Hybrid Plasmonic Nanoantennas: Fabrication, Characterization, and Application

Shengjie Zhai
University of Nevada, Las Vegas

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HYBRID PLASMONIC NANOANTENNAS:
FABRICATION, CHARACTERIZATION AND APPLICATION

by

Shengjie Zhai

Bachelor of Science
Nanjing University of Science & Technology, China
2005

Master of Science
Chongqing University, China
2008

A dissertation submitted in partial fulfillment of
the requirements for the

Doctor of Philosophy in Electrical Engineering

Department of Electrical and Computer Engineering
Howard R. Hughes College of Engineering
The Graduate College

University of Nevada, Las Vegas
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Shengjie Zhai

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Department of Electrical and Computer Engineering

Biswajit Das, Ph.D., Committee Chair
Mei Yang, Ph.D., Committee Member
Yingtao Jiang, Ph.D., Committee Member
Hui Zhao, Ph.D., Graduate College Representative
Tom Piechota, Ph.D., Interim Vice President for Research &
Dean of the Graduate College

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ABSTRACT

Hybrid Plasmonic Nanoantennas: Fabrication, Characterization and Applications

by

Shengjie Zhai

Dr. Das, Biswajit, Examination Committee Chair
Professor of Electrical and Computer Engineering
Director of Nevada Nanotechnology Center
University of Nevada, Las Vegas

As optical counterpart of microwave antennas, plasmonic nanoantennas are important nanoscale devices for converting propagating optical radiation into confined/enhanced electromagnetic fields. Presently, nanoantennas, with a typical size of 200-500 nm, have found their applications in bio-sensing, bio-imaging, energy harvesting, and disease cure and prevention. With the device feature size of next generation IC goes down to 22 nm or smaller, and biological/chemical sensing reaches the Gene’s level, the sizes of the corresponding nanoantennas have to be scaled down to sub-100nm level. In the literature, these sub-100nm nanoantennas are referred as deep subwavelength nanoantennas as size of such miniaturized nanoantennas is only a fraction of the wavelength of applied visible light range (390nm-750nm).

One big problem of such small deep subwavelength nanoantennas lies in the fact that due to high propagation loss at this scale, signal attenuates so quickly that the propagation distance is only a few hundred nanometers. One feasible solution to overcome this propagation loss problem is through signal enhancement that explores hybrid plasmonic effect: plasmon polarization (SPP) coupled with localized surface plasmon (LSPR). In this dissertation, we designed a novel deep subwavelength
nanoantenna structure which can effectively couple the SPP, which is excited by a thin metal film (around 50nm in thickness) under certain light wavelength, with LSPR located between any coupled nanoparticles.

Current top-down fabrication methods using E-beam lithography and FIB cannot be used to manufacture the proposed deep subwavelength nanoantennas. In response to this fabrication problem, we invented a hybrid plasmonic nano-printing method that combines lithography and a direct metal nanoparticle patterning technique. This metal nanoparticle patterning technique allows the metallic nanoparticles to be dropped into the nanoantenna’s grooves at the same time when this nanoantenna is being patterned. Different from the conventional top-down fabrication method, our method explores the convective assembly to achieve a desired surface morphology in well-ordered, rapid, and controllable deposition on practically relevant scales.

Using this proposed fabrication method, we successfully fabricated two hybrid plasmonic nanoantenna devices. These two devices were fully characterized through optical measurement and scanning electronic imaging. These fabricated plasmonic nanoantennas were applied to enhance the signals from three applications: bio-fluorescence, surface enhanced Raman spectroscopy, and next generation System on Chip (SoC). The results have confirmed that signal enhancement up to 100 times has been achieved.
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This dissertation is dedicated

to

my family and everybody who stood steadfast beside me,

and provided assistance I have received either directly or indirectly from them.

