorption spectroscopy was used as a convenient and sensitive method to detect the effect of the fs-pulse on the nanoprisms. The amount of energy that is transferred to the prism (1.0 W/cm²) is well below the threshold of ejection reported in air (~5.0 W/cm²)

69. When prisms are in an atmospheric environment, they access a cooling pathway that slightly ablates the nanoparticle surface atoms, resulting in a blue-shift in nanoparticle peak LSPR from 815nm to 740nm (Figure 3.1.A). However, when submerged into an aqueous medium, the prisms do not remain on the surface of the substrate, but are transferred into solution. This results in a decrease of the absorption band at 815nm from the surface bound nanoparticles (Figure 3.1.B) and the appearance of an absorption band from transferred nanoparticles in solution at 750 nm (Figure 3.1.C). The LSPR band in solution is similar in shape and peak position to the LSPR band of particles that are irradiated in air. This suggests that the decrease in particle dimension that occurs in air at this laser fluence also occurs in solution, with an additional ejection of the particle when submerged into solution. The absorption peaks in water located at 530nm and 960nm are due to melting of the prisms into spheres and a small degree of nanoparticle aggregation, respectively.
Figure 3.1

A

B

C

Figure 1: Absorption spectra of NSL fabricated nanoprisms on substrate before (black) and after (red) irradiated with a femtosecond pulse at 800nm in (a) air and (b) water. Insets are SEM images of the substrates after irradiation. (c) Absorption spectrum of nanoprisms in aqueous solvent irradiated in Figure 1b. Inset is TEM image of transferred particles in water (c). Laser intensity used was 1 W/cm².
Images of ejected nanoprisms on the substrate surface after irradiation in solution show similarities to prisms that were ejected in air. In addition to fully dissociating from the surface of the substrate, prisms “jump”, “twist”, and “flip” over one anchored edge or point, indicating that the mechanism for ejection in solution is similar to the ejection mechanism in air, resulting from an intense build up to pressure at the particle-substrate interface. This is shown in Figure 3.2, with examples of each phenomenon selected. In air, this pressure is caused by the gold itself as the particle uses ablation of surface atoms to cool, fueling nanoparticle ejection. These conclusions were drawn from AFM measurements taken of the particles after ejection, indicating an average decrease in nanoparticle thickness of 3nm upon irradiation and subsequent ejection. An AFM

Figure 3.2

Figure 3.2: SEM image of substrate after irradiation, depicting several ejection phenomena that occur due to femtosecond excitation at 800nm (Fluence = 1 W/cm²). Similar images were used for statistical analysis of the dissociation process in varying solvents (EtOH shown).
measurement was carried out on the nanoprisms after irradiation in solution (Figure 3.3). An increase, not a decrease, in nanoparticle thickness following ejection was observed, suggesting that melting occurs during nanoprism irradiation. The average nanoparticle thickness of ejected prisms was measured to be 39.3 ± 2.1 nm while the average thickness of the unirradiated particle was measured to be 35.1 ± 1.3 nm. This 4.2 nm increase in nanoprism thickness does not rule out the ablation mechanism here, but might suggest an additional mechanism to explain the ejection phenomenon in solution.

Evidence of the responsible mechanism is found by altering the nature of the interface between the gold prism and substrate. Particles were thermally pre-heated prior to irradiation in water, and the amount of particles that were ejected was spectroscopically seen to decrease in solution. (Figure 3.4.A) The decrease in absorbance from nanoparticles bound to the substrate upon irradiation (indicating the degree of nanoparticle ejection from the substrate) was also seen to be less for pre-annealed prisms than for unannealed prisms (Figure 3.4.B). When the particles are preheated, the metal-surface slightly anneals (confirmed by a 40 nm blue shift in substrate bound particle LSPR maximum after heating, not shown) and the particle adhesion to the substrate surface will be increased. We propose that nanoscopic cavities are formed at the gold-substrate interface in the NSL method during vaporization of gold atoms onto and between the polystyrene spheres on the substrate. Weak interactions between particle and substrate have been reported previously in the use of NSL due to a combination of lattice mismatches between the metal and quartz substrate and defects in the substrate surface. If these cavities are large enough, solvent molecules have the opportunity to diffuse underneath the particle. When the electronic gas of the prism is excited at resonant frequency, inelastic electron tunneling from the particle to coupling molecules occurs and these molecules quickly build-up pressure between the prism and substrate, causing nanoparticle ejection if the transferred energy is great enough. When the prisms are annealed prior to laser exposure, the number density and size of these cavities is
decreased and the interface will have a smaller solvent density, and therefore a smaller likelihood exists of pressure build-up and subsequent particle ejection.

**Figure 3.3**

![Figure 3.3: AFM measurements of irradiated (a) and unirradiated (b) areas of the substrate bound array, showing that the irradiated nanoprisms are thicker than the unirradiated ones (not thinner as displaced particles in air). This suggests that a melting process occurs during the nanoprism transfer and not ablation.](image)

During nanoparticle excitation at the resonant frequency of the particle, Bauer et al.\textsuperscript{72,73} have reported evidence of a bi-directional inelastic tunneling of the hot electron gas...
into vacant electronic states of adsorbed molecules. This tunneling imparts energy to the molecules and retards the e-e internal thermalization of the particle. These studies were done for covalently bonded adsorbates, which possess a strong chemical bond to the nanoparticle-surface. However, even non-covalently bonded molecules such as alcohols are known to weakly couple with noble metal surfaces through non-bonding electron donation from the oxygen atom. Likewise, water has an affinity for the gold surface and similar coupling would occur on a frequent basis, more than previously reported due to the lack of a capping agent protecting the nanoprism surface.

To more fully understand the specific role of the solvent on prism ejection into solution, a number of solvents are examined. The ejection process cannot solely be monitored by the number of particles transferred to solution because the solvation ability of the solvent plays a crucial role in the number of particles that completely leave the surface to dissolve in the solution phase. Thus the absorbance signal strength in solution could be a misleading value. For this reason, nanoparticle ejection in solution is broken into two separate processes:

- **Nanoparticle-Substrate Dissociation**, where the nanoparticle physically separates from the substrate surface, and the photothermal energy that is absorbed by the particle is just enough to break the nanoparticle-surface bonding. The amount of energy that is needed to create this separation is represented by $\Delta H_{\text{Diss}}$.

- **Nanoparticle Solvation and Diffusion into Solution**, where the nanoparticle is dissolved into the solvent and taken away from the original substrate position. This process is represented by an enthalpy change, $\Delta H_{\text{Solv}}$.

Direct nanoparticle “ejection” into the environment is not needed, since dissociation can certainly occur in the absence of nanoparticle solvation.
Figure 3.4

(a) Absorption spectra of separate water solutions after irradiation of pre-annealed (black) and unannealed (blue) substrate bound prism arrays at 800nm. (b) Absorption spectra of substrate bound array before (black) and after (red) irradiation of pre-annealed (top) and unannealed (bottom) samples. Annealing was done at 60 C for 15 minutes prior to irradiation. These spectra suggest that annealing the sample prior to irradiation decreases the amount of cavities at the particle-substrate interface, greatly reducing the ejection process.
Nanoparticle-Substrate Dissociation

The degree of nanoparticle dissociation from the substrate is determined by the amount of energy that is transferred from the irradiated nanoprism to the solvent environment at the nanoparticle-substrate interface. The intensity threshold of dissociation is then defined as the laser fluence at which \( \Delta H_{\text{Transfer}} = \Delta H_{\text{Dissociate}} \). (See Figure 3.5.) At this intensity, the particles absorb and transfer the minimum amount of energy to adsorbed solvent molecules at the interface to dissociate the particles from the substrate. The laser fluence that produces this thermodynamic equivalence is nearly impossible to accurately determine experimentally, due to variation in the individual particles’ absorbance cross section at 800nm (the amount of energy that the particle absorbs) and the varying degrees of defect cavities at the particle-substrate interface (creating a variation in the density of solvent molecules coupling to the particle at the interface). However, for all solvents used in this report, spectroscopic evidence suggests nanoparticle ejection occurs around 0.3 ± 0.1 W/cm\(^2\). At this laser fluence, a small decrease in substrate absorbance and/or increase in solution absorption of the nanoprism absorption band was observed after irradiation.

Nanoparticle dissociation was quantitatively measured at a fluence = 1 W/cm\(^2\) through microscopic analysis of substrates irradiated in alcohol and nitrile solvents. This fluence was chosen for statistical purposes, due to a higher amount of particles dissociating compared to the threshold intensity reported above. A group of 15 SEM images (such as the one in Figure 3.2) were taken randomly throughout each substrate after irradiation, resulting in more than 1000 particles counted for each solvent. Analysis of the nanoprism positions was done and each prism was categorized as having “moved” or “not moved” from its initial location. As metallization is done over the NS mask, small nucleation sites form around each particle due to scattering of gold atoms, giving each prism a distinct “footprint”. For each “footprint” that was present on the sample without the accompanying prism, it was counted as a moved particle. The assumption is
made that any movement due to separation will be noticeable movement, detectable through SEM imaging of the substrate surface.

**Figure 3.5**

**Ejection Thermodynamics**

- **\( \Delta H_1: \text{Dissociation} \)**
  
  \[
  (\text{Particle-Substrate}) + h\nu (\text{at } 800\text{nm}) \rightarrow (\text{Particle}) + (\text{Substrate})
  \]

- **\( \Delta H_2: \text{Solvation} \)**
  
  \[
  (\text{Substrate}) + (\text{Particle}) + 2(\text{Solvent}) \rightarrow (\text{Particle-Solvent}) + (\text{Substrate-Solvent})
  \]

**Coupling Solvent**

- **Good Coupling:** \(|\Delta H_2| > kT\)  
  - **Solvation**

**Non-Coupling Solvent**

- **Poor Coupling:** \(|\Delta H_2| < kT\)  
  - **No/Poor Solvation**

**Figure 5:** Thermodynamic description of the nanoparticle ejection process in a liquid environment. Variation in solvent results in a variation in \( \Delta H_{\text{Solvation}} \) that determines the degree of nanoparticle solvation.
Within experimental error, the number of particles that were dissociated from the substrate remained relatively constant for all solvents used here, resulting in ~60% of the particles dissociating. The similarity in the dissociation process (both the threshold intensity of dissociation and the percentage of dissociated particles at a higher intensity) for varying solvents suggests that particle ejection into a solvent is not greatly determined by the dissociation process, and that the average energy of dissociation is sufficiently overcome by the laser pulse used (1.0 W/cm$^2$) for the present solvents.

**Nanoparticle Solvation**

Upon dissociation, a second change in enthalpy occurs as the unsolvated particle becomes fully solvated and the substrate area, previously contained the nanoprism, becomes solvated. This process is exothermic and produces a decrease in enthalpy. The degree of change in the system’s enthalpy upon full solvation, and hence the degree of solvation and diffusion of the nanoparticle into and throughout the solvent, is dependent on the nature of the coupling between the solvent and nanoparticle. If a particle is weakly solvated, and $\Delta H_{\text{Solvation}}$ is not sufficiently negative ($\Delta H_{\text{Solvation}} \leq kT$), the particle theoretically should not remain solvated if a more stable state exists (such as particle aggregation). (See Figure 3.5.)

Generally, interactions between gold and molecules are described using the Hard-Soft Acid-Base (HSAB) principle$^{71}$. The principle qualitatively divides up substances as an acid (electron acceptor) or a base (electron donor) and classifies them as having hard character (non-polarizable) or soft character (polarizable). Metallic nanoparticles are categorized as soft acids$^{71}$ that will accept electron donation from a secondary species, while solvents are categorized here as bases, with a range of hard to soft character. Soft-base/soft-acid interactions are strongest because coupling occurs through covalent bonds, in this case to unsaturated surface atoms of the particle. Generally, covalent bond formation has been the classification of nitrile-gold nanoparticle coupling$^{71}$ as a result of
electron donation from the nitrile to the gold particle, likely from the \( \pi \)-molecular orbitals in the carbon-nitrogen triple bond. Alcohol solvents are characteristically harder than nitriles, and are not known to donate much electron density to the particle. However, coupling has been reported to occur between alcohols and metallic nanoparticles\(^{71}\), most likely from an induced dipole between the molecule and particle. A comparison of solvent-nanoparticle coupling is presented in Table 3.1.

### Table 3.1 - Bonding Character of Different Solvents & the Effect on the Ejection Process

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Type of Bonding to Au</th>
<th>Relative Bonding Strength to Au</th>
<th>Role of Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>Weakly Covalent</td>
<td>Strong</td>
<td>Ligand</td>
</tr>
<tr>
<td>Propionitrile</td>
<td>Weakly Covalent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butynitrile</td>
<td>Weakly Covalent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl Alcohol</td>
<td>Induced Dipole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethyl Alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propyl Alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyl Alcohol</td>
<td>Non-Specific</td>
<td>Weak</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Table 3.1: List of solvents used and their relative HSAB characteristics with the resulting bonding character and relative bonding strength to Au and their function with respect to the nanoparticle.

The degree of nanoprism solvation was qualitatively monitored by measuring the area of the LSPR absorption peak in solution after irradiation. This is proportional to the amount of particles that are transferred from the substrate into solution. In alcohol solvents, the area decreases as the chain length of the alkane group increases from one carbon to four (methyl – butyl alcohol). This is shown in Figure 3.6.a and 3.6.b. As
Figure 3.6: (a) Absorption spectra of transferred nanoprisms in alcohol solvents after irradiation. (b) Amount of solvation of transferred nanoprisms in each solvent (measured by integration of LSPR peak) compared to each alcohol’s polarizability. (c-e) SEM images of the substrate-bound monolayer array after irradiation in (c) methanol, (d) ethanol, and (e) propanol. Indicates a decrease in particle solvation and an increase in particle aggregation as solvent polarizability increases for alcohols.

described above, coupling of the alcohol group to the nanoparticle surface is weak. The decrease in particle absorption in solution occurs because the alcohol functions as a solvation medium without any specified covalent bonds to the nanoparticle surface. As
the alcohol alkane chain increases in length, the polarizability of the solvent molecule increases, thus increasing the coupling between solvent molecules. This increased solvent-solvent coupling results in a decrease in the degree of particle-solvent coupling and an increase in particle aggregation which is observed on the surface of the substrate. SEM images show a qualitative increase in particle groupings as the alkane chain of the alcohol increases in length. (Figure 3.6c-e) Thermodynamically, the enthalpy change upon particle solvation ($\Delta H_{\text{Solvation}}$) is not great enough to solvate the particle for extended periods of time at ambient conditions. In addition, steric hindrance cannot be neglected as a contributing factor in the decrease of nanoparticle solvation.

For nitrile solvents, solvation was not observed to be dependent on the solvent’s alkane chain length between one carbon to three (aceto – butyr nitrile). This is shown in Figure 3.7.a and 3.7.b. Coupling between the nitrile group and metallic nanoparticle has previously been suggested to occur from electron donation to the nanoparticle, forming a covalent bond. The solvent molecules are bound to the nanoparticle surface and function as chemically bound ligands $^{73}$, capping and protecting the particle as it is solvated. This interaction is evidenced by the shifted Raman band of the CCN bending mode between 375 and 400 cm$^{-1}$ in Figure 3.8.A. This explains the insensitivity of alkane chain length in the nitrile solvents to the solvation ability of the particle. For all nitrile solvents $\Delta H_{\text{Solvation}} > kT$ and the particle is sufficiently stabilized in solution.
Figure 3.7: (a) Absorption spectra of transferred nanoprisms in nitrile solvents after irradiation. (b) Amount of solvation of transferred nanoprisms in each solvent (measured by integration of LSPR peak) compared to the polarizability of each solvent. Indicates no change in nanoparticle solvation upon lengthening of the nitrile alkane chain.
Figure 3.8

A.  

B.  

Figure 3.8: Raman bands of the CCN bending mode (A) and the CN stretching mode (B). The presence of a shifted band in A provides evidence of chemical bonding between the CN triple bond and the gold nanoprisms in solution.

Ejected Nanoparticle Stability

The major benefit of this technique is to utilize the bare nanoparticles that are fabricated using lithography in a solution phase environment, which has many applications including but not limited to biological and in vitro studies. For this reason, the stability of the nanoparticles in solution after ejection was monitored. Figure 3.9.A demonstrates the stability of the nanoparticles in three different solutions (water, ethanol, and acetonitrile) without any capping agents by plotting the peak intensity of the plasmon resonance as a function of time over a two-week period. Within experimental error, the particles are relatively stable over the first three days. After that time, the particles begin to fall out of solution and the peak intensity decreases. Figure 3.9.B plots the stability of ejected nanoprisms in an aqueous solution in the presence of two different capping agents; sodium citrate and cety trimethylammonium bromide (CTAB).
Figure 3.9

(A) Stability of ejected nanoprisms in three solvents, water, ethanol, and acetonitrile. The dashed lines are inserted for the eye to follow. (B) Stability of ejected nanoprisms in water with three different capping agents; CTAB, sodium citrate, and no capping agent.

**Conclusion**

In conclusion, photothermal ejection of gold nanoprisms was observed for the first time in a liquid medium, occurring at a fraction of the energy required for the ejection of nanoparticles in air. Ejected particles in solution were observed to increase in thickness upon irradiation, instead of decreasing as ejected particles in air were previously observed to do. This suggested a different ejection mechanism in solution involving the hot solvent molecules present in the cavities located at the particle-substrate interface. These hot solvent molecules result from the transfer of photothermal nanoparticle energy to the solvent molecules upon excitation at the particle’s LSPR. The mechanism was supported by an observed decrease in nanoparticle ejection upon annealing the substrate bound particles prior to irradiation.

Nanoprism ejection was proposed to occur in two separate processes, nanoparticle-substrate dissociation and nanoparticle solvation and diffusion into solution.
By studying these two phenomena individually, we were able to explain how the solvent properties and the immediate environment of the particle affect the ejection process. Nanoparticle–substrate dissociation was not seen to be sensitive to the solvents used and the energy threshold for dissociation was similar, suggesting little dependency of the dissociation on the solvent. Particle solvation was observed to be extremely sensitive to the solvent properties, namely the nature of the coupling to the metal and the polarizability. Alcohols were suggested to be loosely coupled to the particle through an induced dipole. As their polarizability increased (increased alkane chain length) the solvent molecules preferentially favor one another over the metallic nanoparticle surface, resulting in a decrease in solvation of the nanoparticles and a subsequent increase in the nanoparticle aggregation. Nitriles were suggested to couple to the nanoparticle surface in a fundamentally different way by donating electrons to the particle surface, functioning as a soft base. This anchors the solvent molecule through the nitrile group to the particle surface, functioning as chemically bound ligands that cap and solvate the particle. Increased length in the alkane chain of the nitrile therefore has little to no effect on the solvation of the nanoparticle into various nitrile solvents.
References


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CHAPTER 4

ON THE USE OF PLASMONIC NANOPARTICLE PAIRS AS A PLASMON RULER: THE DEPENDENCE OF THE NEAR-FIELD DIPOLE PLASMON COUPLING ON NANOPARTICLE SIZE AND SHAPE

Abstract

The localized surface plasmon resonance (LSPR) spectral band of a gold or silver nanoparticle is observed to shift as a result of the near-field plasmonic field of another nanoparticle. The dependence of the observed shift on the interparticle distance is used as a ruler in biological systems and gave rise to a plasmonic ruler equation in which the fractional shift in the dipole resonance is found to decrease near exponentially with the interparticle separation in units of the particle size. The exponential decay length constant was observed to be consistent among a small range of nanoparticle sizes, shapes, and types of metal. The equation was derived from the observed results on discs and spherical nanoparticles and confirmed using results on a DNA conjugated nanosphere system. The aim of the present paper is to use electron beam lithography and DDA calculations to examine the constancy of the exponential decay length value in the plasmonic ruler equation on particle size and shape of a number of particles including nanoparticles of different symmetry and orientations. The results suggest that the exponent is almost independent of the size of the nanoparticle but very sensitive to the shape. A discussion of the nanoparticles most suitable for different applications in biological systems and a comparison of the plasmonic ruler with FRET is mentioned.
Introduction

Metallic nanoparticles are of great interest due to their optical and radiative properties. The interaction of a noble metal nanoparticle with incident light of a specific energy induces intense localized fields at the surface of the particle. These fields are induced when conduction band electrons of the noble metal nanoparticle couple with the electric field of incident light at a resonant frequency, generating a plasmonic oscillation localized on the surface of the nanoparticle, known as the localized surface plasmon resonance (LSPR)\(^1\text{-}^4\). This plasmonic oscillation occurs at a specific resonance wavelength that is dependent on the particle’s properties (dielectric function, size, and shape) and the dielectric constant of the host medium. By changing these parameters, one can tune the optical properties of the noble metal nanoparticles to optimize them for different applications. The intense localized field at the nanoparticle surface and the tunability of the LSPR in noble metal nanoparticles gives them enormous potential in medical\(^5\text{-}^8\), optical\(^9\text{-}^{12}\), and sensor\(^13\text{-}^{17}\) applications.

When two nanoparticles come into close contact (separations of less than 2 particle diameters), the near-field dipole plasmonic fields couple with one another, reducing the overall resonance energy of the particle pair\(^18\text{-}^{20}\). Colloidal studies have provided initial qualitative data on the near-field coupling between plasmonic nanoparticles, and many groups\(^13,21,22\) have reported on the effect of aggregation on the optical extinction of nanoparticles in solution. To achieve quantitative measurements of the coupling of two plasmonic metal nanoparticles, it is necessary to use lithographic techniques to fabricate nanoparticles of homogeneous size, shape, and interparticle separation. However, only recently has it been technologically possible to fabricate nanoparticles of high homogeneity and low feature size thanks to advancements in electron beam lithography (EBL).

Quantitative studies on the near field dipole plasmon coupling between two nanoparticles as a function of interparticle separation were independently first reported
by Su et al.\textsuperscript{23} and Rechberger et al.\textsuperscript{18} in a spheriodal gold nanoparticle. They concluded that “when the [LSPR] peak shift is scaled by the peak wavelength and the gap is scaled by the particle’s length, all data points fall on a common curve.” The common curve was an exponential decay of the coupling, measured by the fractional shift in the plasmon resonance $\left( \frac{\Delta \lambda}{\lambda} \right)$, as a function of the scaled interparticle separation. It was later shown that while the true dependence of the dipole coupling on the scaled interparticle separation goes as $(s/D)^3$, a single exponential of the form $\left( \frac{\Delta \lambda}{\lambda} \right) = A \times e^{\left( \frac{-s/D}{\tau} \right)}$ very nearly approximates the dependence\textsuperscript{24}. This exponential approximation is also useful for quantifying the relative strength of the dipole field by the magnitude of the pre-exponential factor $A$ and the decay length of the field away from the particle surface by the magnitude of $\tau$.

Using DDA calculations, our group has examined the plasmonic decay law for nanospheres\textsuperscript{24,25}, nanoshells\textsuperscript{26,27}, nanoellipses\textsuperscript{25}, and nanodiscs\textsuperscript{24}, and using electron beam lithography (EBL) the gold nanodisc was studied and the exponential decay length value was found to agree with the DDA results and with the results of silver nanodiscs\textsuperscript{28}. From these studies it was concluded that this common coupling trend has a scaled decay length that is largely independent of the particle material, dielectric environment, size, and shape\textsuperscript{24-27}. We have also loosely shown mathematically why this decay of the scaled quantities should be largely independent of the nanoparticle properties\textsuperscript{24}. By using this common coupling behavior a plasmon ruler equation was developed. Work from Reinhard et al.\textsuperscript{22} demonstrated experimentally controlled separation of two 40nm nanospheres in solution by using conjugated DNA. Accurate control over the nanosphere separation was obtained by conjugating one colloidal solution with a single strand of DNA and conjugating a second colloidal solution with the complimentary single strand of DNA. When the two colloidal solutions were mixed, the resulting DNA hybridization
formed a rigid molecular spacer between two nanospheres of a well-defined length. Jain et al. applied the developed plasmon ruler to this system and calculated the interparticle separation accurately using only the optical extinction of the particles\(^{24}\). This plasmonic ruler technique possesses advantages over the traditionally used FRET (fluorescence resonance energy transfer) technique such as a larger range of measurement on the order of 1-100 nm (1-10 nm in FRET\(^{29,30}\)) and no photobleaching from the reporter system since nanoparticles utilize absorption and scattering to optically measure separations\(^{22}\).

While these conclusions were made based on extensive simulated data using well-established DDA calculations and several experimental systems, these systems were generally isosymmetric, most particles having at least one \(C_\infty\) axis of symmetry and all particles possessing a center of inversion. The symmetrical similarities of the shapes that have been studied thus far (nanospheres, nanodiscs, nanoellipses, and nanoshells) have neglected to truly investigate the “independent” nature of the exponential decay length. Moerner et al.\(^ {31}\) have reported on the coupling between two nanoprisms oriented tip-to-tip (“bowtie” particles) fabricated on silicon using EBL. A similar qualitative exponential decay in the plasmonic coupling was observed as the tip-to-tip separation was increased. FDTD calculations were preformed and a good agreement was reported between the simulated and the experimental data points.

In the present report, we show experimentally that the quantitative decay of the dipole plasmon coupling between two nanoparticles is dependent on the nanoparticle shape, but is generally not highly sensitive to nanoparticle size. We reexamine previous reports on the existence of a universal constant that governs the near exponential decay of the coupling between the surface plasmons of two nanoparticles. While there is no universal decay constant for all nanoparticle shapes, the exponential decay length and amplitude that express the dipole coupling can often be approximated as constants over a range of sizes for a given shape.
Experimental

Nanoprism arrays were fabricated using a JEOL JBX-9300FS 100kV electron beam lithography (EBL) system. The substrates used to support the nanoprisms were prefabricated free standing silicon nitride membranes whose fabrication has been described in detail elsewhere. Briefly, silicon wafers with a <100> orientation were purchased from University Wafer and cleaned and placed in a Tystar Furnace. Si$_3$N$_4$ was deposited onto the wafer surface using a low-pressure chemical vapor deposition process at a deposition rate of 5 nm / min to a final thickness of 50 ± 3 nm. A combination of optical photolithography and dry etching with CF$_4$ removed selected areas of the membrane from one side of the wafer. These areas were exposed to KOH to anisotropically etch the silicon wafer through to the other side, exposing the other silicon nitride membrane. This produced an array of silicon nitride membrane windows freely supported that were 150 x 150 µm$^2$. Each window was used for a single design pattern and each pattern array was 300 x 300 µm$^2$ in order to ensure pattern overlap with the window. A poly-methyl methacrylate (PMMA) positive electron resist was spin coated onto the top Si$_3$N$_4$ side of the wafer to a thickness of 80nm. A dose of 2750 µC/cm$^2$ was used to write the pattern at a beam current of 1.98 nA. Development of the exposed areas was carried out in a 1:3 methyl isobutyl ketone: isopropyl alcohol (MIBK:IPA) solution for 10 seconds. The sample was then washed in IPA for 30 seconds before gently drying in a stream of N$_2$. A thin chrome layer (0.5 nm @ 0.1 A/sec) was evaporated onto the sample using a CVC electron beam evaporator followed by a 20.0 nm layer of gold at a rate of 0.5 A/s. The Cr served as an adhesion layer between the Si$_3$N$_4$ surface and the Au nanoparticles. Final lift-off and removal of the PMMA mask was accomplished by placing the sample in 1165 remover purchased from MicroChem for 24 hours. The array was designed so that the nanoparticle dimer pairs were spaced more than 800 nm from one another to reduce far-field coupling that has been observed by Rechberger et al. in 150 nm diameter gold nanodisc arrays. This far-field coupling has been shown by the
Moerner group to exist at large separations (4-7 prism bisector separations) for tip-to-tip nanoprisms. For this reason, individual particle pairs were experimentally spaced no less than 8 particle diameters apart and no interparticle separations were used greater than 3 particle bisectors. In these experimental samples with small interparticle gaps (15-200 nm), the near-field coupling can be expected to be much stronger than any far-field grating effects.

The supported nanoprisms were imaged using a Zeiss Ultra60 Scanning Electron Microscope (SEM). Absorption measurements were done on a Craic 1100 microabsorption spectrophotometer in transmission mode under polarized light using a 20x magnification. The collection spot was ~8.0 x 8.0 μm² and several different areas were collected from the center of the array and averaged to produce the reported spectra. A comparison between magnified SEM images from various membrane windows show excellent homogeneity in the particle shapes as the spacing is increased from 15 to 200 nm.

The optical response of the nanoparticle shapes have been calculated using the DDA method with the DDSCAT 6.1 code publicly offered by Draine and Flatau\(^{33}\) and modified by Goodman\(^{34}\). The method has been described in great detail elsewhere\(^{1}\). Briefly, the method approximates the desired particle shape as a 3-dimensional point dipole array of pre-programmed dipole-dipole spacing. The program self-consistently solves the Mie equation for a sphere at each dipole point in response to an incident polarization of light and from the fields associated with all the other dipoles present. The bulk values of the dielectric constants reported by Johnson and Christy\(^ {35}\) for gold were used. The DDA method has been demonstrated by many groups\(^ {36-39}\) to be suitable for optical calculations of the extinction spectrum and the local electric field distribution in metal particles with different geometries and environments. The incident light is always polarized parallel with the interparticle axis in this report and the dielectric of the host medium was set at \(\varepsilon_m = 1.00\). As discussed by Rechberger et al.\(^ {18}\), it is reasonable to
consider in the calculations of a single particle pair instead of the entire 2-D array. This consideration is justifiable because the particle pairs in the experiment are separated from each other by large distances on the order of 8 particle diameters, large enough so that no coupling occurs between different particle pairs. This ensures that only the interactions between the two particles within the dimer are measured.

**Results**

**Nanosphere**

We begin with DDA calculations on the nanosphere, since it is the easiest gold nanoparticle shape to synthesize and has been previously utilized in numerous applications, including the plasmon ruler equation. This application fundamentally requires a well-developed understanding of the coupling between two nanospheres and knowledge of how the plasmon resonance of the particle pair depends on the interparticle separation. DDA calculations were performed on simulations of two identical gold nanospheres with diameters throughout the range $5 > D > 50 \text{nm}$ at various interparticle separations. For each nanosphere size, the plasmon dipole resonance was calculated for 6 various interparticle separations. Representative calculated spectra are shown in **Figure 4.1.A**. Each separation results in a unique SPR extinction maximum. The fractional shift of the SPR maximum wavelength ($\Delta\lambda/\lambda$) is plotted as a function of the interparticle separation scaled by the size of the nanoparticle (diameter of the sphere), shown in **Figure 4.1.B**. Additional spectra and dipole coupling fits can be found in Appendix A.

This dependence has previously been explored$^{24}$ and mathematically found to obey the dependence:

$$\frac{\Delta\lambda}{\lambda} \left(\frac{s}{D}\right) = \frac{1}{\left(12\Lambda(s/D + 1)^3 - (1 + \gamma)\right)}$$

Equation 4.1
This dependence is very closely approximated as a single exponential decay of the form:

\[
\frac{\Delta \lambda}{\lambda} = A \times e^{-\left(\frac{s/D}{t}\right)}
\]

Equation A.2

Figure 4.1

Figure 4.1: (A) DDA simulation of the optical extinction of two nanospheres (D=40nm) at various interparticle separations. (B) The dipole plasmon coupling of two nanospheres measured as the fractional shift in the plasmon resonance (\(\Delta \lambda/\lambda\)) plotted as a function of the interparticle separation scaled by the diameter of the nanosphere. The red line is a single exponential decay best-fit to the data (\(R^2=0.98\)) of the form \(y = A\times\exp(-x/t)\). The values for the amplitude (A) and decay (t) are 0.04 and 0.22, respectively.

It is this exponential approximation that led to the formulation of the plasmon ruler equation \(^2^4\), where \(A = 0.18\) and \(t = 0.23\), which was successfully used to measure separations of nanosphere particles in solution using their optical extinction. Table 4.1 lists the decay values and amplitudes of the best-fit exponential decay approximation for a range of nanosphere sizes calculated using the DDA method. The decay values are plotted in Figure 4.2 as a function of the nanosphere volume. Over this size range (5 > D > 50 nm) the decay value has a negligible dependence on the size of the nanosphere. The
plasmon ruler equation is not greatly affected by the weak dependence of these fitting values on the nanosphere size when the size is D<50nm. The exponential decay length previously reported (t = 0.23) is the average value over this range. While this decay length does not significantly vary at small sizes (D < 50nm), caution is recommended when using nanospheres larger than 50nm in diameter since the deviation in the plasmon coupling could become significant.

Figure 4.2

Figure 4.2: The variation in the plasmon coupling decay length (t) and amplitude (A) of two gold nanospheres as a function of the nanosphere volume. Variation in both values as a function of volume is negligible within error.

Nanodiscs

Previously we have referred to the decay of the dipole plasmon coupling between particles as “universal”, being independent of the particle’s size and shape. This
conclusion was largely based on similarities in the value of the best-fit exponential decay for other shapes in addition to nanospheres, specifically nanodiscs, which were experimentally and theoretically determined. Here we have varied the dimensions of the nanodisc and computed the influence of the dimensions of the disc (thickness, volume) on the dipole plasmon resonance coupling. Table 4.2 displays various nanodisc dimensions and the respective decay values and amplitudes associated with them.

Table 4.1 – Au Nanospheres (DDA):

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Amplitude*</th>
<th>Decay Length*</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.039 ± 0.004</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>10.0</td>
<td>0.038 ± 0.003</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td>20.0</td>
<td>0.042 ± 0.006</td>
<td>0.22 ± 0.04</td>
</tr>
<tr>
<td>30.0</td>
<td>0.040 ± 0.003</td>
<td>0.24 ± 0.02</td>
</tr>
<tr>
<td>40.0</td>
<td>0.045 ± 0.004</td>
<td>0.22 ± 0.03</td>
</tr>
<tr>
<td>50.0</td>
<td>0.045 ± 0.004</td>
<td>0.21 ± 0.03</td>
</tr>
</tbody>
</table>

*εm = 1.00 (air)

The exponential values listed in Table 4.2 for nanodisc pairs are plotted in Figure 4.3. Variation in the nanodisc volume has a negligible effect on the nanodisc dipole coupling constants until the nanodisc diameter exceeds 75nm. When the diameter of the nanodisc becomes large (100nm) the decay constants slightly increase. As the thickness of the nanodisc is varied, there is also a negligible deviation in the exponential decay coupling values. It is worth noting, while the dependence of the dipole plasmonic decay values on the nanoparticle volume is extremely weak, there can be significant variation in the values when the nanodisc dimensions or aspect ratio (diameter / thickness) are excessively varied. The average exponential decay length for a nanodisc of an aspect ratio of 5 is 0.22 ± 0.02 (Figure 4.3.A) while the average exponential decay length of a large nanodisc (D = 100nm) averaged over several different aspect ratios is 0.30 ± 0.02 (Figure 4.3.B). These significant variations are attributed to an extreme change in the
nanodisc dimensions (shape), which has a significant effect on the strength of the induced plasmonic field\textsuperscript{40}. However, within a reasonable size range (Diameter = 10-75nm), the effects of the size on the nanodisc exponential coupling of a set aspect ratio and particle shape are negligible.

Figure 4.3

(A)

![Graph A](image1.png)

Variation in the Plasmon Coupling Decay of Nanodisc Thickness

- Decay Length
- Amplitude

Nanodisc Thickness (nm\textsuperscript{3})

(B)

![Graph B](image2.png)

Variation in the Plasmon Coupling Decay of Nanodisc Thickness

- Decay Length
- Amplitude

Nanodisc Volume (nm\textsuperscript{3})

Figure 4.3: (A) The dependence of the decay length (red diamonds) and amplitude (blue squares) of the dipole plasmon coupling between two nanodiscs as a function of nanodisc thickness. The diameter is held constant at 100nm. (B) The dependence of the decay length (red diamonds) and amplitude (blue squares) of the dipole plasmon coupling between two nanodiscs as a function of nanodisc volume. The aspect ratio of the discs (D/T) is held constant at 5.

It is worth noting that the experimental value for the decay length previously found for gold nanodiscs of D = 88nm and T = 25nm was 0.18 ± 0.02 and does not match the values reported here. We believe that this value does not fall within the range found in Table 4.2 because there are only a few data points provided to obtain the data experimentally\textsuperscript{24}, and none of the points fall around s/D = 1 where the greatest deviation occurs between the exponential fit and the true x\textsuperscript{3} dependence. Experimental data points in this region should result in a slightly larger best-fit single exponential decay length, consistent with our findings here.
Table 4.2 – Au Nanodisc (DDA)

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Thickness (nm)</th>
<th>Amplitude*</th>
<th>Decay Length*</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.0</td>
<td>20.0</td>
<td>0.17 ± 0.01</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td>75.0</td>
<td>15.0</td>
<td>0.13 ± 0.01</td>
<td>0.24 ± 0.03</td>
</tr>
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<td>50.0</td>
<td>10.0</td>
<td>0.11 ± 0.01</td>
<td>0.23 ± 0.03</td>
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<td>30.0</td>
<td>6.0</td>
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<td>0.22 ± 0.03</td>
</tr>
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<td>4.0</td>
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<td>0.21 ± 0.02</td>
</tr>
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<td>10.0</td>
<td>2.0</td>
<td>0.09 ± 0.01</td>
<td>0.21 ± 0.02</td>
</tr>
<tr>
<td>100.0</td>
<td>10.0</td>
<td>0.14 ± 0.01</td>
<td>0.33 ± 0.04</td>
</tr>
<tr>
<td>100.0</td>
<td>14.0</td>
<td>0.16 ± 0.02</td>
<td>0.30 ± 0.05</td>
</tr>
<tr>
<td>100.0</td>
<td>20.0</td>
<td>0.17 ± 0.01</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td>100.0</td>
<td>24.0</td>
<td>0.17 ± 0.02</td>
<td>0.27 ± 0.03</td>
</tr>
<tr>
<td>100.0</td>
<td>30.0</td>
<td>0.18 ± 0.02</td>
<td>0.26 ± 0.04</td>
</tr>
</tbody>
</table>

*ε_m = 1.00 (air)

Nanoprisms

We now move on to discuss the prismatic shaped nanoparticle and the effect of dimensional changes on the decay of the coupling between two nanoprisms oriented tip-to-tip. This dimer system is of interest to the field of molecular sensing due to predicted high fields at the nanop prism tip upon excitation at the surface plasmon resonance frequency\(^40\). This intense field is the foundation of surface enhanced spectroscopies on metallic surfaces, which have gained enormous attention recently\(^15,41,42\). Specifically, the enhancement factor for a surface enhanced Raman scattered photon is proportional to the enhancement of the field to the fourth power. The nanoprism is also of interest to the discussion here because of its unique symmetry compared with the other nanoparticle shapes studied, lacking a center of inversion.

The optical extinction for several equilateral nanoprism dimers of various volumes were theoretically computed using the DDA method. Table 4.3 lists the decay length and amplitude values of the best-fit single exponential curves fit to the fractional shift in the plasmon resonance wavelength as a function of scaled interparticle separation...
for various equilateral nanoprisms. The coupling values are plotted in Figure 4.4 as a function of the total volume.

Table 4.3 – Au Nanoprism (DDA)

<table>
<thead>
<tr>
<th>Bisector (nm)</th>
<th>Base (nm)</th>
<th>Thickness (nm)</th>
<th>Amplitude*</th>
<th>Decay Length*</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.4</td>
<td>81.0</td>
<td>19.8</td>
<td>0.11 ± 0.01</td>
<td>0.36 ± 0.05</td>
</tr>
<tr>
<td>57.1</td>
<td>66.6</td>
<td>16.3</td>
<td>0.10 ± 0.01</td>
<td>0.35 ± 0.04</td>
</tr>
<tr>
<td>38.1</td>
<td>44.4</td>
<td>13.0</td>
<td>0.09 ± 0.01</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td>17.3</td>
<td>20.2</td>
<td>5.9</td>
<td>0.09 ± 0.01</td>
<td>0.30 ± 0.03</td>
</tr>
</tbody>
</table>

*ε_m = 1.00 (air)

Similar to the nanodisc, there is a negligible increase in both coupling constants as the total volume of the nanoprism is increased. This is again due to higher order multipoles strengthening the dipole plasmon fields during plasmonic coupling. The interesting result here is that the average decay length is much higher for nanoprisms (0.33) than it is for either the nanodiscs (0.22) or the nanospheres (0.23). Physically, this result indicates that the surface field extends further out from the particle in nanoprisms than in nanodiscs and nanospheres, quantitatively 50% further. This phenomenon is due to high field intensities at the surfaces of nanoprisms due to the high curvature tip region.