If you put your mind and perseverance into it, the sky is the limit.
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Chapter 1
INTRODUCTION

1.1 RF antenna and Nanoantenna

RF antenna is an electrical device which converts electric power into radio waves, and vice versa. It is usually used with a radio transmitter or radio receiver. Analogous to RF antenna, nanoantenna (also called plasmonic nanoantenna, or plasmonic nanoantenna) is an enabling technology for manipulating and controlling optical radiation at subwavelength scales [2]. As so, the objective of nanoantenna design is to optimize the energy transfer between nanoantenna and the free-radiation field (figure 1).

![Image](image)

**Figure 1** Red arrows indicate the direction of energy flow. The two configurations are related by the principle of reciprocity.

Despite the widespread use of radio-wave and microwave antennas in our daily life, nanoantenna has not yet made its debut in commercial applications, primarily because of its small size requirement as determined by its characteristic dimension. According to classical antenna theory, the characteristic dimension of a nanoantenna needs to be analogous to the optical radiation wavelength (<100nm). Consequently, fabrication
accuracy down to a few nanometers is required to fabricate functional nanoantennas.

Fortunately, this level of fabrication accuracy has become possible with the continuing refinement of nano-fabrication tools. This opens the door to make finer nanoantennas for the enhancement of photodetection efficiency [3,4], light emission [5,6], sensing [7], heat transfer [8,9] and spectroscopy [10]. At present, prototype nanoantennas have been fabricated by either top-down nanofabrication methods using focused ion/electron beam milling [11,12] or electron-beam lithography [13,14], or by bottom-up self-assembly methods [15,16]. These fabrication methods, however, suffer from slow fabrication speed, high cost, and poor reliability. As a result, a new fabrication method that can overcome the all these existing methods needs to be developed.

1.2 Evolution of Nanoantenna Research

The concept of the nanoantenna has its roots in near-field optics [17]. In 1928, Edward Synge proposed the use of a colloidal gold particle for localizing optical radiation on a sample surface and thereby surpassing the diffraction limit in optical imaging [18]. In 1985, John Wessel perceived that a single gold particle can function as an antenna [19]. It was until 1995 that the first experimental demonstrations of John Wessel’s idea were made by Dieter Pohl and Ulrich Fischer [20]. Since then, research on nanoantenna has been flourished, and all these works [20-27] broadly fall into three main areas: 1).nanoantenna manufacturing, 2).surface plasmon effects modeling and simulation, and 3).development of nanoantenna applications.

1.3 Nanoantenna Manufacturing

As the device feature size in modern ICs goes down to sub-100 nanometer scale, it becomes increasing challenge to fabricate desired nanostructures in a precise and
controllable manner. Various fabrication techniques have been studied, developed and
refined to address this fabrication challenge, and they mainly fall into three categories:
top-down approaches (TDA), bottom-up approaches (BUA) and Template-based
Approaches. Each of these fabrication methods has its own pros and cons in terms of
feature resolution, controllability yield, productivity and fabrication cost.

1) Top down approaches

A top down approach (TDA) in nanofabrication starts from a macroscopic scale and
works down toward microscopic details by shaping the material, in the way similar to
sculpturing a blank piece of stone, and removing materials from where they are not
required. Compared with bottom-up and template-based fabrication approaches, top
down approaches are relatively matured, making them the de facto fabrication strategy in
large scale industrial production. A typical TDA fabrication method involves the use a
number of techniques, including lithography, thin-film deposition, dry/wet etching and
mechanical/chemical mechanical polishing [16]. The advantages of TDA include: (I)
excellent controllability of the fabricated structures, in terms of the feature size, shape
and position; and (2) excellent parallel processability of identical features, qualifying it
as a better choice for mass commercial production. The disadvantage of TDA mainly lies
in the increasing difficulties and cost as the feature size reduction continues to sub-
lithographic scale [22].