These DDA simulations are compared to experimental nanoprism dimers of various separations fabricated by EBL. We have fabricated a near equilateral nanoprism shape that possesses some of the most extreme dimensions of this study, which results in the more extreme coupling values. Nanoprisms with large volumes and low aspect ratios (bisector/thickness) were used for this purpose. Scanning electron microscopy (SEM) images of the nanoprism dimers fabricated by electron beam lithography (EBL) are shown in Figure 4.5. Statistical analyses of the nanoprism dimensions were taken for more than 200 particles at the center of each array, in the same location where the optical spectra were taken. The average dimensions of two samples are given in Table 4.4. The radius of curvature for the nanoprisms was roughly 10 nm.
Figure 4.4

![Graph showing the dependence of decay length and amplitude on nanodisc volume.](attachment:image.png)

Figure 4.4: The dependence of the decay length (red diamonds) and amplitude (blue squares) of the dipole plasmon coupling between two nanoprisms as a function of nanoprism volume. The aspect ratio of the prisms (Bisector/Thickness) is held constant at 3.5. The “average” line drawn over the decay length data (red) includes the experimental data.

**Figure 4.6.A** shows the unaltered micro-absorption spectra of several nanoprism dimers from 200 nm to 14 nm interparticle separations. The irradiation light was polarized parallel to the interparticle axis for all spectra. The large decrease in intensity for the closest particles (14.4 nm separation) is due to some particle pairs fusing together at these shortest separations. When fusing occurs to form one large particle the optical extinction maximum shifts far to the red, outside of the field of analysis, and therefore does not affect the plasmon band position of the separated particles. For the least separated nanoprisms, the separation gap was $14.4 \pm 3.9$ nm. These measurements did not include the fused particle pairs with a gap = 0nm. For all other arrays of particle separations the error for the reported interparticle separation was less than 3.9 nm. **Figure 4.6.B** shows the experimental relationship between the coupling of the dipole plasmon resonance of the nanoprisms, monitored by the fractional shift in the plasmon resonance...
\(\Delta \lambda / \lambda\), as a function of the interparticle separation scaled by the nanoprism size. The experimental data is fit to a best-fit single exponential decay. We find that the exponential fit is a good approximation for nanoprism particles, evidenced by the high \(R^2\) fitting of 0.98. We report for the first time experimental evidence of the non-universality of the coupling decay constant seen in so many previous cases with more symmetric nanoparticle systems, which have a value between \(0.18 \leq \tau \leq 0.23 \pm 0.04\). It is clear that the experimental data for nanoprism does not fit this exponential decay value but decays with a value roughly 50% higher \((\tau = 0.35 \pm 0.02)\), as predicted by the DDA calculations.

**Table 4.4 – Au Nanoprism (Experimental)**

<table>
<thead>
<tr>
<th>Bisector (nm)</th>
<th>Base (nm)</th>
<th>Side (nm)</th>
<th>Thickness (nm)</th>
<th>Amplitude</th>
<th>Decay Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>87.0 ± 3.6</td>
<td>79.7 ± 2.8</td>
<td>89.2 ± 3.8</td>
<td>20 ± 1</td>
<td>0.13 ± 0.01</td>
<td>0.34 ± 0.02</td>
</tr>
<tr>
<td>83.0 ± 5.1</td>
<td>72.2 ± 2.7</td>
<td>81.4 ± 4.1</td>
<td>20 ± 1</td>
<td>0.12 ± 0.01</td>
<td>0.36 ± 0.02</td>
</tr>
</tbody>
</table>

The size of the nanoprism is defined by the prism bisector, which is used to scale the interparticle separation. It is beneficial to discuss the appropriateness of using the nanoprism bisector to describe the size. For all nanoparticles investigated in this way to date, the size of the particle has been intuitively defined as the length of the particle along the interparticle axis. For example, the size of a nanodisc is defined as the diameter of the disc. The loss in inversion symmetry for nanoprism requires that we justify the use of the bisector, since the plasmon oscillation occurs as two dipoles along each of the nanoprism sides, which has been both theoretically\(^{1,43}\) and experimentally\(^{40}\) determined when the polarization of the light is parallel to the nanoprism bisector, as is true in our case. This unique situation is not observed for the higher symmetry nanoparticles such as discs, spheres, and shells. Even the nano-ellipses studied by Su et al.\(^{23}\) possess only one established dipole that is parallel to both the interparticle axis and the incident polarization of light. Although the induced dipoles in the nanoprism are not oriented
parallel to the interparticle axis, the net summation of the vectors is along that axis and is the reason that the resonance coupling between the electrons of the metal nanoparticle and the electric field of the light occurs.

Figure 4.5

Figure 4.5: Nanoprism dimers fabricated by EBL with increasing interparticle separation 14.4, 23.1, 30.2, 34.7, 124.8, and 202.1 nm separation for A-F, respectively. The insert in 1A is one of many highly magnified SEM images that were used to take statistical measurements of the particle dimensions.
The optical extinction spectra for similar sized nanoprisms are simulated in Figure 4.7.A and the dipole plasmon coupling dependence on the interparticle separation is plotted in Figure 4.7.B. The blue shift in simulated spectra compared with the experimental spectra is likely due to the dielectric constant surrounding the nanoprisms. The experimental nanoprisms are supported on a silicon nitride substrate in ambient conditions, while the theoretical calculations assumed an environmental dielectric constant equal to that of air. While this has a great effect on the absolute plasmon resonant energies, the decay length and amplitude of the dipole plasmon coupling is nearly identical in the experimental and theoretical work.

Figure 4.6

Figure 4.6: (A) Experimental extinction spectra of selected nanop prism dimer pairs with various tip-to-tip interparticle separations. (B) Experimental results of the dipolar plasmon resonance coupling (Δλ / λ) between two nanoprisms oriented tip-to-tip as a function of the interparticle separation scaled by the particle size.

We also observed in all theoretical calculations and experimental spectra a strong deviation from the exponential approximation when the interparticle separation is equal to the nanoparticle size, \( \left( \frac{S}{D} = 1 \right) \). This deviation is very pronounced in the experimental
work, as can be seen in Figure 4.6, where the error bars for the data point \( \frac{S}{D} \approx 1 \) do not overlap the single exponential best-fit. This deviation was also observed for other theoretical studies for various particle shapes\(^{24,25,27}\), but this is the first reported experimental confirmation of that deviation. It has previously been explained as a deviation of the exponential approximation from the true cubic equation, derived elsewhere\(^{24}\). Caution is given when using the plasmonic ruler equation in the region of \( \frac{S}{D} \approx 1 \) due to the large deviation from the exponential approximation.

**Figure 4.7**

(A) DDA simulation of two nanoprism particles oriented tip-to-tip with various interparticle separations. Nanoprism dimensions match those of the experimental samples. (B) Single exponential best-fit curve demonstrating the theoretical relationship between the fractional dipole plasmon shift as a function of the scaled interparticle separation. Black squares are the data points obtained from DDA calculations.

**Nanocubes**

To emphasize the effect that intensified surface fields have on the dipole plasmon coupling between two nanoparticles, we have investigated the effect of size on the exponential coupling between two gold nanocubes. The fractional shift in the dipole
plasmon wavelength was plotted as a function of the interparticle separation scaled by the edge length of the nanocube when the nanocube sides are facing one another. The exponential decay values for the best-fit single exponential for various nanocube volumes are given in Table 4.5 and plotted in Figure 4.8 as a function of nanocube edge length. Similar to other shapes explored here, the size of the nanocube has a negligible effect on the decay length of the dipole plasmon coupling.

**Figure 4.8**

![Graph showing the dependence of the decay length (red diamonds) and amplitude (blue squares) of the dipole plasmon coupling between two nanocubes oriented side to side as a function of nanocube volume.](graph)

Figure 4.8: The dependence of the decay length (red diamonds) and amplitude (blue squares) of the dipole plasmon coupling between two nanocubes oriented side to side as a function of nanocube volume.

Like nanoprisms, the nanocube has regions of high curvature and it has been shown through electrodynamic calculations that the rectangular shape possesses strong fields around these high curvature areas\(^{44}\), more intense than a nanoprism. These intense fields lead to an even higher dipole plasmonic coupling decay length (0.37), larger than the nanoprism.
Table 4.5 – Au Nanocube (DDA)

<table>
<thead>
<tr>
<th>Edge Length (nm)</th>
<th>Volume (nm$^3$)</th>
<th>Amplitude*</th>
<th>Decay Length*</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1000</td>
<td>0.05 ± 0.01</td>
<td>0.35 ± 0.02</td>
</tr>
<tr>
<td>20</td>
<td>8000</td>
<td>0.05 ± 0.01</td>
<td>0.35 ± 0.02</td>
</tr>
<tr>
<td>30</td>
<td>27000</td>
<td>0.06 ± 0.01</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>40</td>
<td>64000</td>
<td>0.07 ± 0.01</td>
<td>0.41 ± 0.04</td>
</tr>
<tr>
<td>50</td>
<td>125000</td>
<td>0.10 ± 0.01</td>
<td>0.38 ± 0.04</td>
</tr>
</tbody>
</table>

* $\varepsilon_m = 1.00$ (air)

**Practical Applications of Nanoparticles as a Plasmon Ruler**

As a concluding discussion, we would like to point out that for general applications of the nanoparticle plasmon ruler the ideal nanoparticle size and shape selection should be a small nanosphere (D<50nm). The exponential decay constants used to approximate the dipole plasmon coupling of nanospheres in this size regime have a negligible dependence on the nanoparticle size, thus errors due to the dispersion in size will be minimized. Gold nanospheres are one of the easiest nanoparticles to homogeneously synthesize, making them practically preferable to other colloidal nanoparticle shapes. Smaller nanoparticles are preferred in biological systems because the structural perturbation of the biological system caused by the conjugated nanoparticles will be minimized.

For completion, it is important to discuss the advantages and disadvantages that the plasmonic ruler possesses compared to the traditionally used FRET technique. As mentioned in the introduction, FRET performs accurately in measuring inter-site distances of 1-10nm$^{29,30}$ while the nanoparticle plasmonic ruler operates on a much wider range of 5-100nm depending on the nanoparticle size and shape$^{24}$. The two techniques are complimentary to one another in this respect. However, the advantage of single molecule FRET is that the optical reporter is very small is size (molecular) and has a minimal perturbation effect on the structure of the system. Metallic nanoparticles used in the
plasmonic ruler technique are much larger than the molecular size used in their FRET counterparts.

While nanospheres generally will be the choice of particle shape in the plasmon ruler applications, the results here demonstrate that less symmetrical particle shapes with high curvature features such as tips and corners can increase the plasmonic coupling range. Particularly the large value of the decay length of the dipole plasmon coupling between nanoprisms oriented tip-to-tip and nanocubes oriented side to side ($\tau \sim 0.37$) compared to nanospheres or nanodiscs ($\tau \sim 0.23$) suggests that the probe range of nanoprisms is roughly 50% larger. **Table 4.6** summarizes the plasmonic near-field coupling between two homogeneous nanoparticles in terms of the best-fit exponential decay length of the coupling as a function of separation. This allows one to obtain the same measurement for smaller nanoprisms that would only be possible using larger nanospheres. For biological samples the smaller the nanoparticle antennas are that perform the measurement the less perturbation is introduced to its structure, and for this reason the prismatic or cubic shape would be preferred, as long as orientational dependence of the particles relative to one another is understood. Presently, a biologist using nanospheres does not need to concern themselves with orientation effects of the two spheres relative to one another. However, future studies are centered on investigating the orientational dependence of the exponential constants in low symmetry nanoparticles and nanoparticle systems to allow the nanoparticles to function not only as a 1-dimensional ruler but also as a 2 or 3-dimensional mapping agent for biological systems.
Table 4.6

<table>
<thead>
<tr>
<th>Nanoparticle Shape</th>
<th>Decay Length (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold Nanosphere</td>
<td>0.23 ± 0.03</td>
</tr>
<tr>
<td>Gold Nanodisc (Dia/Th = 5)</td>
<td>0.22 ± 0.03</td>
</tr>
<tr>
<td>Gold Nanoprism (tip-to-tip)</td>
<td>0.35 ± 0.03</td>
</tr>
<tr>
<td>Gold Nanocube (side to side)</td>
<td>0.37 ± 0.03</td>
</tr>
</tbody>
</table>

Conclusions

We have found experimental evidence and computational support of the shape dependence of the dipole plasmon coupling on distance between pairs of gold nanoparticles. This coupling has been quantitatively described by the fitting parameters of a best-fit single exponential decay of the fractional shift in the wavelength of the dipole surface plasmon resonance of the particle pair as a function of the interparticle separation scaled by the nanoparticle size. The two fitting parameters are the amplitude and the decay length. The amplitude physically describes the maximum fractional shift, which occurs at zero separation of the pair and is proportional to the maximum value of the overlapping field strength of the two particles. The decay length is the length over which the combined field decays as the pair moves away from one another. From these results, we conclude that nanospheres below D=50 are generally the most practical nanoparticle shape to use as a plasmonic ruler. Other nanoparticle shapes of stronger plasmonic fields (such as nanocubes and nanoprisms) can be used to extend the measurement to longer inter-sight binding separations. However, orientational control over these less symmetric particles must be understood, since variations in the particle orientations can likely result in changes in the exponential plasmonic coupling decay length. Work is currently being carried out to better understand the dependence of the exponential decay length on the particle orientations.
Acknowledgment

This work was supported by the Materials Research Division of the National Science Foundation (no. 0138391). We thank B. T. Draine and P. J. Flatau for use of their DDA code, DDSCAT 6.1 and Cheng-Tsung Lee for supplying the Si$_3$N$_4$ substrates.

**Note: For all plots that include a near-exponential dependence, the data can also be plotted on a logarithmic scale with a best-fit linear function. Several plots such as these are presented in Appendix B with the corresponding linear plot for comparison.**
References


(9) Huang, W.; Qian, W.; El-Sayed, M. A. Advanced Materials (Weinheim, Germany) 2008, 20, 733-737.


CHAPTER 5

THE EFFECT OF ORIENTATION ON PLASMONIC COUPLING BETWEEN GOLD NANORODS

Abstract:

Radiative coupling of induced plasmonic fields in metal nanoparticles has drawn increasing attention in the recent literature due to a combination of improved experimental methods to study such phenomena and numerous potential applications, such as plasmonic nanoparticle rulers and plasmonic circuitry. Many groups, including ours, have used a near-exponential fit to express the size-scaling of plasmonic coupling. Firstly, we show experimental agreement between previously simulated nanorod coupling and plasmonic coupling in electron beam lithography (EBL) fabricated nanorods using the near-exponential expression. Next, we study the effect of nanoparticle orientation on plasmonic coupling using EBL and DDA simulations. We develop a mathematical relationship that is consistent with our findings, and quantitatively describes plasmonic coupling between nanorods as a function of orientation, separation, induced dipole strength, and the dielectric constant of the medium. For applications utilizing plasmonic coupling to become viable with particle shapes that do not have spherical symmetry, such as nanoprism and nanorods, comparison of the experimental and theoretical results of how particle orientation affects plasmonic coupling is essential.
Introduction

Noble metal nanoparticles are exciting materials because their conduction band electrons couple with light in the visible to near IR region of the electromagnetic spectrum. The electric field of the light induces a coherent oscillation of electrons on the surface of the particle that is resonant with the excitation frequency. The resonance reaches a maximum value at specific frequencies, identified as dipole, quadrupole, etc… For particles that are small with respect to the wavelength of light (r < ¼*λ), the dipole resonance dominates the spectral signature of the particle. The resonant energy of this dipole transition in a single nanoparticle is a function of the dielectric medium in which the nanoparticle is embedded, the shape and size of the nanoparticle, and the specific plasmonic metal. By changing these variables, one can tune the optical properties of a single noble metal nanoparticle. This tunability of the localized surface plasmonic resonance (LSPR) frequency and the intense localized field induced at the nanoparticle surface in noble metal nanoparticles gives them enormous potential in medical\textsuperscript{1-3}, optical\textsuperscript{4-7}, and sensor\textsuperscript{8-12} applications.

As two particles approach one another, the intense near-fields at the surface of the particles overlap and couple with one another strongly affecting the plasmonic resonance energies. The coupling between two degenerate plasmonic modes has been discussed as an analogy to molecular exciton coupling theory (MECT)\textsuperscript{13-16}, which describes the splitting of an excited state energy level into two eigenmodes, one at higher energy and one at lower energy, whose separation is approximated by the Simpson-Peterson equation. Similarly, when two nanoparticles come into contact with one another, the individual dipole modes couple to produce two new dipole resonances, one at a higher energy and one at a lower energy, associated with the dimer system. For tip-to-tip oriented rods, the higher energy hybrid dipole is forbidden, due to the net dipole being equal to zero. The lower energy hybrid dipole is stronger in intensity and the fractional
shift in the resonance wavelength is a measure of the degree of coupling between the two particles.

While there are commonalities between the Simpson-Peterson approximation with near-field coupling of plasmonic nanoparticles, this model assumes that the excitation is a single dipole state, and the coupling occurs only between these two dipoles. Plasmonic excitations, while predominantly dipolar at large separations, have contributions from higher order multipoles as well, especially at decreasing separations. These higher order resonances can be seen clearly in anisotropic particles such as nanoprisms. This point has been evidenced in the literature by numerous researchers that fit the decay of the plasmonic field coupling with separation to an exponential function instead of the $R^{-3}$ functional dependence predicted by the dipole-dipole model. In these papers, the exponential fit is only used to approximate the functional dependence of the dipole coupling on separation and should be used prudently, since the exponential fit to the data in the range of $1.5 \times S \leq R \leq 2.5 \times S$ and $R \leq 1.1 \times S$ is poor. However, the near-exponential description of the plasmonic coupling does facilitate its application by providing a straight-forward model that expresses the relationship, and this model has been used to predict the separation of plasmonic nanoparticles using their optical signal.

The shift in the resonance energy with decreasing interparticle separation was first studied by Su et al. and Rechberger et al., who independently demonstrated that near-field coupling red-shifts the dipole resonance frequency. The near-field coupling was quantitatively measured by the fractional shift in the dipole resonance wavelength ($\Delta\lambda/\lambda$), which decayed near-exponentially with separation. Later, the exponential decay length ($\tau$) in units of the particle size was found to be consistent among several nanoparticle shapes (Equation 5.1), such as nanospheres, nanodiscs, and nanoshells. This method of describing the plasmonic coupling as a near-exponential function of separation was an attempt to simplify the convoluted coupling that occurs not only between plasmonic dipoles (which theoretically couple as a function of separation such as: $R^{-3}$).
but also higher order multipoles as the separation decreases. This near-exponential trend also highlighted the common size scaling of many symmetric nanoparticle shapes by reporting the decay length of the coupling ($\tau$) in units of the particle size and the commonality of this value for various nanoparticle sizes. It was first postulated that this decay length was universal for all shapes of nanoparticles, however it has since been shown in the literature that this value can vary with particle shape, and is larger for some shapes, such as the nanoprisms.  

$$ \left( \frac{\Delta \lambda}{\lambda} \right) = A \times e^{\left( \frac{-s/D}{\tau} \right)} $$  

**Equation 5.1**

While these studies have investigated the coupling between two plasmonic nanoparticle dimers, they have all been limited in scope to ideally oriented particles, save for one recent publication. In this work, Funston et al. found a nice correlation between the single particle / dimer optical signal of distributed colloidal nanorod dimers and DDA simulations of various orientations. They found that for very small separations ($R/S < 0.09$) that the exponential fit is not accurate. In addition, some very nice hybridization schemes were presented for particular orientations of nanorods with respect to one another. For applications such as the plasmonic ruler and sub-wavelength optics, it is helpful to investigate the plasmonic near-field coupling of nanoparticles with anisotropic shapes when the orientation is systematically varied and at larger separations.

In this paper, we use electron beam lithography to form two-dimensional arrays of pairs of nanorods with different distances and orientation and measure the positions of their surface plasmon extinction. We discuss the observed plasmonic coupling in nanorod dimers, with systematically varied separations and rotational geometries, in order to understand and model the coupling between less than ideally oriented anisotropic nanorods, specifically when one rod is rotated around its center of mass. We discuss the
advantages to modeling plasmonic coupling with the plasmonic hybridization model (the analog to MECT) and modify the Simpson-Peterson approximation to incorporate the plasmonic near-field coupling dependence on four variables; separation, orientation, induced dipole size, and medium dielectric. We also discuss previous observations of nanoprisms that possess a stronger coupling at larger distances compared with discs and spheres of the same size as additional support for the model.

**Experimental**

Nanorod arrays were fabricated using a JEOL JBX-9300FS 100kV electron beam lithography (EBL) system. The substrates used to support the nanoprisms were prefabricated free standing silicon nitride membranes whose fabrication has been described in detail elsewhere\(^3\). Briefly, silicon wafers with a <100> orientation were purchased from University Wafer and cleaned and placed in a Tystar Furnace. \(\text{Si}_3\text{N}_4\) was deposited onto the wafer surface using a low-pressure chemical vapor deposition process at a deposition rate of 5 nm / min to a final thickness of 50 ± 3 nm. A combination of optical photolithography and dry etching with \(\text{CF}_4\) removed selected areas of the membrane from one side of the wafer. These areas were exposed to KOH to anisotropically etch the silicon wafer through to the other side, exposing the other silicon nitride membrane. This process produced an array of silicon nitride membrane windows freely supported that were 150 x 150 \(\mu\text{m}^2\). Each window was used for a single design pattern and each pattern array was 300 x 300 \(\mu\text{m}^2\) in order to ensure pattern overlap with the window. A poly-methyl methacrylate (PMMA) positive electron resist was spin coated onto the top \(\text{Si}_3\text{N}_4\) side of the wafer to a thickness of 80nm. A dose of 2750 \(\mu\text{C/cm}^2\) was used to write the pattern at a beam current of 1.98 nA. Development of the exposed areas was carried out in a 1:3 methyl isobutyl ketone: isopropyl alcohol (MIBK:IPA) solution for 10 seconds. The sample was then washed in IPA for 30 seconds before gently drying in a stream of \(\text{N}_2\). A thin chrome layer (0.5 nm @ 0.1 A/sec) was
evaporated onto the sample using a CVC electron beam evaporator followed by a 20.0 nm layer of gold at a rate of 0.5 A/s. The Cr served as an adhesion layer between the Si₃N₄ surface and the Au nanoparticles. Final lift-off and removal of the PMMA mask was accomplished by placing the sample in 1165 remover purchased from MicroChem for 24 hours. The array was designed so that the nanoparticle dimer pairs were spaced more than 800 nm from one another to reduce far-field coupling that has been observed by Rechberger et al.²² in 150 nm diameter gold nanodisc arrays. This far-field coupling has been shown by the Moerner group to exist at large separations (5-7 particle lengths). For this reason, individual particle dimers were experimentally spaced no less than 8 particle diameters apart and no interparticle separations were used greater than 5 particle lengths. In these experimental samples with small interparticle gaps (20-300 nm), the near-field coupling can be expected to be much stronger than any far-field grating effects.

The supported nanorods were imaged using a Zeiss Ultra60 Scanning Electron Microscope (SEM). Extinction measurements were performed on a Craic 1100 microspectrophotometer in transmission mode under polarized light (along the interparticle axis) using a 5x magnification. The collection spot was ~32.0 x 32.0 µm² and several different areas were collected from the center of the array and averaged to produce the reported spectra. A comparison between magnified SEM images from various membrane windows show excellent homogeneity in the particle shapes and sizes as the spacing and orientation is varied.

The optical response of the nanoparticle dimer systems has been calculated using the DDA method with the DDSCAT 6.1 code publicly offered by Draine and Flatau³¹ and modified by Goodman³² and Schatz³³. The method has been described in great detail elsewhere³⁴. Briefly, the method approximates the desired particle shape as a 3-dimensional cubic lattice of polarizable point dipoles of pre-programmed dipole-dipole spacing. The program solves for the scattering and absorption of each polarizable point self-consistently in response to an incident plane polarized field and polarization of
neighboring dipole points. The bulk values of the dielectric constants reported by Johnson and Christy\textsuperscript{35} for gold were used. The DDA method has been demonstrated by many groups\textsuperscript{36-39} to be suitable for optical calculations of the extinction spectrum and the local electric field distribution in metal particles with different geometries and environments. The incident light is always polarized parallel with the interparticle axis in this report and the dielectric of the host medium was set at $\varepsilon_m = 1.00$. As discussed by Rechberger et al.\textsuperscript{22}, it is reasonable to consider the calculations of a single particle pair instead of the entire 2-D array. This consideration is justifiable because the particle pairs in the experiment are separated from each other by large distances on the order of 8 particle diameters, large enough so that no coupling occurs between different particle pairs. This ensures that only the interactions between the two particles within the dimer are measured.

**Results & Discussion**

**Tip-to-tip coupling between nanorods**

We first investigated nanorods oriented tip-to-tip and the relationship between interparticle separation and the degree of coupling between the longitudinal plasmon resonances. This has previously been studied qualitatively in colloidal solutions\textsuperscript{13,40,41} and quantitatively through DDA simulations\textsuperscript{19,24}, but has not yet been systematically reported experimentally. A few representative SEM images of the nanorod dimers oriented tip-to-tip are shown in Figure 5.1 (A-C). Statistical measurements were performed on all of the nanorod arrays to ensure that the size distribution was homogeneous. The average magnitude for the length and width of the nanorods was 66.4 ± 1.7 and 37.6 ± 1.8 nm, respectively and the thickness was 18nm. By measuring the extinction spectra of the nanorod dimers, we verified that the plasmonic coupling obeys the predicted red-shift in a near-exponential fashion. The experimental data points are shown in Figure 5.1.D (black squares) and a DDA simulation of the exact particle size and shape is shown for
completion (green triangles). Using the best-fit exponential function shown in Equation 5.1, the decay length was confirmed to be $\tau = 0.20 \pm 0.03$, in agreement with previous simulations$^{24}$ (dashed blue line). **Figure 5.1.E** shows the experimental extinction spectra of 7 nanorod samples with varying interparticle separation.

**Figure 5.1**

![Figure 5.1](image)

Figure 5.1: (A-C) SEM images of gold nanorod dimer arrays fabricated by EBL with various interparticle separations: 20.9, 72.3, and 286.7nm. The scale bar in the top left corner of A is 100nm. The inset in A is a 400kX magnification of a nanorod dimer. The scale bar in the inset is 30nm. (D) Plasmonic coupling ($\Delta \lambda / \lambda$) shown as a function of interparticle separation in units of the nanorod length for experimental EBL fabricated (black squares) and DDA simulated particles (green prisms). Two fits are presented, the exponential model with a decay length of $\tau = 0.20$ (red solid line) and a derived fit shown in Equation 2 of the paper (blue dashed line). (E) Experimental extinction spectra of 7 different nanorod dimers showing the spectral plasmonic shift from 757-804 nm.
While the exponential fit has been used to nearly approximate the decay of plasmonic coupling with separation, it has consistent deviations from the data, which have been discussed previously. A more accurate relationship has been derived in the supplementary information of Ref. 21. This functional relationship between the fractional shift in the resonance wavelength and the separation between particles is presented in Equation 5.2:

\[
\left( \frac{\Delta \lambda}{\lambda} \right) = \frac{1}{12\Lambda \left(1 + \frac{R}{S}\right)^3 - (1 + \gamma)}
\]  

\textbf{Equation 5.2}

where \(\Lambda\) and \(\gamma\) are shape factors that are determined by the shape and size of the plasmonic nanoparticle, \(R\) is the separation between the centers of the plasmonic fields (typically approximated as the centers of the nanoparticles) and \(S\) is the size of the nanoparticle. Figure 5.1.d shows a second best-fit line using Equation 5.2 (blue dashed line), which has a much better fit to the data, both experimental and theoretical, compared with the exponential fit. The comparison between these two fits demonstrates two points; (1) the approximation of the exponential model in predicting separations between nanoparticles and (2) the necessity for a better mathematical description of the plasmonic field coupling as a function of particle separation. While the exponential decay model has been used to successfully approximate plasmonic coupling\textsuperscript{21}, we point out here that a more accurate mathematical relationship, such as Equation 5.2, would provide a better fit and be an improvement in the critical regions such as center-to-center separations of 1.5-2.5 in units of the particle size. An interesting note is that the parameter \(\Lambda\) is equal to \(1/3\) in the fit using Equation 5.2, which is nearly the value predicted for a nanorod of this size (\(\Lambda = 1/\text{aspect ratio}\)). The small divergence probably exists due to the shape not being an ideal oblate spheroid, but a flattened rod.
According to MECT, the energy splitting ($2U$) between two hybridized modes was originally discussed for molecular dipole excitations by Kasha et al.\textsuperscript{16} and is given by the Simpson-Peterson approximation\textsuperscript{15} (Equation 5.3),

$$U = \frac{|\mu|^2}{\eta^2 \times R^3} \times |\kappa|$$  \hspace{1cm} \text{Equation 5.3}

where $\mu$ is the transition dipole moment of the system, $\eta$ is the refractive index of the medium, $R$ is the center-to-center separation between dipoles, and $\kappa$ is an orientation factor. Previously, plasmonic coupling has been qualitatively described using a hybridization model analogous to MECT\textsuperscript{14,19}, shown in Figure 5.2. An analogous equation to the Simpson-Peterson approximation is developed here that quantitatively describes the hybridized energy levels using independent variables, separation ($R$), dipole module ($\mu$), medium refractive index ($\eta$), orientation ($\kappa$). The Simpson-Peterson approximation will be used as a starting point for the development of such an equation.

\textbf{On the role of nanoparticle orientation on Plasmonic Field Coupling}

Next, we report on the plasmonic coupling between non-ideally oriented nanorods. The anisotropic nature of the nanorod and other anisotropic nanoparticle shapes could lead to superior plasmonic applications\textsuperscript{19}, like the plasmon ruler and plasmonic waveguides. However, for anisotropic nanoparticles to be useful in plasmonic applications, the coupling must be understood as a function of particle orientation. We systematically studied the normalized optical extinction of the nanorod dimer pairs with polarized light along the interparticle axis with one nanorod positioned at varying angular orientations with respect to the interparticle axis. Representative SEM images of the nanorod dimers at different orientations are presented in Figure 5.3. The extinction
wavelength for each rotation in Figure 5.3 was measured using a micro-spectrometer and the spectra are shown in Figure 5.4.A. As one of the nanorods is rotated around its center of mass and the incident polarization is held constant along the interparticle axis, the hybridized plasmonic dipole along the interparticle axis blue shifts as the coupling between the nanorods is reduced.

Figure 5.2

A.) Molecular Exciton Coupling Theory:

B.) Plasmonic Hybridization Theory:

Figure 5.2: A.) Molecular exciton coupling theory (MECT) scheme depicting hybridized excited energy levels separated by 2U, where U is given in Equation 5.3. B.) Plasmonic hybridization theory (PHT) scheme depicting the analogous hybridized excited energy levels separated by 2V, where V is given below in Equation 5.10.
Figure 5.3: SEM images of nanorod samples fabricated by EBL with one rod rotated with respect to the interparticle axis by various angles (θ) indicated in the top left corner of each image.

The localized surface plasmon resonance is strictly a surface event, where-by the conduction band electrons oscillate in resonance on the surface of the nanoparticle. Therefore we investigate the possibility that the decoupling of the plasmonic modes as one rod is rotated is due to a resulting increase in separation between the nanorod surfaces. The experimental data depicting the relationship between plasmonic coupling and the minimum surface-to-surface separation is plotted in Figure 5.4.B. The data for
the unrotated nanorod dimers with increasing separation is plotted with black squares. The red line is the best-fit curve in this region. The blue diamonds are the smallest surface-to-surface separation in the nanorod dimers where one rod is rotated. A linear best-fit line is shown in blue for the eye to follow. It is clear from this data that the plasmonic coupling dependence on orientation is distinct from the dependence on strict surface-to-surface separation.

The relationship between the angle of rotation and the fractional shift in the wavelength is shown in Figure 5.4.C. The experimental data points are shown as black squares and the DDA simulations are shown in green triangles. The fractional wavelength shift is normalized to the maximum shift (0°, 180°, and 360°) and the red line is the best-fit \( \cos^2(\theta) \) function, with an \( R^2 \) fitting value of 1.00 and 0.96 for the simulated and experimental data, respectively. We note here that the data was also fit to a \( \cos(\theta) \) function, but the agreement with the data was much poorer.

This relationship can be explained using the orientation factor \( (\kappa) \) presented in the Simpson-Peterson approximation in MECT,

\[
\kappa = \cos \theta_{12} - 3 \cos \theta_{1R} \cos \theta_{2R} \tag{Equation 5.4}
\]

The value \( \theta_{12} \) is the angle between the two dipole vectors and the values \( \theta_{1R} \) & \( \theta_{2R} \) are the angles between respective dipole vectors 1 & 2 and the interparticle axis that connects the dipole centers. In the case presented here, \( \kappa \) is simplified to \( \kappa = -2 \cos \theta \), where \( \theta \) is the rotation of one nanorod around a fixed point with respect to the interparticle axis.
Figure 5.4: (A) Optical extinction of two gold nanorods separated by a center-to-center distance of 110nm with various relative orientations. The light is polarized parallel to the interparticle axis as is depicted in the inset while one nanorod is rotated by some angle (θ) from the interparticle axis. When θ = 0° the long axes of the nanorods are parallel and when θ = 90° the long axes of the nanorods are perpendicular. (B) Fractional wavelength shift of the coupled nanorods as a function of surface-to-surface separation. The blue data points are the nearest separation between the nanoparticle surfaces as one nanoparticle is rotated, indicating that the coupling is not functionally dependent on the surface-to-surface separation. (C) Experimental (black squares) and simulated (green triangles) plasmon coupling between two nanorods as a function of relative rotation of one nanorod around its center of mass. The plasmon coupling dependence follows a $\cos^2(\theta)$ dependence due to the coupling of the vector components of the dipole plasmons along the interparticle axis. The best fit functional dependence is $(\Delta \lambda / \lambda) \propto \cos^2(\pi \theta / w)$, with an $R^2 = 0.96$ & 0.99 for the experimental and simulated data, respectively.
Additionally, when the light is polarized along a fixed direction, as is the case in both the DDA simulation and the experimental work presented here, the magnitude of the hybridized transition dipole modulus of the dimer system is a function of the orientation of the rods in the dimer. This value can be calculated by summing the oscillator frequencies or the two rods. The oscillator frequency \( f \) is directly proportional to the square of the transition dipole modulus \( \mu \), where the modulus is a function of the rotation angle of the one nanorod as it is rotated around its center of mass.

\[
\mu = \varepsilon_m \hat{E} \alpha
\]  
\text{Equation 5.5}

In \textbf{Equation 5.5}, \( \varepsilon_m \) is the electric permittivity of the medium, \( \hat{E} \) is the incident electric field applied to the nanoparticle system, and \( \alpha \) is the dipole polarizability of the nanoparticle, shown in \textbf{Equation 5.6};

\[
\alpha = 3\varepsilon_0 \left( \frac{\varepsilon - \varepsilon_m}{\varepsilon + \kappa \varepsilon_m} \right) V
\]  
\text{Equation 5.6}

Here, \( \varepsilon \) is the dielectric permittivity of the nanoparticle material, \( \kappa \) is a shape dependent variable, and \( V \) is the volume of the particle.

The total oscillator frequency \( f_{TOT} \) of the nanorod dimer can be calculated by summing the component oscillator frequencies of each dimer pair\textsuperscript{16}:

\[
f_{TOT} = f_1 \cos \theta_1 + f_2 \cos \theta_2
\]  
\text{Equation 5.7}

For all dimers in this work \( f_1 = f_2 \) since the nanorods in the dimer are identical. In the case where the nanorods are oriented tip-to-tip \( \theta_1 = \theta_2 = 0 \) and
\( f_{TOT} = f_1 + f_2 = 2f \). In the case where one nanorod is rotated by some angle \( \theta \) away from the interparticle axis, the oscillator strength along that axis is reduced by a factor \( \cos(\theta) \), and
\( f_{TOT} = f (1 + \cos(\theta)) = 2f \). Therefore, the square of the allowed component of the total dipole transition modulus is expressed in Equation 5.8.

\[
\mu_{TOT}^2 \propto f_{TOT} = f (1 + \cos(\theta)) \quad \text{Equation 5.8}
\]

The full dependence of the hybridized energy separation on the rotation of one nanorod in a nanorod dimer away from the interparticle axis by \( \theta \) is thus,

\[
V[\theta] = |1 + \cos(\theta)| \times |\cos(\theta)| = |\cos(\theta) + \cos^2(\theta)| \quad \text{Equation 5.9}
\]

In summary, the two contributions \(|1 + \cos(\theta)| \) and \(|\cos(\theta)| \) to the rotational dependence in Equation 5.9 originate from 1.) the induced transition dipole \( (\mu) \) coupled with the incident field polarization and 2.) the orientation factor \( \kappa \), which accounts for the coupling between the two fields with respect to one another. As mentioned previously, MECT predicts that the degenerate excited states of excitons in a dimer are split into two energy levels, one at higher energy and one at lower corresponding to the symmetric and anti-symmetric relative dipole orientations, respectively (shown in Figure 5.2). Equation 5.9 is plotted in Figure 5.5 for hybridized mode 1 (anti-symmetric mode) and hybridized mode 2 (symmetric mode) and is shown to very nearly overlap with the \( \cos^2(\theta) \) dependence fit to the data in Figure 5.4.C (black line). Note that due to symmetry hybridized mode 2 is 180° out of phase with hybridized mode 1.
Figure 5.5: The close agreement between a $\cos^2(\theta)$ which fits the data in Figure 5.4 (black line) and the mathematically derived full functional dependence of the plasmonic hybridized energy level (fractional shift in the plasmonic resonance wavelength) on rotation angle of one nanorod around a central pivot point. There are two hybridized modes, anti-symmetric (HM1) and symmetric (HM2). The only net contribution occurs when both dipoles are constructively interfering.

The diagram in Figure 5.2.B depicts two plasmonic resonance modes at different energy levels. We have predominately discussed the anti-symmetric mode (lower energy) of the dimer system so far in this article. The symmetric mode (higher energy) is often
referred to as the “dark plasmon” mode since the net dipole moment of the system is zero and is not spectroscopically observable. Upon rotation of one nanoparticle the net dipole of the dark plasmon becomes non-zero. However, this resonance mode remains unobservable here in the experimental and simulation, which is consistent with the mathematical derivation in Equation 5.9, as the constructively coupling mode (HM 1 when \(0 < \theta < 90^\circ\) & \(270 < \theta < 360^\circ\); HM 2 when \(90 < \theta < 270^\circ\)) is the dominant mode. This is more clearly observed in Figure 5.5 where the contribution to the energy shift of the destructively coupling mode is very small.

The effect of the dipolar modulus on plasmonic coupling

An important issue of the plasmonic nanoparticle ruler application has been the report of a slower decay of the plasmonic coupling than predicted by either the exponential or \(R^3\) relationships. This can be observed in the spectra reported here (Figure 5.1.D) and many other reported simulation and experimental data sets, generally around \(R/D \sim 2\). Additionally, it was pointed out that at very small interparticle separations (surface-to-surface separations < 5nm) the lower energy hybridized plasmonic band shifts more rapidly to lower energy than is predicted by the single exponential function used by many groups. Both of these phenomena need to be accounted for to obtain a more practical model of the plasmonic near-field coupling. The Simpson-Peterson approximation (Equation 5.3) indicates that the shift in energy from the monomer excited dipole energy to the hybridized excited dipole energy is proportional to the square modulus of the transition dipole for MECT. However, for near-field plasmonic coupling, the x-component of the transition dipole (along the interparticle axis and parallel with the electric field of light) increases nearly exponentially as the separation between nanoparticles decreases (not shown), due to increased coupling between the dipole and quadrupole modes. Qualitatively, this phenomenon explains the
increased energy shift in the hybridized excited plasmon resonance compared with the $R^{-3}$ dependence for two coupling dipoles.

Recently we published an article investigating the near-field dipole coupling between nanoprisms, and the induced energy shift of the hybridized excited plasmonic mode. We reported that the range of plasmonic coupling was larger for nanoprisms compared to nanospheres and nanodiscs of comparable size. This was quantitatively measured by the decay length of the plasmonic coupling ($\tau$) using the best-fit exponential decay function, and was quantitatively reported to be 50% larger in prisms ($\tau = 0.35$) compared to discs ($\tau = 0.22$). Pragmatically, this means that nanoprisms have a larger measurement range than nanodiscs and nanospheres with comparable sizes, and smaller particles can be used which lead to less perturbation in the substrate. This result is qualitatively explained by comparing the transition dipole modulus of the nanoprisms to the transition dipole modulus of the nanodisc of relatively the same size.