Recently, several groups used the TDA methods to realize various nanoantennas,
such as dipole nanoantenna fabricated using E-Beam lithography; Bow-tie nanoantenna
fabricated by focus ion beam; or Bow-tie and Yagi hybrid nanoantenna fabricated using
E-Beam lithography and then configured using focused ion-beam milling.
2) Bottom-up Approaches

Opposite to TDA, in a bottom up approach (BUA), construction of the final structure starts from the microscopic level of the fundamental building blocks, such as atoms, molecules and nanoparticles. A bottom-up fabrication process is usually carried out by self-organization or self-assembly, through which an ordered structure is formed from a disordered system as a consequence of specific, local interactions without the presence of external direction. Features of the obtained structure can be engineered by tailoring the parameters of the environment, in terms of temperature, pressure, chemical concentration, and so on so forth, as well as the properties of the build blocks.

The main advantage of BUA is its capability of accessing features down to the size of 10 nanometers or even less with a reasonably low cost. Besides, most BUAs offer massively parallel processability as photolithography; the self-assembling nature allows all desired structures to form spontaneously and simultaneously. The major disadvantage of BUA is its lack of precise controllability over the size, shape and position of the features produced. As a result, BUA has found little applicability in commercial and industrial processes, a sharp contrast to its more matured TDA counterparts.

Common examples of BUAs in nanofabrication include synthesis of nanoparticles or quantum dots [4] in solution process, catalytic growth of nanowires and nanotubes [5], nanopatterning by self-assembly of nanoparticles, and block copolymer patterning by self-organization [6].

3) Template-based Nanofabrication

Template-based nanofabrication is quite different from conventional top down/bottom up fabrication. It may involve either TDA or BUA or both. The key concept
of template-based fabrication is that the fabrication is an indirect process in which the final structure is achieved with the assistance of a pre-defined template. The reason to create such a template is that direct fabrication of the targeted structure is problematic or impractical for the material of interest. Instead, a secondary material that is easier to work with is used to create the template with desired features first, on top of which the final structure of the original material may be constructed.

In nanofabrication, a template can serve several purposes:

(1) To define the feature size (e.g., in [7], a bio-template with cavities of certain size is used to form 30 nm nanoparticles);

(2) To define the feature position and/or alignment (e.g., growth of nanowires on a patterned template [8];

(3) To define the shape and aspect ratio (e.g., growth of nanowires or nanotubes using a template made of porous anodic aluminum oxide (AAO) [9], which is one of the most important materials used in template-based fabrication).

1.4 Techniques used in Nanoantenna Characterization

In recent years, a wide range of techniques have been utilized for characterizing plasmonic nanoantennas’ both near-field and far-field behaviors. Figure 2 lists four types of characterization techniques based on the nature of the input source and output detector: photon to photon, photon to electron, electron to photon, and electron to electron: (see in fig.2 and table 1). In this dissertation, three of them are employed to characterize plasmonic nanoantenna, (1) optical spectrum meter, (2) scanning electron microscopy, and (3) confocal microscopy.
Figure 2  Characterization techniques for plasmonic nanoantennas [38]

Table 1  Classification of nanoantennas’ characterization techniques

| Photon to Photon | 4WM: Four-wave mixing  
SNOM: Scanning near-field optical microscopy  
aSNOM: Apertureless SNOM  
SHG: Second-harmonic generation  
TPPL: Two photon photoluminescence  
Confocal: Confocal microscopy  
Optical: Spectrum meter |
|------------------|---------------------------------------------------------------------|
| Photon to Electron | nPPE: n-photon photoemission  
PEEM: Photoemission electron microscopy  
SEM: Scanning electron microscopy |
| Electron to Photon | CL: Cathodoluminescence |
| Electron to Electron | EELS: Electron energy loss spectroscopy  
EF-TEM: Energy-filtered TEM  
STEM: Scanning TEM |

1.5  Nanoantenna Simulations

The electrodynamics of plasmonic nanoantennas have been simulated by several groups using Green’s tensor technique [1], the finite element method (FEM) [2], finite difference time domain (FDTD) methods [14,19,20,24], the Fourier modal method [25], discrete dipole approximations (DDA) [22,26,28], and the boundary element
method[18,28]. Although some simulation results were compared to experimental results [19, 24], there is still a lack of direct matching between theoretical and experimental results in the visible range that can verify the validity of the simulation methods.