Using the DDA method, we have compared the transition dipole moduli of these two shapes in Figure 5.6, which is directly proportional to the intensity of the extinction band. The simulated nanoprism and nanodisc shapes both had a size of 75nm, which corresponds to the respective bisector and diameter, and a thickness of 20nm, (inset of Figure 5.6). The intensity of the dipole resonance extinction band for the nanoprisms is roughly 80% larger than that of the nanodisc of equal size. Thus, the fractional shift in the hybridized plasmonic mode for two nanoprisms will be more strongly shifted at a given interparticle separation than for two nanodiscs, for equally sized particles.

There has been a recent publication from our group describing the affect of varying the dielectric medium of the nanoparticles on the sensitivity or degree of plasmonic field coupling. This report indicates that the near-field dipole coupling between particles increases with an increasing dielectric medium. This conclusion is consistent with the Simpson-Peterson approximation. The hybridized energy shift is predicted to be inversely proportional on the square of the refractive index of the medium
and directly proportional to the transition dipole modulus. As defined in Equation 5.5, the transition dipole modulus is directly proportional to the electric permittivity of the medium ($\varepsilon_m$), which is nearly equal to the square of the refractive index of the medium in the limit of the magnetic permeability equal to 1. Thus the full dependence of the hybridized energy shift ($V$) on the refractive index of the medium should be $U \propto \eta^2$.

Figure 5.6

Figure 5.6: Comparison of the extinction intensity of a nanodisc (red dashed) and a nanoprism (black solid). The intensity of the dipole plasmonic mode is ~80% stronger for the nanoprism than for the nanodisc, and thus the nanoprism transition dipole modulus is roughly 80% greater. The sizes of the particles are comparable (bisector = diameter = 75nm, height = 20nm) and the dipole spacing in both cases is 1nm.

With these considerations, in addition to the orientation and separation results discussed in the previous sections, the Simpson-Peterson approximation that
quantitatively describes the hybridized energy level splitting in MECT can be modified to approximate the hybridized energy level splitting between near-field coupled plasmonic fields. **Equation 5.10** gives the modified version of this equation for identical nanoparticles:

\[
V \approx \frac{\Delta \lambda}{\lambda} \propto \eta^2 \times |\mu|^2 \times |\kappa| \times \Gamma
\]

**Equation 5.10**

where \(\eta\) is the refractive index of the medium, \(\mu\) is the transition dipole module, \(\kappa\) is the orientation factor and is defined as:

\[
\kappa = \varphi * (\cos \theta_{12} - 3\cos \theta_{1R}\cos \theta_{2R})
\]

**Equation 5.11**

where \(\varphi = (\cos \theta_{1P} + \cos \theta_{2P})\), and 1 and 2 represent the axis of the induced plasmonic dipole, \(R\) is the interparticle axis, and \(P\) is the polarization axis of the light. The last term in **Equation 5.10**, represents the functional dependence on the separation of the plasmonic fields. Several different functions can be used, including an exponential (**Equation 5.1**) or a more complex but fundamentally derived fit, for example **Equation 5.3**.

The two functions presented here (**Equations 5.1 & 5.2**) are limited in scope and have certain drawbacks that must be considered when using them. The exponential fit is only a near approximation and has a poor fit when \(1.5 < R/D < 2.5\), while **Equation 5.3** has two variables that must be accurately computed for the shape of the particle. Both equations must be taken as approximations only above moderate separations \((s > 1.1*D)\), since below this separation the coupling increases more rapidly than either model predicts, due to higher order multipole coupling. Future work should focus on analytically deriving this function that includes higher order multi-pole coupling and the
influence of separation on the transition dipole module, \( \mu \). This would prove to be a beneficial addition to the model and assist towards the integration of plasmonic nanoparticles in applications.

**Conclusion**

In conclusion, we report that the near-field electromagnetic coupling of two plasmonic nanorods can be modeled as a function of orientation by using the \( \kappa \) function that is taken from the Simpson-Peterson approximation that is used in MECT. The plasmonic field coupling was experimentally shown to have approximately a \( \cos^2(\theta) \) dependence on the orientation of one nanorod with respect to a neighboring nanorod, where \( \theta \) is the angle between the interparticle axis and the axis of the longitudinal plasmonic mode of the rotated nanorod. This relationship was also theoretically confirmed using DDA simulations. A model equation was presented, based on the Simpson-Peterson approximation, whereby the coupling of the plasmonic fields is a function of four variables, namely the, the separation between nanoparticles, the transition dipole module induced, the refractive index of the medium, and the relative orientations of the nanoparticles. In agreement with previous DDA work\(^{25}\), the best-fit exponential decay length was experimentally verified to be \( \tau = 0.22 \) in units of the nanorod length. From this work, we present some of the first systematic studies of orientation dependence of the plasmonic coupling between two nanoparticles, identifying a new method to not only map nanometer distances in 1 dimension, but potentially expanding the application to a powerful 2 or 3 dimensional mapping technique solely utilizing optical spectra of the nanoparticles.
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CHAPTER 6

SERS ENHANCEMENT BY AGGREGATED SILVER NANOCUBE MONOLAYERS ASSEMBLED BY THE LANGMUIR-BLODGETT TECHNIQUE AT DIFFERENT SURFACE PressURES

Abstract

The surface-enhanced Raman scattering spectrum of poly(vinyl) pyrrolidone (PVP) molecules capping 50 nm silver nanocubes assembled in a monolayer via the Langmuir-Blodgett (LB) technique is studied at different surface pressures (at different nanoparticle densities). The observed correlation between the intensity of different SERS bands of the PVP with the nanoparticle density and those of the extinction intensity of the localized surface plasmon resonance bands (as a measure of the surface plasmon field) suggest the following: 1) the observed SERS enhancement results mostly from surface fields of the aggregated nanoparticles; 2) the relative intensities of the different Raman bands are in reasonable agreement with those expected from the electromagnetic mechanism of enhancement. Beside the large surface plasmon field used in the Raman scattering enhancement, the broad SPR band of the aggregated nanocubes provides an additional advantage in the analytical applications of Raman spectroscopy.
Introduction

Raman spectroscopy is a well-established analytical technique that uses an intense light source (generally a laser source) to induce electronic excitations in a molecule that subsequently relax to emit a photon. If the electron relaxes to a different vibrational energy level the associated scattered photon is shifted in frequency compared with the initial incident photon. By subtracting the energies of the two photons it is possible to measure the vibrational energies of the molecular analyte. This spectroscopic information is then used to uniquely identify, follow, and characterize the molecule. However, the shortcoming of Raman spectroscopy has always been the low sensitivity of the technique. The small Raman cross-section of most molecules leads to roughly only 1 in $10^6$ photons being Raman scattered. Traditionally this has required a large concentration of analyte to produce a measurable Raman spectrum.

Surface enhanced Raman scattering (SERS) has recently alleviated the low sensitivity limitation of Raman spectroscopy\(^1\). SERS was first observed using pyridine on the surface of a roughened silver electrode by Fleischman et al.\(^2\) but the large signal was attributed to normal Raman scattering with a substrate that had a large surface area. It was discovered independently by Van Duyne et al.\(^3\) and Creighton et al.\(^4\) that an increased surface area was not sufficient to produce the large Raman intensity. More recently, this same phenomenon was observed to occur for molecules adsorbed onto plasmonic metal nanoparticles, and enhancement factors as large as $10^{14}$-$10^{15}$ have been reported\(^5-8\). Herein, we examine the SERS phenomenon as related to SERS-active substrates composed of plasmonic metal nanoparticles.

Two mechanisms have emerged from the literature to explain the high enhancement of the Raman signal, namely the chemical mechanism\(^9,10\) and the electromagnetic mechanism\(^11,12\). The chemical mechanism of enhancement has been applied to molecules adsorbed onto the surface of nanoparticles\(^10\) at adatoms. The induced electron-hole pairs within the metal nanoparticle are proposed to influence the
Raman polarizability of the adsorbed molecule that is being probed\textsuperscript{13}. This influence can be in form of a charge-transfer (CT) between the molecule and the conducting metal\textsuperscript{14}. This mechanism is often invoked to explain SERS phenomena such as (1) large SERS intensity variations from molecules of similar Raman cross-sections\textsuperscript{15}, (2) unexpected SERS intensity variations of different vibrations of the same molecule\textsuperscript{15,16}, and (3) poisoning of the SERS signal by small concentrations of various ions\textsuperscript{9,17}.

The electromagnetic mechanism of enhancement, while not ruling out the chemical mechanism, is proposed to account for the majority of the large Raman enhancement (up to $10^{12}$-$10^{13}$)\textsuperscript{18,19}. When metallic particles of a small size (compared with the wavelength of light) are excited by an electric field of light, the conduction band electrons of the metal oscillate in resonance with the field, creating a large field strength on the surface of the particle\textsuperscript{20-22}. This large surface field enhances the incident and Raman scattered photons. The intensity of the Raman scattered photon ($I_{\text{SERS}}$) is mathematically described\textsuperscript{1} in Equation 6.1 and is proportional to the square of the enhancement of the near field at the incident frequency ($g$) and the square of the enhancement of the near field at the scattered frequency ($q$). (This equation is derived in more detail in the discussion section.) The term $\alpha_R$ is the Raman polarizability of the Raman scatterer.

$$I_{\text{SERS}} \propto \alpha_R^2 g^2 (v_0) q^2 (v_R) I_0$$  \hspace{1cm} (6.1)

While there has been a large amount of nanoparticle sizes, shapes, and materials\textsuperscript{23-25} used to study SERS, gold spheres\textsuperscript{26} and rods\textsuperscript{8} and silver nanoparticles and aggregates\textsuperscript{27} have been the most utilized. Silver has superior optical properties compared with gold since it has a longer dephasing time (thus sharper surface plasmon band) due to the separation of the interband transitions from the plasmon resonance\textsuperscript{28,29}. Although many researchers have reported that the SERS enhancement requires aggregation of the nanoparticles\textsuperscript{30-32}, single particles have also been investigated and reported to exhibit
single molecule detection.\textsuperscript{33,34} Nie et al.\textsuperscript{5} showed that there are active hot spots that are responsible for SERS, which was later shown by Brus et al.\textsuperscript{31} to likely occur at interstitial spots between two nanoparticles. Theoretical models\textsuperscript{18,35} have predicted that these hot spots can have enhanced field intensities that are as high as $5 \times 10^4$, depending on the curvature and shape of the particle. Nanocubes have a strong plasmon field concentrated at the coroners and edges\textsuperscript{36}, which should lead to a substantial enhancement of the Raman signal.\textsuperscript{35} Techniques for synthesizing silver nanocubes have been previously reported\textsuperscript{36,37} that result in particles that possess eight sharp corners in which the charges are concentrated and the field intensity becomes much higher than for corners or edges that are more rounded\textsuperscript{38}.

Since the plasmonic field is responsible for the electromagnetic mechanism of SERS, it is very helpful to assemble plasmonic nanoparticles, in order to increase the plasmon intensity and thereby increase the field that enhances the Raman scattered photons. The assembly of plasmonic nanoparticles (gold and silver) leads to enhancement of the plasmonic field in-between the nanoparticles.\textsuperscript{6} Several model systems composed of aggregated nanoparticles have been investigated. A monolayer from silver nanowires was shown by Tao et al. to be a good SERS platform\textsuperscript{39,40}. The 2D-assembling of nanoshell arrays, with plasmon resonance in the NIR, with sub-10 nm interparticle gaps were used to enhance both Raman and IR spectra\textsuperscript{41}. This assembling leads to the formation of hot-spots in the interparticle junctions in both NIR and mid-IR\textsuperscript{42}.

A very convenient method of assembling plasmonic nanoparticles is the Langmuir-Blodgett (LB) technique\textsuperscript{37,43,44}. In this manner, large Raman enhancement can be accomplished. In this report, we assemble 50nm silver nanocubes (AgNCs) on the surface of a quartz substrate by creating a LB monolayer film with different inter-particle distances. The average strength of the plasmon field (and thus the plasmon coupling between the particles) as well as the relative amounts of the monomer and aggregated nanoparticles was followed optically as Blodgett pressure (nanoparticle density)
increases. SEM and AFM are used to monitor the particle surface coverage and the
degree of aggregation on the substrate. Surface enhanced Raman scattering (SERS)
spectra of the PVP adsorbed on the surface of the AgNCs were measured as a function of
the average nanoparticle density (the percent of the surface covered area). The
electromagnetic enhancement mechanism of SERS is concluded from the observed
relationship between the relative intensities of the different Raman bands and the surface
plasmon extinction intensities of the aggregate band at those Raman frequencies.

**Experiment and Theoretical Simulation**

The synthesis of the silver nanocubes has been previously described elsewhere.
Briefly, 30 mL of ethylene glycol (EG) was heated to 150 °C for 1 hour, followed by
addition of 0.2 of poly(vinyl) pyrrolidone (MW = 55k) dissolved in 10 mL EG. The
resulting solution was heated until the temperature rose to 150 °C. Sodium sulfide (3
mM) dissolved in 0.4 mL of EG and 3.5 mL of 282 mM silver nitrate dissolved in EG
were injected slowly into the reaction mixture. Silver ions were reduced completely after
15 minutes, producing AgNCs. For purification of AgNCs, a 5 mL aliquot of the AgNCs
solution was diluted with acetone and centrifuged. The particles were then re-dispersed in
water. Finally, the solution was centrifuged and the AgNCs were dispersed in 10 mL
chloroform.

The Langmuir-Blodgett monolayer was prepared using a Nima 611D trough filled
with deionized water. The surface pressure was measured with a Wilhelmy plate attached
to a D1L-75 model pressure sensor. AgNCs in chloroform (2 mL) were sprayed over the
water surface and the monolayer was left 30 minutes to dry and reach the equilibrium
state. The surface pressure was measured as a function of area at which the particles are
dispersed. The LB film was transferred to quartz and silicon substrates (cleaned with
piranha solution 30% H₂O₂+70% H₂SO₄ volume ratio) by the vertical dipping method at
different pressures (25, 20, 15, 10, 5, and 0 mN/m). A Holoprobe Raman microscope
(Kaiser Optical Systems) with 785 nm laser excitation was used for surface Raman measurement. For the UV-vis. absorption measurements, an Ocean optics HR4000Cg-UV-NIR was used. A Zeiss Ultra60 was used for SEM measurement and the Picoscan 5 Molecular Imaging instrument was used for AFM measurements.

The optical response of the nanocubes has been calculated using the DDA method with the DDSCAT 6.1 code publicly offered by Draine and Flatua\textsuperscript{45} and modified by Goodman\textsuperscript{46}. The method has been described in great detail elsewhere\textsuperscript{19}. Briefly, the method approximates the desired particle shape as a 3-dimensional cubic lattice of polarizable point dipoles of pre-programmed dipole-dipole spacing. The program solves for the scattering and absorption of each polarizable point self-consistently in response to an incident plane polarized wave light and polarization of neighboring dipole points. The bulk values of the dielectric constants reported by Johnson and Christy\textsuperscript{47} for silver were used. The DDA method has been demonstrated by many groups\textsuperscript{38,48-50} to be suitable for optical calculations of the extinction spectrum and the local electric field distribution in metal particles with different geometries and environments. The dielectric of the host medium was set at $\varepsilon_m = 1.00$.

**Characterization of the silver nanocube assemblies**

**Surface plasmon resonance spectra**

The extinction spectra of silver nanocubes dispersed in water and chloroform are shown in Figure 6.1.A. Silver nanocubes of 50nm edge length have previously been reported to possess four overlapping resonance bands between 300-500nm, where the strongest peak is the lowest in energy and is assigned to the dipole resonance. There is a red-shift in the dipole plasmon resonance after the phase transfer of the nanocubes from water to chloroform (due to the increased refractive index of chloroform compared to water). During this process, no additional bands appear at lower energy and no change in the spectral width of the dipole resonance band is observed, which is evidence for a
successful phase transfer from water to chloroform without particle aggregation. The discrete dipole approximation (DDA) calculation for a AgNC with edge lengths of 50 nm.

Figure 6.1

A.)

B.)

C.)

Figure 6.1 A) The surface plasmon spectra of AgNCs dissolved in water (black) and chloroform (red). B) Experimental and DDA calculated (extinction, scattered, and absorption) optical spectra of 50nm silver nanocubes. The experimental spectrum is taken from surface supported particles on a quartz substrate deposited via the LB trough technique at a surface pressure of 0 mN/m (blue). C) The surface plasmon resonance spectra of silver nanocubes adsorbed onto the surface of quartz substrate via the LB technique as a function of surface pressure (25, 20, 15, 10, 5, and 0 mN/m).
is shown in Figure 6.1.B. The AgNCs have four plasmon peaks at 416, 387, 371, and 349 nm. Due to the large size of the AgNCs, the scattering process dominates the extinction spectrum, as has been predicted for nanorods and nanospheres\textsuperscript{49}.

Deposition of the AgNCs into a monolayer on the surface of the LB trough affects the shape and position of the surface plasmon resonance spectrum. Figure 6.1.C shows the surface plasmon resonance of the LB film AgNCs on the surface of a quartz substrate irradiated with unpolarized light when transferred at different surface pressures (25, 20, 15, 10, 5, 0 mN/m). The plasmon spectrum was found to be much sharper on the quartz substrate, compared to the plasmon spectrum of the AgNCs in solution, likely due to a more homogeneous positioning of the cubes with one face lying flat on the substrate, as shown in the SEM images. Moreover, an overall blue shift is observed in the band positions due to the lower dielectric environment of air compared to the aqueous environment. The assembled AgNCs have five plasmon resonance peaks. Four of these peaks are assigned to the individual nanocubes and were observed in solution (Peaks 1-4) while Peak 5 is a result of the assembly process due to the aggregation of nanocubes on the surface of the quartz substrate during LB monolayer deposition. Some of these peaks shift in wavelength as the surface pressure of the monolayer increases during the deposition process. As the surface pressure is increased, Peak 3 red-shifts while Peak 2 does not noticeably change position. The most intense plasmon peak (peak 4) that assigned to the dipole resonance band of the nanocube red-shifts as the surface pressure is increased, which is expected due to previous studies on dipole plasmonic coupling. After deposition of the AgNC monolayer onto the quartz substrate, peak 5 appears at lower energy, far to the red of the previously observed plasmon resonances. This peak has a broad shape and was not observed in the DDA calculation for the single AgNC. This broad peak corresponds to aggregated nanocubes on the surface of the particle that have a small variation in interparticle separations. These aggregates are shown in the SEM images Figure 6.2(A-F) at different particle densities. Each aggregates contains certain
number of nanocubes and has a unique aggregate plasmon frequency in addition to the higher energy plasmon resonances of the individual particles. The combination of these aggregate plasmon resonances form the broad plasmonic peak observed in the spectrum.

**Imaging studies**

To investigate the red-shift in the surface plasmon resonance of AgNCs, the topography of the sample was imaged by SEM in Figure 6.2(A-F). As the surface pressure during deposition is increased, the density of particles on the surface of the substrate increases and the interstitial distance between the particles decreases. Additionally, the number of aggregate clusters increases, but at a disproportionately faster rate, as the surface pressure increases. The increase in the number of aggregates accorded well with the optical measurement shown in Figure 6.1, in which the intensity of the aggregate plasmon band (peak 5) increases as the surface pressure increases.

The insets of Figure 6.2 show the dark field images of the respective LB monolayers deposited onto the quartz substrates. These images provide a visual analysis of the disproportionate increase in the aggregate plasmon peak that scatters red light compared with the single particle plasmon bands that scatter blue light. As the surface pressure increases upon deposition, the amount of red light that is observed in the dark field increases and the dominant scattered color changes from blue to red. However, in all of the dark field images, there are different regions that scatter different wavelengths of light. The scattered light from the isolated particles and small aggregates has a faint blue appearance (shorter wavelength), while the smaller clusters scatter at a longer wavelength (yellow and green colors). The larger aggregates scatter at the longest wavelength (reddish color spots). The reddish colored scattering points are attributed to strong coupling inside the aggregates while the yellow appeared due to lower coupling. The weakest coupling produces faint blue scattering. The amount of reddish and yellowish
spots increase at the expense of faint blue spots, as the surface pressure (which is a function of coverage area) is increased.

**Figure 6.2**

![Sem images of silver nanocubes adsorbed onto the surface of quartz substrates prepared at different surface pressure 25, 20, 15, 10, 5, and 0 mN/m (A-F, respectively). The dark field images corresponding to each SEM image are inset. A high-resolution image of the nanocubes is shown in the inset of F.]

The SEM produced a good description for the topography of the surface (the number and the size of aggregates). However, to obtain more details about the aggregate shape (if it is 2D or 3D) AFM measurements of two samples deposited at different surface pressures (20 and 5 mN/m) were taken and are shown in **Figure 6.3**. The AFM
images show that the aggregates lie in the same plane of measurement parallel to the surface of the substrate and are therefore 2-D. No evidence for a multilayer aggregate is observed. Moreover, the number of aggregates assembled in the sample deposited at the surface pressure of 20 mN/m is much higher than the number of aggregates in the sample deposited at 5 mN/m. This confirms that there is an increased amount of coupling and thus increased surface plasmon fields) in samples that are deposited at a higher surface pressure.

Figure 6.3

![Figure 6.3: AFM images of the AgNCs adsorbed onto the surface of a silicon substrate, prepared at surface pressures of 20 (A) and 5 (B) mN/m. The false color represents thickness in the Z-direction and indicates a uniform thickness (monolayer).](image)

SERS of the PVP capping molecules of the Ag nanocubes

Poly(vinyl) pyrrolidone (PVP) was used as the capping agent during the silver nanocube preparation and was spectroscopically investigated using surface enhanced Raman scattering (SERS). The SERS spectrum of PVP adsorbed onto the surface of the AgNCs at various nanoparticle densities is shown in Figure 6.4.A. The incident laser wavelength was 785 nm, which is far away from the sharp SPR bands below 500 nm that are assigned to individual particles. However, there is substantial overlap of the broad
aggregate band with the laser wavelength and thus the observed enhanced Raman spectrum is expected to arise from the PVP capping molecules on the aggregated nanoparticles.

The observed SERS spectrum of PVP is altered from the normal Raman spectrum of PVP\textsuperscript{51,52}. Several vibrational bands are red-shifted in energy from the normal Raman spectrum of the solid PVP, namely the O=C-N bending mode of the amide (654 cm\textsuperscript{-1}), C-C ring breathing mode (850 cm\textsuperscript{-1}), the CH\textsubscript{2} scissor mode (1461 cm\textsuperscript{-1}), and N-H bending mode (1371 cm\textsuperscript{-1}). In a complimentary fashion, two bands blue-shift in energy in the SERS spectra, namely the O=C-N bending mode (573 cm\textsuperscript{-1}) and the in-plane C=O bending mode (545 cm\textsuperscript{-1}). All of these vibrational modes, along with the unshifted bands, are broader in energy in the SERS spectra compared with the normal Raman spectrum.

Interestingly, several vibrational modes are “activated” or “deactivated” in the SERS spectra compared with the normal Raman spectrum of solid PVP. Vibrational bands assigned to PVP that are “deactivated” in the SERS spectra (present in the normal Raman) are the C-C stretches (750 and 810 cm\textsuperscript{-1}), the C=O, C=N stretch (1674 cm\textsuperscript{-1}), and the CH\textsubscript{2} wag, C-N stretch (1280 cm\textsuperscript{-1}). (The 366 cm\textsuperscript{-1} band observed in the normal Raman, which is unassigned, also does not appear in the SERS spectra.) Vibrational bands assigned to PVP that are “activated” in the SERS spectra (not present in the normal Raman) are the out-of-plane C=O bend (472 cm\textsuperscript{-1}), C-N stretch (630 cm\textsuperscript{-1}), C-C stretch (687 cm\textsuperscript{-1}), and several CH\textsubscript{2} vibrations (1070, 1167, 1425, and 2922 cm\textsuperscript{-1}).

In addition to the energetic shifts of the PVP modes and the “activation” / “deactivation” of some modes, several bands are observed in the SERS spectra that have not previously been assigned to PVP. These bands are observed at frequencies 500, 726, 958, 1142, 1410, 1542, and 1600 cm\textsuperscript{-1}. These new bands are likely due to the breaking and/or formation of some molecular bonds in the PVP during the synthesis of the silver nanocubes, which is done at high temperatures (150ºC) in the presence of ethylene glycol.
Figure 6.4

A.)

Figure 6.4: (A) Surface enhanced Raman spectra of bulk solid PVP and PVP adsorbed onto the surface of silver nanocubes deposited onto a quartz substrate at surface pressures of 0, 5, 10, 15, 20, and 25 mN/m. (B) The relationship between the percent of coverage area and the plasmon peak intensities of peak 3, 4 and 5 at 785 nm. (C) The relationship of SERS band intensity of five well-resolved bands and the corresponding percent of coverage.
It has been previously demonstrated\textsuperscript{5,53} that the SERS frequency of molecular vibrations can fluctuate in frequency and intensity. This phenomenon has been attributed to the chemical enhancement mechanism previously described. It has been reported that PVP chemically adsorbs to the metal surface via oxygen\textsuperscript{52}, although other binding motifs are possible. Thus, the increased breadth of the SERS bands of PVP compared with the bulk normal Raman bands could be due to (1) the variation in chemical binding between the PVP molecules and the AgNC particles and / or (2) the electronic fluctuations between the molecule and the particle during plasmon excitation\textsuperscript{53}. The first possibility supports the electromagnetic enhancement mechanism due to the variation of the molecule located in the plasmonic field (due to different particle aggregation sites or molecular locations on the nanoparticle) while the second possibility supports the chemical enhancement mechanism. Therefore, both mechanisms are valid and can explain the observed increase in the spectral breadth of the Raman bands. However, the appearance of some PVP vibrations (“activation”) in the SERS spectrum and the disappearance of other PVP vibrations (“deactivation”) compared with the normal Raman spectrum of bulk PVP is difficult to ascribe to the electromagnetic enhancement, as has been true in the past\textsuperscript{5,13,53}. For this reason, we do not rule out the chemical mechanism of enhancement here, but examine the relationship between electromagnetic field enhancement (which is fundamental to the EM mechanism) and the observed intensity of the SERS bands.

The SERS band intensities are found to increase as the surface pressure during particle deposition increases, as shown in section III. Increasing the surface pressure during LB deposition increases the density of the aggregated particles on the quartz substrate surface and in turn increases the PVP concentration on the substrate. The plasmon extinction intensity is a linear function of particle concentration, and will have a linear dependence on the particle coverage on the substrate. This is evident in the monomer plasmon bands below 500nm and the linear increase in these bands as a
function of particle coverage is shown in Figure 6.4.B (solid lines). However, the relationship between the plasmon band of the aggregate and the particle coverage is not linear (dashed line in Figure 6.4.B). Likewise, the intensity of the Raman bands normally correlates linearly with the analyte concentration, which is why SERS can be used as an analytical tool. As the surface pressure increases, the SERS band intensities are found to non-linearly increase with the particle density on the surface of the substrate, as shown in Figure 6.4.C, similar to the fast increase in the plasmon band associated with the nanocube aggregates. Therefore, the concentration is not solely responsible for the SERS enhancement, and appears to be dependent on the plasmon extinction intensity of the aggregated particles.

The induced localized surface plasmon resonance of the nanoparticles enhances the electromagnetic field of the light at the surface of the particle. As the plasmon field increases the degree of amplification of the SERS increases. While charge transfer (chemical mechanism) could be partially responsible for the shift and broadening of the bands, it does not explain the non-linear relationship between the concentration of PVP and the SERS intensity. This is better understood using the electromagnetic mechanism. It is shown in Figure 6.4.C that the least Raman shifted vibrational bands have the largest slope and therefore are enhanced the most. This occurs because the field enhancement, represented by the plasmon intensity, is strongest at the incident photon frequency and progressively diminishes at lower frequencies where the Raman shifted photons are scattered.

The induced localized plasmon resonance of the nanoparticle generates a strong electric field at the surface of the particle ($E_{LSP}$) that enhances the electric field of the incident photon ($E_0$) by a factor $g(\nu_0)$. The magnitude of the electric field of the photon that excites the molecule to a virtual state is $E_{LSP}$. The electric field associated with the Raman scattered photon is then proportional to the exciting field multiplied by the Raman polarizability of the scatterer. It is worth noting that the scatterer in normal Raman
spectroscopy is the molecule, and the polarizability is referred to as the Raman polarizability of the molecule. However in SERS, the scatterer is the molecule / particle system and the polarizability value could be affected by the metal. It is here that the chemical enhancement would contribute to the SERS enhancement. When the Raman scattered photon is scattered from the particle surface, it is enhanced again by the plasmonic field by a factor \( q(\nu_R) \) that is a function of the shifted frequency at which the photon is scattered, \( \nu_R \). The measured SERS photon then has an associated electric field \( (E_{SERS}) \) that is described in **Equation 6.4**. This relationship can also be written in terms of the measured intensity of the SERS scattered photon \( (I \propto E^2) \) as a function of the incident intensity, polarizability, and the field enhancement factors at both the incident and Raman scattered frequencies (**Equation 6.5**). These processes are shown in the schematic diagram in **Figure 6.5**.

\[
E_{LSP} = g(\nu_0)E_0 \\
E_R \propto \alpha_R E_{LSP} = \alpha_R \left[ g(\nu_0)E_0 \right] \\
E_{SERS} \propto q(\nu_R)E_R = q(\nu_R) \times \left[ \alpha_R g(\nu_0)E_0 \right] \\
I_{SERS} \propto \alpha_R^2 q^2(\nu_R) g^2(\nu_0)I_0
\]

**Equation 6.5**

For any Raman active vibration, the intensity of the SERS band is only dependent on the electromagnetic field enhancement at the incident and Raman shifted frequencies, given constant incident photon intensity. Taking the natural logarithm of **Equation 6.5**, we show in **Equation 6.6** the linear relationship between the natural log of the SERS intensity \( (I_{SERS}) \) of a specific Raman frequency and the natural log of the product of the field enhancements \( (g(\nu_0) \& q(\nu_R)) \) squared. For a specific Raman frequency, the Raman polarizability \( (\alpha_R) \) and the incident photon intensity \( (I_0) \) are constant, and are contained in the y-intercept \( (k) \).
\[ \ln(I_{\text{SERS}}) = k + \ln(g^2(\nu_0) \times q^2(\nu_R)) \] (6.6)

Figure 6.5

Figure 6.5 Schematic representation of the field enhancement steps of the incident and Raman scattered photons due to the localized surface plasmon field around the particle. This field is represented by the halo surrounding the particle. The field enhancement factors \( g(\nu_0) \) and \( q(\nu_R) \) act on the respective incident and Raman scattered photons at the indicated times.

The electromagnetic field that is responsible for enhancing the incident and scattered photons is generated due to plasmonic resonances of the nanoparticle. These plasmonic resonances are measured and shown in Figure 6.6.A through the spectral range of 300-1050nm. The plasmonic resonance bands have been assigned in the previous section. While it is obvious that there is a relationship between the plasmonic extinction efficiency of the nanoparticle and the strength of the generated field, to our knowledge this relationship has never been fully developed. In Figure 6.6.B, we plot the
Figure 6.6
A.)

![Plasmon extinction spectra of the nanocubes in a monolayer supported on a quartz substrate at varying concentrations. The incident laser energy is marked by the red dashed line at 785 nm and each Stokes-shifted Raman vibration of PVP is shown at lower energies.](image)

B.)

![Linear relationship between the natural logarithm of the SERS intensity and the natural logarithm of the product of the plasmon extinction intensities at the incident and Raman shifted vibrations is plotted. The slope of each line is equal to one, demonstrating the proportional relationship between the extinction intensity and the average surface field enhancement factor.](image)

Figure 6.6: (A) Plasmon extinction spectra of the nanocubes in a monolayer supported on a quartz substrate at varying concentrations. The incident laser energy is marked by the red dashed line at 785 nm and each Stokes-shifted Raman vibration of PVP is shown at lower energies. (B) The linear relationship between the natural logarithm of the SERS intensity and the natural logarithm of the product of the plasmon extinction intensities at the incident and Raman shifted vibrations is plotted. The slope of each line is equal to one, demonstrating the proportional relationship between the extinction intensity and the average surface field enhancement factor.

dependence of the natural logarithm of the SERS intensity for 5 Raman active vibrational bands as a function of the natural logarithm of the product of the plasmon extinctions at
the incident and scattered frequencies. This relationship is mathematically shown in **Equation 6.7**.

\[ \ln(I_{SERS}) = k + m \times \ln(P_0 \times P_R) \]  

(6.7)

From the plot in **Figure 6.6.B**, the slope of each line \( m \) is measured to be 1, while the y-intercept \( k \) is unique for each Raman active band. This result allows us to draw a relationship between the extinction efficiency of the plasmon resonance at the incident and the Raman scattered frequencies \( (P_0 \text{ and } P_R, \text{ respectively}) \) and the average field enhancement factors at the incident and Raman scattered frequencies \( (g(\nu_0) \text{ and } q(\nu_R), \text{ respectively}) \). This relationship is shown in **Equations 6.8a & b**.

\[ P_0 \propto g^2(\nu_0) \quad \& \quad P_R \propto q^2(\nu_R) \]  

(6.8a & 6.8b)

The slope and intercept of the lines plotted in **Figure 6.6.B** are indicated on the graph. The consistency in the slope value of 1.0 for various Raman bands supports the electromagnetic enhancement mechanism of SERS. We propose that the variation in the y-intercept is due only to the variation in the Raman polarizability of the different vibrational bands of the PVP analyte molecule / nanoparticle system (since the incident light intensity is constant). This treatment thereby qualitatively separates the electromagnetic mechanism from the chemical mechanism of enhancement. The Raman polarizabilities for the molecule / particle system are calculated relative to one another in **Table 6.1** by dividing the y-intercepts of each molecular vibration by the y-intercept of the 660 cm\(^{-1}\) vibration. We have compared the relative normal Raman polarizabilities of two bands that appear in the bulk Raman sample (660 and 933 cm\(^{-1}\)) in column 3 of **Table 6.1**. The relative bulk normal Raman polarizabilities are different than the SERS polarizabilities, which could be attributed to the chemical mechanism of enhancement.
However, because the majority of the bands that are enhanced during SERS are not normally Raman active, it is difficult to identify the chemical enhancement here.

**Table 6.1**

<table>
<thead>
<tr>
<th>Frequency (vibration)</th>
<th>Relative SERS Polarizability $\left( \alpha_R / \alpha_{660} \right)$</th>
<th>Relative Normal Raman Polarizability $\left( \alpha_R / \alpha_{660} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>660 cm$^{-1}$ (N-C=O) bend, ring def</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>933 cm$^{-1}$ (CH$_2$) ring breathing</td>
<td>0.31</td>
<td>0.43</td>
</tr>
<tr>
<td>1001 cm$^{-1}$ (C-C), (CH$_2$) rock</td>
<td>0.54</td>
<td>N/A</td>
</tr>
<tr>
<td>1765 cm$^{-1}$ amide (C=O)</td>
<td>0.38</td>
<td>N/A</td>
</tr>
<tr>
<td>2938 cm$^{-1}$ Sym. CH$_2$ Stretch, chain</td>
<td>0.36</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**Conclusion**

In conclusion, we have demonstrated that the deposition of silver nanocubes on the surface of a quartz substrate provides an excellent platform to study the surface enhanced Raman scattering from adsorbed molecules on the nanoparticle surface. The natural aggregation that occurs in the monolayer of nanocubes is beneficial to SERS spectroscopy because of the broad localized surface plasmon resonance band that strongly enhances both the incident exciting photon and the Raman scattered photon for a wide range of Raman vibrations of the adsorbed or nearby molecules to the surface. In addition, the aggregation itself increases the surface plasmon field. The natural logarithm of the intensity of the SERS bands was experimentally shown to linearly depend on the
natural logarithm of the product of the plasmon intensities at the incident frequency and at the scattered frequency within the observed aggregation spectrum. This work experimentally showed evidence of the electromagnetic mechanism of SERS. In addition, we were able to demonstrate mathematically a relationship between the intensity of the surface plasmon extinction and the average field enhancement at the particle surface. We experimentally determined the Raman polarizabilities of each vibrational band of the SERS scatterer relative to the strongest Raman band at $660 \text{ cm}^{-1}$ and compared two of these relative polarizabilities to the normal Raman polarizabilities of the individual molecule.

**Acknowledgment**

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CHAPTER 7

CATALYSIS WITH TRANSITION METAL NANOPARTICLES IN COLLOIDAL SOLUTION: HETEROGENEOUS OR HOMOGENEOUS?

Abstract

Surface atoms on nanoparticles are valencely unsaturated, and due to the surface curvature, their bonds to the nanoparticle can be weaker. Thus, they become chemically active and physically dynamic. This could be good or bad. It makes nanoparticles more active as catalysts. However, they might become too active and become reactants. In addition, individual atoms can dissolve and catalyze the reaction in solution. Therefore, depending on the nanoparticle shape, size, the reaction conditions and the type of reactants involved, colloidal nanocatalysis can be heterogeneous (if it takes place on the nanoparticle surface), homogeneous (if it takes place in solution), or both.
Background

Heterogeneous catalysis in solution-phase historically was rarely viewed as being profitable due to the much higher yield (i.e. conversion × selectivity) afforded by homogeneous catalysts. This paradigm has begun to change due to an increased interest in nanoparticle synthesis. Colloidal nanocatalysts combine the advantages of heterogeneous and homogeneous catalysis while circumventing many of their individual drawbacks. The drawbacks of homogeneous catalysts include poor recycling potential and contamination of the products by the catalyst (with sometimes significant loss of catalyst). Heterogeneous catalysis in solution alleviates these drawbacks because the contamination of the products is low and the catalysts can be phase separated from the reaction media and reused. However, the turnover frequency (TOF), or the reaction rate normalized to some indicator of the number of sites (reported in units of reactions per site per unit time), of these catalysts are highly inferior to their homogeneous counterparts. The inferior catalytic ability of heterogeneous catalysts is attributed to the low number of active sites per volume of catalytic material because only surface atoms directly participate in catalysis. The use of colloidal nanoparticles alleviates the dimensional limitations of heterogeneous catalysts because they have high surface-to-volume ratios and expose a greater number of surface atoms per unit volume compared to supported heterogeneous catalysts.

A heterogeneous catalyst exists in a physical state different from that of the reactant(s), while homogeneous catalysts are in the same physical state. It is important to recognize the subjective nature of this definition when applied to nanocatalysis. The traditional definition of a heterogeneous catalyst may have evolved in 1985 in a paper by Schwarz, in which the nature of the catalyst was classified based on the number of different catalytically-active sites available on a single catalyst. A catalyst with only one type of active site was termed homogeneous, while a catalyst with various types of active sites was termed heterogeneous. This definition was proposed by Schwartz and further
utilized by others\textsuperscript{2-4} in order to classify nanoparticles as heterogeneous and distinguish them from homogeneous counterparts since colloidal nanoparticles possess solution-phase properties, such as mobility in solution, as well as solid-phase properties, such as a liquid-solid interface. Nanoparticles inherently have multiple catalytically active sites (corners, edges, and different exposed crystal facets) and were categorized as heterogeneous. However, confusion has arisen from this definition. The work on “single-site” heterogeneous catalysts is one example (see chapter by Raja and Thomas). Metallic complexes bound to a macroscopic solid support that can be easily separated from the reaction solution are inherently contradictory to Schwartz’s definition. Schwartz’s definition lacks applicability throughout the nanocatalytic field; therefore, we shall adopt the traditional definition of heterogeneous catalysis with a few clarifications related to catalysis by nanomaterials. If catalysis takes place on the surface of the nanoparticle it is defined herein as heterogeneous, regardless of the catalytic species (i.e. active site on the nanoparticle surface or a metallic complex bound to the nanoparticle surface). If the nanoparticle supplies the solution with a complex that subsequently conducts the catalysis at a distance from the nanoparticle surface, the catalysis is classified as homogeneous. This definition is consistent with the International Union of Pure and Applied Chemistry (IUPAC) definition of heterogeneous/homogeneous catalysis\textsuperscript{5}.