1.6 Nanoantenna Applications

During recent years, enormous progress has been made in the study of the properties of various nanoantenna structures/patterns. One particular property that nanoantennas’ surface plasmon resonance effect is strong at select frequencies has made nanoantennas extremely useful in two types of application [29–31].

(1) Photodetection and photovoltaics.

When a nanoantenna is applied to a photodetector, the absorption cross-section (antenna aperture) area is increased, which directly increases the light flux that impinges on the detector. Theoretical and experimental studies have shown that intensity enhancements of $10^4$–$10^6$ are readily achievable [14, 36, 37], which enables photodetection for single molecule imaging. Another big advantage of using antennas is to reduce the detector area 100-fold, thus gaining at least an order of magnitude in sensitivity [3, 25, 29, 46].

Based on the same concept, nanoantennas have also been explored for enhancing the efficiency of photovoltaic devices, particularly for solar energy harvesting [1, 48]. Because of the increase of absorption cross-section area, the photovoltaic layer thickness in thin-film devices can be reducing to lower the carrier collection length and reduce impurity recombination. [48].

(2) Biosensing and Bioimaging.

Biosensing and Bioimaging are two commonly used analytical tools for the detection
of an analyte that combines a biological component with a physicochemical detector. Their functions to detect the presence of specific chemical or biomolecules makes it extremely important in today’s clinical diagnosis, drug discovery, environmental monitoring, food and water supplies and homeland security. Because the metal nanoparticles can be employed to significant generate the localized surface plasmon reasonace electromagnetic field above the metal thin film (eg Au, Ag). There are two major limitations to the performance of biosensing and bioimaging [3-7, 14-22, 30]:

- Lower sample concentration (which imposes a challenge to the instrument resolution)
- Higher background noise

1.7 Organization of the Dissertation

Although nanoantennas have found their great applications in biosensing and IC manufacturing, as described in early sections, more effective means to further improve nanoantennas’ surface Plasmon effects need to be sought. Correspondingly, three main areas are addressed in this dissertation: (1) development of a low cost fabrication method with good repeatability that can be used to design and fabricate nanostructures with the smallest possible features, (2) theoretical study and experimental characterization of the nanostructures in terms of their optical and electromagnetic properties, and (3) explorations of applying nanoantennas in novel areas.

The remaining of the dissertation is organized as follows. Chapter 2 presents the physics governing the nanoantenna principles and behaviors, which guides us to design the hybrid plasmonic nanoantenna. Chapter 3 describes a novel fabrication method that is a combination of the top-down and bottom-up methods. By applying this new fabrication
method, a few hybrid plasmonic nanoantennas have been fabricated. Characterization results of these fabricated nanoantennas are reported in Chapter 4. In Chapter 5, three important applications using this hybrid plasmonic nanoantenna are suggested. In the end, Chapter 6 concludes this dissertation along with suggestions for future studies.
Chapter 2

PRINCIPLES OF NANOANTENNAS

Although many plasmonic nanoantennas have similar shapes as their RF and microwave counterparts, there are crucial differences in their respective physical properties and scaling behavior. Most of these differences arise from the fact that metals are not perfect conductors at optical frequencies, but instead they are strongly correlated plasmas described as a free electron gas.

The collective fluctuation of surface free electrons at the interface between the conductors and the dielectrics is called surface plasmons (SPs) or surface plasmon resonance (SPR) [32-33]. The word ‘plasmon’ was coined by David Pines in 1950s [33], who theoretically described the energy loss caused by the collective oscillation of free electrons in the metal, and borrowed the concept from the plasma physics. The free electrons in metal can be treated as an electron liquid of high density, and the collective electron fluctuation can be considered as plasma oscillation [32]. A generic term for this is “surface plasmon polaritons” [34], since it involves the interaction between surface charge and electromagnetic field (light) applied.