Determination of the catalytic nature (i.e. heterogeneous or homogeneous) of a reaction is not trivial in catalysis by nanomaterials in solution. The interfacial region at the nanoparticle surface is not clearly understood and prompts the question as to whether the catalysis is heterogeneous in nature and takes place on a well-defined surface or homogeneous due to an unstable surface. Nearly every experiment that has been performed has been unable to fully eliminate the possibility of one catalytic nature. Some reports have suggested that metal salts such as palladium (II) chloride or tetrachloroplatinate\textsuperscript{6,7} rather than nanoparticles\textsuperscript{8,9} are the true active catalysts—
acceptance of such conclusions is not widespread. The intent of this review is not to elucidate the mechanism(s) of nanocatalysis, but to provide a general overview of the current understanding of colloidal nanocatalysts and how their functioning catalytic nature (heterogeneous or homogeneous) gives rise to their potential as model catalysts in solution-based reactions.

**Experimental Techniques to Determine Catalytic Nature of Colloidal Nanoparticles**

The best approach to investigate the nature of a reaction catalyzed by colloidal nanoparticles is to utilize multiple experimental techniques and to arrive at a conclusion that supports all of the data. The most direct analysis is a kinetic measurement of the reaction. Reaction rate constants directly describe the reaction and can be used to derive intensive activation energies that do not depend on the catalyst concentrations. However, this technique is not always useful, such as in reactions involving species not easily measured analytically using spectroscopy and/or chromatography.

A second technique used to analyze the nanoparticles is transmission electron microscopy (TEM). The existence of particles as well as their size/shape distributions in solution can be followed during the course of the reaction by examining aliquots of the solution at intervals throughout the reaction. TEM can confirm the existence of nanomaterials in solution as well as accurately monitor nanoparticle size, shape and crystallography with high resolution. However, TEM cannot straightforwardly determine if the nanoparticle surface is responsible for the catalysis. Exemplifying this point, it is accepted that the metallic center of a homogeneous catalyst evolves through a redox cycle in order to catalyze many carbon-carbon bond formation reactions. This means there are always zero-valent metal atoms [M(0)] present in solution that can aggregate with one another to form nanoparticles. The formation of nanoparticles may be foundational to catalysis, where particle formation occurs prior to product formation,
or it could be (2) a consequence of catalysis, where particle formation results as the metal ions transition through the redox cycle and aggregate.

A third technique that has been used to study colloidal nanocatalysis is the Collman test or the “3-Phase Test” \(^{16}\). One reactant is chemically bound to a solid support (Phase 1) and the catalyst is chemically bound to a second solid support (Phase 2). Phases 1 and 2 are suspended in solution (Phase 3), into which a second reactant is also dissolved (not substrate bound). Direct contact between Phase 1 and Phase 2 is restricted due to the fact they are both substrate bound. If the heterogeneous catalyst in Phase 2 is required for the reaction to proceed there will not be any product formation. If the heterogeneous catalyst (Phase 2) leaches homogeneous complexes into solution (Phase 3), the reaction will proceed and in this way the nature of the active catalyst can be investigated. However, there are limitations to this experimental setup since the formation of products does not rule out heterogeneous catalysis. The formation of secondary particles from leached species is possible, so at best, this test supplies evidence for atomic leaching.

These three techniques are employed along with others not mentioned here to investigate the catalytic nature of a reaction. It is difficult to obtain positive confirmation for one catalytic nature over another because of the ability for small amounts of homogeneous catalyst (concentrations below current detection methods) to catalyze reactions \(^{11}\). Leached atoms can re-adsorb rapidly to heterogeneous structures, either to a substrate or to the surface of the nanoparticles \(^{17,18}\). In the following sections, we review some of the major results involving colloidal nanoparticles in solution-phase catalysis. The two reaction types that will be discussed in this chapter are redox reactions and carbon-carbon bond formation reactions.
**Redox Reactions**

Many redox reactions by colloidal nanoparticles have been reported. Three of the most-studied reactions are (1) the catalyzed electron transfer between ferricyanide and thiosulfate $^{8,19-21}$, (2) the catalytic reduction of fluorescent dyes by sodium borohydride $^{22,23}$, and (3) the catalytic reduction of organic compounds (e.g. nitro-aryls $^9$ and alcohols $^{24}$). These reactions have been studied extensively because they are easy to follow spectroscopically allowing for straightforward measurement of reaction kinetics. The third set of reactions have enormous industrial significance, where nitro compounds are reduced to their less toxic nitrate or amine counterparts $^{25,26}$ and the electro-oxidation of methanol is utilized for methanol fuel cells $^{27,28}$.

Several metals have been used to catalyze redox reactions; the most commonly studied are platinum and gold. There is debate concerning the exact catalytic nature – homogeneous or heterogeneous – of these catalysts. We summarize the results on the dependence of the reaction rate and TOF for redox reactions catalyzed by colloidal nanoparticles on (1) particle size, (2) local particle environment, (3) particle concentration, and (4) particle shape.

**Particle Size Dependence**

The rate of many catalyzed redox reactions decrease as the gold nanoparticle increases in size $^{9,23,24}$. The work of Panigrahi et al $^9$ demonstrates this in Figure 7.1a, with particles synthesized by the Frens method (sodium citrate reduction of a gold salt and subsequent protection of the formed nanoparticles by citrate ions) $^{29}$. This trend occurs because as the size of the nanoparticle decreases, the surface atoms are less coordinatively-saturated and thus more reactive. Several authors $^{9,30}$ have concluded this data is evidence for heterogeneous catalysis; however, it is premature to conclude solely from catalytic kinetics that correlate with nanoparticle size that the catalysis is
heterogeneous in nature. This increase in the coordination unsaturation of surface atoms would lead to their decreased stability (due to weaker/fewer metal-metal bonds) increasing the probability atoms (which are catalytically active) leach into solution.

In addition to the size-dependent comparison, Panigrahi et al.\(^9\) reported the dependence of the reaction rate on the surface area of the gold particle. This dependence on surface area was reported to be linear for a particle diameter between 8 and 55 nm, as shown in Figure 7.1b. The linear dependence suggested that the increased number density of defect sites on the particle surface had a negligible effect on catalysis, demonstrating that the catalysis occurs on the surface of these colloidal particles, and the defect sites (which would be the primary source of atomic leaching from the surface into solution) are not the active sites for the reaction\(^9\). However, this size regime is quite large and the atomic defect density for particles between 8 and 55 nm doesn’t vary significantly. Catalysis could occur at the defect sites because the defect site density remains constant (within experimental error) over this size regime. Since the concentration of the complex in solution is dependent on the density of defect sites, homogeneous catalysis due to the release of soluble complexes from the particle surface at the defect sites can also explain these results.
Figure 7.1

Figure 7.1: Panigrahi et al show (a) the dependence of the catalyzed reaction rate on colloidal gold nanoparticle size from 8-55nm and (b) the dependence of the reaction rate on the total available surface area of the colloidal nanoparticles. The linear dependence shows that the surfaces are the same from 8 – 55nm colloidal particles, but does not prove if catalysis is heterogeneous (surface catalyzed) or homogeneous (solution catalyzed). The total gold atom concentration was kept constant in each experiment. Reprinted with permission from. Reprinted with permission from 9.

There have been fewer reports on the particle size dependence of catalysis by platinum-catalyzed redox reactions. A report by Sharma et al 21 showed that platinum colloidal nanoparticles do not demonstrate the same dependence on particle size as gold nanoparticles do for the reduction of hexacyanoferrate (III) by thiosulfate 19. Platinum nanoparticles protected by sodium di(2-ethylhexyl) sulfosuccinate (synthesized by a reverse micelle technique) exhibit an optimum size (~38 nm) for the reduction of ferricyanide by thiosulfate (Figure 7.2). The reason for an optimum particle size is not fully understood; however, they proposed the following explanation: a shift in the Fermi level occurs as the diameter is increased, which decreases the energy barrier for electron transfer to and from the nanoparticle surface, while the decrease in catalytic activity for nanoparticles >38 nm is attributed to an overall decrease in the available surface area. The proposed heterogeneous surface-directed reaction involves the adsorption of
ferricyanide to the particle surface and subsequent reduction by bound thiosulfate through electron transfer mediated by the platinum nanoparticle.

Figure 7.2

![Graph showing the catalyzed reaction rate for the reduction of ferricyanide by thiosulfate as a function of colloidal platinum nanoparticle size](image)

Figure 7.2: Sharma et al report on the dependence of the catalyzed reaction rate for the reduction of ferricyanide by thiosulfate on the colloidal platinum nanoparticle size, indicating that an optimum size exists where the catalytic rate is greatest, ~38 nm. The total concentration of Pt atoms was kept constant for each experimental point. Reprinted with permission from 21.

Effect of Capping Material

The growth of colloidal nanoparticles is restricted using growth-inhibiting molecules (herein referred to as capping agents) that bind to the particle surface and exert control over size and/or shape. This control is conducted via steric interactions (e.g. polymers such as poly(vinylpyrrolidone) (PVP)) or electrostatic interactions (e.g. citrate or cetyl trimethylammonium bromide (CTAB)). The impact of the capping agent on the
catalytic function of protected nanoparticles has been reviewed \textsuperscript{31}; the general trend is the more protected the particle is by the capping molecules the less catalytically active it is. Yang et al \textsuperscript{32} reported on the influence of primary alkylamines and alkylthiols bound to the platinum surface on the electrocatalytic oxidation of methanol. The binding affinity of thiols to the Pt nanoparticle surface increased with increasing particle size, whereas the binding affinity of amines to the Pt nanoparticle surface decreased as the particle size increased. This is likely due to the electron-donating nature of the Au-S bond, which strengthens as the fraction of terrace binding sites on the particle increases, compared with the electron-withdrawing nature of the Au-N bond, which weakens as the fraction of terrace binding sites on the particle increases \textsuperscript{33,34}. An inverse relationship between the strength of the capping agent and the catalytic activity was reported. Amine-protected Pt particles are more active as their size increases due to a decreased binding affinity between the capping agent and the metallic surface, whereas thiol-protected Pt particles become less active as the size increases due to an increased binding affinity between the capping agent and the metallic surface. Di et al. have also reported \textsuperscript{8} on the effect of the capping agent bound to gold colloids on the reduction of ferricyanide by thiosulfate. Using alkylthiols of various alkyl chain lengths, they concluded that a shorter capping molecule increased the rate of reaction compared to longer alkylthiols.

**Concentration dependence of the colloidal nanoparticles**

Most experimental reports on the dependence of the rate of reaction on the concentration of nanoparticles in solution provide similar conclusions. The earliest study on this dependence sums up these conclusions and was conducted by Freund and Spiro \textsuperscript{19} using colloidal gold solutions to catalyze the reduction of ferricyanide by thiosulfate. As the concentration of nanoparticles increases, there is a linear increase in the reaction rate, which is expected whether the catalytic mechanism is heterogeneous or homogeneous.
They reported that the strength of this dependence on concentration was dependent on the size of the gold nanoparticles. While it was postulated that the catalysis occurred on the surface of the particle, these results do not prove that the catalysis is heterogeneous, but only that the catalyst concentration increases as the particle concentration is increased.

Particle Shape Dependence

**Effect of Particle Shape on the Activity of the Reaction**

There are several reports on the dependence of nanoparticle shape on the rate of reaction using metal colloids\textsuperscript{14,20}. Surface atoms on nanoparticles of shapes of high curvature have a higher defect density compared to nanoparticles of low curvature geometries\textsuperscript{35}. The ratio of the coordinatively unoccupied sites (edges and corners) to the number of terrace atoms of the close-packed surface is very small for particles larger than 10 nm. In addition, different shapes are terminated by different crystal facets which exhibit a large variation in surface energy\textsuperscript{36}.

Researchers have developed procedures to synthesize transition metal nanoparticles with a number of different shapes\textsuperscript{35,37}. The most stable thermodynamic shape is a sphere, which displays both (100) and (111) crystal facets. A perfect tetrahedron exposes (111) crystal faces providing a more reactive surface than the mixture of (100) and (111) facets on a sphere for the electron transfer reaction between ferricyanide and thiosulfate\textsuperscript{35}. The importance of exposed crystal facets was demonstrated in a report by Tian et al\textsuperscript{38} on the electrochemical synthesis of platinum nanoparticles with surfaces exposing a large number of high-index facets. These facets contained a high fraction of undercoordinated surface atoms, resulting in a catalyst that was \textasciitilde 400\% more active than an equivalent platinum surface area for the catalytic electrooxidation of ethanol.
Tetrahedral nanoparticles had a much higher catalytic activity and lower apparent activation energy for the reduction of ferricyanide by thiosulfate compared with their spherical counterparts. Narayanan and El-Sayed compared the catalytic activity associated with tetrahedral, cubic, and spherical platinum nanoparticles for the electron transfer reaction between hexacyanoferrate (III) ions and thiosulfate ions to form hexacyanoferrate (II) ions and tetrathionate ions. The catalytic activity correlated with the fraction of surface atoms located on the corners and edges of the platinum nanoparticles. The tetrahedral nanoparticles have the highest fraction of corner and edge surface atoms and correspondingly the highest catalytic activity ($E_A = 14.0 \pm 0.6 \text{ kJ/mol}$) while the cubic platinum nanoparticles have the lowest fraction of corner and edge surface atoms and have the lowest catalytic activity ($E_A = 26.4 \pm 1.3 \text{ kJ/mol}$). Spherical platinum nanoparticles have an intermediate fraction of surface atoms on corners and edges and therefore have an intermediate catalytic activity ($E_A = 22.6 \pm 1.2 \text{ kJ/mol}$).

**Influence of Catalysis on the Stability of Particle Shape**

Narayanan and El-Sayed investigated the effect of the electron-transfer reaction between ferricyanide and thiosulfate on the stability of the particle shape. The change in shape of the nanoparticle was time-dependent; this change was in the form of a thermodynamic “rounding” of the particle into a sphere due to the dissolution of platinum atoms from the corners and edges of the tetrahedral and cubic platinum nanoparticles. Figure 7.3 demonstrates that the tetrahedral particle evolves into a distorted tetrahedral particle after one reaction cycle (Figure 7.3a and b). For the cubic platinum nanoparticles (Figure 7.3c), the rate of dissolution of platinum atoms was slower, and distorted cubic platinum nanoparticles (Figure 7.3d) were dominant after two reaction cycles.
Figure 7.3: Narayanan and El-Sayed show an example of a HRTEM image of a tetrahedral PVP-Pt nanoparticle before electron-transfer reaction (a), after second cycle of electron transfer reaction (b), cubic polyacrylate capped Pt nanoparticle before electron-transfer reaction (c), and after second cycle of electron-transfer reaction (d). The scale bars are 1 nm in length.

The effect of individual reactants on the tetrahedral and cubic platinum nanoparticles was investigated in order to determine which reactants were responsible for the distortion of the nanoparticles \(^{40}\). There was significant dissolution of atoms from the corners and edges of both the tetrahedral and cubic platinum nanoparticles upon exposure to hexacyanoferrate (III) ions. Distorted tetrahedral and cubic platinum nanoparticles became the dominant shape (Figure 7.3b and d, respectively). The distortion in shape of the nanoparticles was proposed to be due to the cyanide ligand of the hexacyanoferrate
ions adsorbing and reacting with the platinum corner and edge atoms of the nanoparticles to form \( \text{Pt(CN)}_4^{2-} \) complexes. The platinum cyanide complexes are more stable in solution than the ferricyanide complex \(^{41}\). Upon exposure to thiosulfate ions, very little change in the shape of the tetrahedral and cubic platinum nanoparticles was observed. It is believed that the binding of thiosulfate via the \( S^- \) group to the nanoparticle surface stabilizes it from dissolution \(^{40}\). The fact that the thiosulfate binds strongly to the nanoparticle surface while ferricyanide dissolves the nanoparticle surface led the authors to propose that the reaction mechanism involves the adsorption of thiosulfate ions onto the nanoparticle surface followed by a surface reaction with ferricyanide ions in solution\(^{40}\).

Narayanan and El-Sayed examined the binding of reactants to the platinum nanoparticle surface with Raman spectroscopy \(^{42}\). There are two possible adsorption configurations of the thiosulfate ions to the platinum nanoparticle surface (through the \( S^- \) ion or the \( O^- \) ion). A shift in the symmetric S-S stretching mode (bound form through \( S^- \)) as well as an unshifted S-S stretching mode (free form in solution) indicates the presence of both bound and unbound forms of thiosulfate. In addition, no shift in the symmetric or asymmetric O-S-O bending or S-O stretching frequencies was observed, indicating binding does not occur via the \( O^- \) group. Raman spectra of the platinum nanoparticles exposed to hexacyanoferrate (III) ions exhibited several bands associated with the formation of platinum complexes. Mahmoud and El-Sayed \(^{43}\) provided spectroscopic evidence for the formation of Prussian blue analogue complexes (with the formula \( \text{Pt}_x\text{Fe}_y(\text{CN})_z \)) on the platinum nanoparticle surface, in addition to \( \text{Pt(CN)}_4^{2-} \) bands. These assignments provide evidence that the strong cyanide ligands of the hexacyanoferrate (III) ions dissolve platinum atoms resulting in the formation of Prussian blue analogue complexes in solution.

In summary, the nature of the catalytic mechanisms (heterogeneous or homogeneous) involving colloidal nanoparticles to catalyze redox reactions are not fully
agreed upon among the scientific community. However, it is clear from numerous investigations that tuning the properties of the colloidal nanoparticles, such as the particle size and shape, composition, and concentration, can greatly enhance the catalytic activity. While the nature of the catalysis is currently being studied, the use of nanoparticles as catalysts in gentle redox reactions is certainly a worthwhile endeavor.

**Carbon-Carbon Bond Forming Reactions**

Organometallic complexes are commonly used in carbon-carbon bond formation reactions, such as Stille\(^{44}\), Sonogashira\(^{45}\), Suzuki\(^{46}\), and Heck\(^{47}\) reactions. The Suzuki and Heck reactions specifically have been studied using transition metal colloidal nanocatalysts. The Suzuki-Miyaura\(^ {46}\) reaction is a coupling reaction between an arylboronic acid and an aryl halide to form a biaryl that is generally catalyzed by a soluble palladium species (although there are some reports using other metal-based catalysts\(^ {48,49}\)). The Mizoroki-Heck reaction\(^ {47}\) is a carbon-carbon bond formation reaction that couples an aryl halide and a terminal alkene over palladium catalysts. The cross-coupling reactions typically occur at high temperatures (although a few exceptions occur) and require long reflux times to complete the reaction. The proposed and generally accepted homogeneous catalytic mechanism for the two coupling reactions includes an oxidative addition of the metal catalyst followed by transmetallation and finally reductive elimination\(^ {15}\).

Several investigators have attempted to identify the nature of the metal species that catalyze these coupling reactions in solution. Due to the harsh conditions of these reactions and the thermodynamic instability of colloidal particles, it is highly possible and probably likely that multiple catalytic mechanisms occur simultaneously. A few review articles on carbon-carbon bond formation reactions catalyzed with colloidal transition metal nanoparticles are available\(^ {7,11}\).
Organic chemists studying carbon-carbon bond formation reactions using homogeneous metallic catalysts observed the formation of nanoparticles during the reaction. These organic chemists began to investigate the possibility that these colloidal nanoparticles, which inadvertently formed in their experiments, were the active catalytic agent. From a different direction, material chemists were simultaneously investigating if the colloidal particles that were intentionally used in their experiments formed homogeneous complexes in solution that were responsible for the catalysis. In this way, investigations into colloidal nanocatalysis began in two different fields with a common goal in mind of elucidating the nature of the catalysis reactions in solution.

**Carbon-Carbon Bond Formation Reactions Catalyzed by Colloidal Nanoparticles**

The first studies that intentionally used colloidal nanocatalysts were reported independently by Beller et al.\(^{50}\) and Reetz et al.\(^{51}\) using chemical reduction and electrochemical techniques, respectively, to synthesize colloidal palladium nanoparticles for the Heck reaction. Both Beller and Reetz concluded that the solution-phase catalysis occurred on the surface of the nanoparticle, without confirming a homogeneous catalytic pathway was non-existent. Le Bars et al.\(^{52}\) demonstrated an inverse relationship between the size of Pd nanoparticles and the TOF (normalized to the total number of surface atoms) for the Heck reaction (Figure 7.4a). After normalizing the rate to the density of defect sites (for each nanoparticle size) (Figure 7.4b), the TOF for all particle sizes was identical. Colloidal PVP-capped palladium nanoparticles synthesized by ethanol reduction are effective catalysts for Suzuki cross-coupling reactions in aqueous solution\(^{53}\). The El-Sayed group reported that the initial rate of reaction increased linearly with the concentration of Pd nanoparticles\(^{53}\) and the catalytic activity was inversely proportional to the nanoparticle size (3.0-6.6 nm)\(^{54}\). Similar to previous results by Le Bars et al.\(^{52}\), the dependence on particle size is a dependence on the number density of defect sites on the
nanoparticle surface. This data further supports catalysis occurs on the surface of the nanoparticles, and defect sites represent the active catalytic species. However, this dependence on the number of defect sites can also be explained by a homogeneous mechanism where defect sites supply metal ions through catalytic complexes that leach into solution.

Figure 7.4

Figure 7.4: Le Bars et al show (a) the dependence of the initial reaction rate of the Heck reaction normalized to the calculated total surface area available on the colloidal nanoparticles of various sizes and (b) the dependence of the initial reaction rate of the Heck reaction normalized to the calculated total number of surface defects on the colloidal nanoparticles. This shows that the apparent dependence of the reaction rate on the surface area is actually a dependence on the number of surface defects on the nanoparticle surfaces. Reprinted with permission from 55.

The coordination unsaturation renders atoms at defect sites more susceptible to dissolution where they could potentially function as homogeneous catalysts. Reetz and Westermann reported the formation of palladium nanoparticles during the Heck reaction in the presence of a phase transfer ion using “ligandless” homogeneous metallic catalysts such as palladium acetate, Pd(OAc)$_2$. The nanoparticles were found in
solution after a 1h induction period. In the absence of a phase transfer catalyst, de Vries et al.\textsuperscript{56} demonstrated that increasing amounts of Pd\textsuperscript{2+} (in the form of Pd(OAc)\textsubscript{2}) in solution resulted in an increase in the reaction rate until a critical Pd\textsuperscript{2+} concentration is achieved after which the rate decreased dramatically due to the formation of Pd(0) species and their aggregation into palladium black. Palladium black was not observed in the presence of ionic salts (phase transfer catalyst) because the salts acted as surfactants which limited nanoparticle growth\textsuperscript{13}.

\textbf{Influence of Catalysis on Particle stability}

Narayanan and El-Sayed\textsuperscript{57} conducted a detailed investigation to determine the fate of PVP-protected palladium nanoparticles during the Suzuki reaction. This reaction takes place at high temperatures (> 80 °C) and requires long reflux times (12-24 h). Tetrahedral platinum nanoparticles transformed into spheres during the course of the reaction\textsuperscript{48}. In addition to the change in shape, the nanoparticles grew in size after a single reaction cycle with a concurrent broadening of the size distribution due to Ostwald ripening. Cassol et al.\textsuperscript{58} reported ripening behavior during the Heck reaction also, which provides evidence that surface atoms from the colloidal nanoparticles leach into solution. This observation is not conclusive proof that the catalysis is homogeneous since the catalysis can be considered homogeneous in nature only if leached atoms are catalytically-active following desorption into solution and prior to readsorption onto the nanoparticle surface. Narayanan and El-Sayed\textsuperscript{57} compared the rate of particle size growth by Ostwald ripening with the formation of the product, biphenyl. During the first hour of the reaction, there is minimal change in the particle size distribution and rapid formation of biphenyl. After the first hour, the concentration of biphenyl increases slowly and the nanoparticles begin to ripen, leveling off after six hours of the reaction. Therefore, it appears that ripening is not correlated with the production of biphenyl.
The molecular species (individual reactants and solvent) responsible for the leaching of Pd atoms from the nanoparticle surface was studied. Palladium nanoparticles and sodium acetate (NaOAc) were refluxed in acetonitrile:water (3:1), while the reactants, phenylboronic acid (PA) and iodobenzene (I), were separately dissolved into solutions of acetonitrile:water containing Pd nanoparticles and NaOAc. The initial average size and the size distribution of the Pd nanoparticles (Figure 7.5a and b) in the solution containing NaOAc increased after refluxing (Figure 7.5c and d) indicating that the leaching process involved in

Ostwald ripening is not caused by the reactants. An identical increase in the average palladium nanoparticle size and a broadening in the size distribution occurred in the solution containing NaOAc and iodobenzene (Figure 7.5g and h) suggesting iodobenzene does not noticeably influence Ostwald ripening. This suggests that iodobenzene does not effectively adsorb to the surface of the nanoparticles. In contrast, in the presence of phenylboronic acid, ripening (Figure 7.5e and f) is inhibited, presumably due to stabilization of the nanoparticle surface by the adsorption of deprotonated phenylboronic acid. This binding was later confirmed by infrared spectroscopy to occur via fully deprotonated O⁻ groups in a bridging mode, with the two O⁻ ions binding to separate Pd atoms. The TEM results and the spectroscopic measurements were used to propose a heterogeneous mechanism in which the phenylboronate anion binds to the surface of the palladium nanoparticle and subsequently reacts with iodobenzene from solution.
Figure 7.5: TEM images and Gaussian fits of the size distribution of the palladium nanoparticles initially (a-b), after being exposed to the solvent (1:3 water:acetonitrile) and the base (sodium acetate SA) (c-d), after being exposed to the base and phenylboronic acid (PA) (e-f), and after being exposed to the base and iodobenzene (I) (g-h). It can be seen that the Ostwald ripening process is inhibited upon exposure to the phenylboronic acid while exposure to iodobenzene results in the growth of the nanoparticles. In addition, refluxing the nanoparticles in the solvent alone also results in the Ostwald ripening of the particles. Reprinted with permission from 40.
Investigations of Atomic Leaching from Colloidal Nanoparticle Catalysts

Pröckl et al. measured the concentration of leached Pd species from palladium nanoparticles supported on a metal oxide via atomic absorption spectroscopy as a function of time in solution. The data indicated that the largest concentration of Pd species in solution (Pd$^{2+}$ and/or Pd(0)) occurred during the reaction (Figure 7.6). As the reaction neared 100% conversion, the soluble Pd concentration returned to the original value, presumably due to re-adsorption onto the metal oxide substrate. The process was concluded by the authors to have “clearly involved heterogeneous reactions”. This data supports a catalytic mechanism that is heterogeneous in nature, where the reaction occurs at the interface and causes the dissolution of surface atoms into solution. This explanation is supported by the report of Pröckl et al. that individual reactants didn’t initiate nanoparticle dissolution but dissolution was observed during the reaction over the 25-50 min time interval when the conversion was the highest (Figure 7.6).

While there is no catalytic activity for the Suzuki and Heck reactions in filtered solutions (which should only contain dissolved molecular Pd species) recent work by Thathagar et al. indicates that leached Pd species are critical participants in the catalysis. Their experimental setup consisted of a cell divided into two sections by a membrane with a pore size of 10nm. The insoluble base, NaOAc, which is necessary for the reaction to occur, was positioned on one side of the membrane, while 15nm colloidal palladium nanoparticles (which were larger than the 10nm pore size of the membrane) were placed on the opposite side of the membrane. This experimental setup allowed the reaction to take place only on the side that contained the base. Since the reaction requires both a palladium catalyst and the insoluble NaOAc base, the reaction can only occur if the catalyst passed through the membrane (via atomic leaching from the nanoparticle colloids) to the opposite side of the cell that contained the base. The results demonstrated that the product was produced on the side of the membrane containing the base. Therefore, the active catalyst passed through the membrane as either an atomic species or
as clusters (less than the 10 nm pore size). This report confirms that the process of atomic leaching from the colloidal particles participates in one catalytic mechanism. However, it doesn’t demonstrate conclusive proof that catalysis occurs only via a homogeneous mechanism. It is possible that particle formation could occur on the side of the membrane where the base is located through aggregation of the leached atomic species.

Figure 7.6: Pröckl et al demonstrate that leached Pd species occur in solution only during the reaction and quickly re-adsorb onto the substrate after the reaction is complete. Reprinted with permission from 61.

The identification of metallic complexes during the palladium catalyzed Heck reaction has been reported by several groups using electrospray mass spectrometry 62 and extended x-ray absorption fine structure spectroscopy 63. The spectroscopic observation of these metallic complexes led de Vries to propose a “Unifying Mechanism” 7 that is homogeneous in nature, which is shown in Figure 7.7. He observed the formation of Pd nanoparticles in a solution containing “ligandless” Pd(OAc)2, but they appeared late (near
100% conversion) in the reaction. He concluded colloidal particles form because reduced Pd atoms aggregate before they reoxidize.

This conclusion remains speculative since a detailed study of the formation of Pd(0) particles throughout the reaction was not reported. Following the mechanistic pathway from the top right corner in Figure 7.7, the first two species (Pd(OAc)$_2$ and H$_2$O-Pd(OAc)$_2$) are the precursors to the active catalytic species, PhPdI$_2$. The existence of a PhPdI$_2$ species has not been confirmed, and it is possible that particles or clusters form early in the reaction and are the active catalyst instead of (or in addition to) the metal complex PhPdI$_2$. Independent x-ray photoelectron spectroscopy studies have confirmed that the surface of the Pd nanoparticles is oxidized completely from Pd(0) to Pd$^{2+}$ during the Heck reaction with iodobenzene, suggesting that the surface of the colloidal nanoparticle could be active.

**Figure 7.7**

![Diagram](image)

Figure 7.7: “Unified mechanism” proposed by de Vries that incorporates several reports of spectroscopically identified species (shown in bold in figure). Reprinted with permission from.
The catalytic nature of colloidal metal nanoparticles during many carbon-carbon bond formation reactions remains unconfirmed. Conclusions from the many studies reported here have demonstrated that scientific evidence is available that supports both homogeneous and heterogeneous catalysis when colloidal nanoparticles are present. The harsh conditions that are often required for these reactions aid in obscuring the identity of the catalytic nature of colloidal nanocatalysts. However, while the nature of the catalysis remains hotly debated, colloidal nanoparticles have become useful in catalyzing many organic reactions that were formerly reserved for homogeneous complexes. Further investigation in this field is certain to lead to exciting and interesting results concerning colloidal nanoparticles as catalysts.

**Summary and Conclusions**

Colloidal nanoparticles are attractive catalysts because they exhibit the advantages of both homogeneous catalysts (high reaction rate on a per atom basis) and heterogeneous catalysts (good recyclability due to ease of separation). The determination of the exact catalytic nature (heterogeneous vs. homogeneous) in the presence of colloidal metal nanoparticles is not trivial. Heterogeneously-catalyzed pathways might occur during mild solution-phase chemical reactions in the presence of nanomaterials (specifically reactions in non-reactive solvents that take place at low temperatures). There is evidence to suggest that in many chemical reactions, especially reactions where the environment is particularly harsh, nanoparticles are likely a source for secondary chemical species (homogeneous catalyst dissolved in solution) that may be responsible for catalysis. While the nature of the catalytic mechanisms involving colloidal metal nanoparticles is currently under scientific investigation by many groups in several different fields, currently the most intriguing attribute of these catalysts is the multi-dimensionality of the nanomaterials, where the catalytic properties can be tuned with the
nanoparticle properties. For this reason, although controversy surrounds the discussion of the nature of nanocatalysis, metallic colloids are an excellent selection for the pursuit of a model catalyst for solution-based reactions.

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APPENDIX A

DDA SPECTRAL SIMULATED SPECTRAL DATA CONDENSED IN
CHAPTER 4

Figure A.1

A) B)

C) D)

Figure A.1: DDA simulations of the optical extinction of four representative nanosphere dimers at various separations. The diameter of the individual spheres are \( D = 5.0 \) (A), 20.0 (B), 50.0 (C), and 80.0 nm (D).
Figure A.2: Best-fit single exponential curves fit to the fractional shift in the surface plasmon resonance wavelength of two nanospheres as a function of the interparticle separation scaled by the nanosphere diameter. Four nanosphere diameters are shown, D = 5.0 (A), 20.0 (B), 50.0 (C), and 80.0 nm (D).
Figure A.3: DDA simulations of the optical extinction nanodisc dimers of three thicknesses (10nm (A), 20nm (C), 30nm (E)) at various separations. Corresponding best-fit single exponential decays fit to the fractional surface plasmon resonance wavelength shift as a function of the interparticle separations scaled by the nanodisc diameter (10nm (B), 20nm (D), 30nm (F)).
Figure A.4

A.)

Figure A.4: DDA simulations of the optical extinction nanoprism dimers of three thicknesses (8nm (A), 24nm (C), 40nm (E)) at various separations. Corresponding best-fit single exponential decays fit to the fractional surface plasmon resonance wavelength shift as a function of the interparticle separations scaled by the nanoprism bisector (8nm (B), 24nm (D), 40nm (F)).
Figure A.5: DDA simulations of the optical extinction nanocube dimers of three volumes (Edge = 10nm (A), 30nm (C), 50nm (E)) at various separations. Corresponding best-fit single exponential decays fit to the fractional surface plasmon resonance wavelength shift as a function of the interparticle separations scaled by the nanocube edge (10nm (B), 30nm (D), 50nm (F)).
APPENDIX B
LOGARITHMIC PLOTS OF THE PLASMONIC COUPLING BETWEEN TWO NANOPARTICLES AS A FUNCTION OF SEPARATION

The data plots in Appendix B are presented for a clearer presentation of the fit between the best-fit near exponential decay law presented in Chapter’s 4 and 5 by utilizing a logarithmic scale. The linear scale is shown for comparison.

Figure B.1

Figure B.1: Plasmonic coupling measured as the fractional shift of the plasmon resonance as two nanospheres approach one another. The simulations here were performed using the Discrete Dipole Approximation. The linear (A) and logarithm (B) scales are used to plot this dependence with the best fit exponential curve shown in red.
Figure B.2

A.)

\[ y = A_1 \exp\left(-\frac{x}{\tau}\right) \]

\[ A_1 = 0.13 \pm 0.01 \]
\[ \tau = 0.34 \pm 0.03 \]

Figure B.2: Plasmonic coupling measured as the fractional shift of the plasmon resonance as two nanoprisms approach one another. The data points are experimentally measured using EBL fabricated samples. The linear (A) and logarithm (B) scales are used to plot this dependence with the best fit exponential curve shown in red.

Figure B.3

A.)

\[ y = A \exp\left(-\frac{x}{t}\right) \]

\[ A = 0.11 \pm 0.01 \]
\[ t = 0.35 \pm 0.05 \]
\[ R^2 = 0.97 \]

Figure B.3: Plasmonic coupling measured as the fractional shift of the plasmon resonance as two nanoprisms approach one another. The simulations here were performed using the Discrete Dipole Approximation. The linear (A) and logarithm (B) scales are used to plot this dependence with the best fit exponential curve shown in red.
Christopher Tabor
Ph.D. Candidate

Curriculum Vitae

Education

Ph.D. Physical Chemistry, Georgia Institute of Technology, Atlanta, GA
(07/04-08/09), Expected Graduation: August 2009 GPA: 3.7

B.S. Chemical Physics, emphasis in Chemistry and Mathematics Centre College, Danville, KY (08/00-05/04) GPA: 3.4

Additional Relevant Graduate Level Courses:
• Management of Technology, Georgia Institute of Technology
• Analysis of Emerging Technologies, Georgia Institute of Technology

Publications

1. Tabor, Christopher; Van Haute, Desiree; El-Sayed, Mostafa A. The Effect of Orientation on Plasmonic Near-Field Coupling Between Gold Nanorods. ACS Nano Submitted.

2. Mahmoud, Mahmoud; Tabor, Christopher; El-Sayed, Mostafa A. SERS enhancement by aggregated silver nanocube monolayers assembled by the Langmuir-Blodgett technique at different surface pressures. Journal of Physical Chemistry ASAP


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7. Narayanan, Radha; Tabor, Christopher; El-Sayed, Mostafa A. Can the observed changes in the size or shape of a colloidal nanocatalyst reveal the nanocatalysis mechanism type: Homogeneous or Heterogeneous? *Topics in Catalysis* 2008 48(1-4) 60-74. (Invited Review Article)

8. Mahmoud, Mahmoud; Tabor, Christopher; El-Sayed, Mostafa A; Ding, Yong; Wang, Zhong L. A new catalytically active colloidal platinum nanocatalyst: The multiarmed nanostar single crystal. *Journal of the American Chemical Society* 2008, 130(14) 4590-4591.


**Technical Skills**

- **Nanoparticle Fabrication/Synthetic Techniques**: Photolithography (PL); Electron Beam Lithography (EBL); Software Pattern Writing for EBL; Nanosphere Lithography (NSL); Colloidal nanoparticle reduction techniques (gold spheres and rods; platinum spheres, cubes, and prisms); Langmuir-Blodgett (LB) Deposition

• Chemical Analysis. Raman and Surface Enhanced Raman Scattering Spectroscopy (SERS), High Pressure Liquid Chromatography (HPLC), FT-IR Spectroscopy, Attenuated Total Reflection (ATR) FT-IR

• Cleanroom Processing: Spin Coating, Reactive Ion Etching (RIE), Wet Chemical Etching, Metal Deposition, Thermal Processing, Nitride Deposition.


• Simulation and Theoretical Modeling. DDA method - DDSCAT6.1 code

Research Presentations

• Tabor, C.; Mahmoud, M.; Dreaden, E.; Murali, R.; El-Sayed, M.; “The Effect of Nanoparticle Shape on Dipole Plasmonic Coupling” Optical Metamaterials Workshop, Boulder, CO (September 2008)


• Tabor, C.; Qian, W.; El-Sayed, M.A.; “The Synthesis of Highly Monodisperse Colloidal Solutions of Nanoprisms: Using Femtosecond Laser Pulses and Nanosphere Lithography”. Georgia Institute of Technology, Graduate Student Symposium, Atlanta GA (March 2007)

• Tabor, C.; Qian, W.; El-Sayed, M.A.; “Photothermal Ejection of Gold Nanoprisms from Quartz Substrates into Liquid Media”. Electronic
Processes in Organic Materials, Gordon Research Conference, Mount Holyoke College (July 2006).

Oral Presentations

- Tabor, Christopher "Some Radiative and Non-Radiative Properties of Plasmonic Nanoparticles: From Plasmon Driven Motion to Plasmonic Coupling for Advanced Plasmonic Rulers". The Ohio State University, Invited Speaker: Coherent Seminar 2009 (February 2009).


- Tabor, C; “Chemical Advances in Nanolithography” Ph. D. Candidacy proceedings. (November 2005)

Research Experience

- Georgia Institute of Technology, Atlanta, GA, USA. Optical and Catalytic Properties of Supported Noble Metal Nanoparticles (June 2004 – Present)


Leadership and Teaching Experience

- Mentor to Undergraduate Research Assistant: Project Title: Plasmonic Coupling in Nanorod Dimer Assemblies as a Function of Orientation (June 2008-Present)

- Summer Mentor to Undergraduate Intern: Project Title: Kinetic Studies of the Catalysis of Platinum Nanoparticles of Various Shapes Analyzed by Raman Spectroscopy (June 2007 – August 2007)

- Summer Mentor to NNIN Undergraduate Intern: Project Title: A Kinetic Study of the Catalysis by Gold Nanoparticles Supported on a Substrate (June 2006 – August 2006)
• **Chemical Waste Management Captain:** Laser Dynamics Laboratory (August 2007-Present)

• **Cleanroom Tour Leader.** Introduced Exceptional High School Students to Current Research Completed inside the Microelectronics Research Center Cleanroom (April 2007)

• **Teaching Assistant.** General Chemistry Experimental Lab, Georgia Institute of Technology (08/04-12/04)

• **General Chemistry Tutor,** General Chemistry Student Tutor, Centre College (08/02-04/03)

**Honors and Awards**

• **Invited Coherent Seminar Graduate Student Speaker** – The Ohio State University, Spring 2009

• **American Chemical Society Outstanding Student Poster** – 236th National ACS Meeting Fall 2008.

• **First Runner-Up** Georgia Institute of Technology Graduate Student Symposium – Competitive Research Poster Competition 2007

• **GAANN** (Graduate Assistance in Areas of National Need) - Financial Stipend Award. (08/04-08/05)

• **Centre Fellowship Award** – (4 years) Financial Award for Outstanding Undergraduates (08/00-05/04)

• **KHEES Scholarship Award** – (4 years) Financial Award for Outstanding Undergraduates (08/00-05/04)