Based on the difference of the excitation condition, there are two different forms of SPs (Figure 3): propagating SPR and localized SPR. SPR is electron density waves that are freely propagating along the metal surfaces, and LSPR is the localized free charge oscillations on metal nanoparticles (MNPs).
2.1 Surface Plasmon Resonance

Surface Plasmon occurs at the metal-dielectric interface, shown in figure 4a. The surface plasmon polaritons (SPP) propagate in the x- and y-directions along this metal-dielectric interface, for distances in the order of tens to hundreds of microns, and decay evanescently in the z-direction with $\frac{1}{e}$ decay lengths in the order of hundreds nanometers [27, 39, 44].
The interaction between the metal surface-confined EM wave and a molecular surface layer of interest leads to shifts in the plasmon resonance condition, which can be observed in three modes: (a) angle resolved; (b) wavelength shift, and (c) imaging [27]. In the first two modes, one measures the reflectivity of light from the metal surface as a function of either angle of incidence (in the case when constant wavelength is applied) or wavelength (in the case when constant angle of incidence is applied). The third mode uses light with both constant wavelength and incident angle to interrogate a two-dimensional region of the sample.

2.1.1 Surface Plasmon Conditions

We consider a classical model consisting of two semi-infinite nonmagnetic media with local (frequency-dependent) dielectric functions $\epsilon_1$ and $\epsilon_2$ with a planar interface at $Z = 0$ (figure 5).

\[ \nabla \times H_i = \hat{\jmath} c \frac{1}{\epsilon} \frac{\partial}{\partial t} E_i \]

(1)

Figure 5 Two semi-infinite media with dielectric functions $\epsilon_1$ and $\epsilon_2$ with a planar interface at $z = 0$.

The governing Maxwell’s equations for the structure shown in Fig. 4 in the absence of external sources can be expressed as follows [169]:
\[ \nabla \times E_i = -\frac{1}{c} \frac{\partial}{\partial t} H_i \quad (2) \]
\[ \nabla \times (\hat{\partial} E_i) = 0 \quad (3) \]
\[ \nabla \times H_i = 0 \quad (4) \]

where the index, i, corresponds to the media; i = 1 at \( z < 0 \), and i = 2 at \( z > 0 \).

Solutions to equations ((1)-(4)) can generally have s-polarized and p-polarized electromagnetic modes \([169][165]\), where the electric field \( \vec{E} \) and the magnetic field \( \vec{H} \) are perpendicular to each other and both of them are parallel to the interface. In the context of SPP, s-polarized surface oscillation waves (thus the s-polarized mode) do not exist, as this is the case for electric field \( E \) perpendicular to the interface. As a result, only p-polarized oscillation wave may propagate along the surface \( (z = 0) \), with both \( \vec{H} \) and \( \vec{E} \) tailing off at \( z \neq 0 \). That is, the electrical (magnetic) field \( \vec{E} \) has only two non-zero vectors, namely \( \vec{E}_i \) and \( \vec{E}_s \) (\( \vec{H}_i \) and \( \vec{H}_s \)).

Assume the wave is propagating along the x-axis. The \( \vec{E} \) and \( \vec{H} \) can be described as:

\[ \vec{E}_i = (E_{i_x}, 0, E_{i_z}) e^{-k \cdot |\vec{q}|} e^{i(q \cdot x - \omega t)} \quad (5) \]

And

\[ \vec{H}_i = (0, E_{i_y}, 0) e^{-k \cdot |\vec{q}|} e^{i(q \cdot x - \omega t)} \quad (6) \]

where \( |\vec{q}| \) represents the magnitude of a wave vector that is parallel to the surface.

Substituting equations (5) and (6) into equations ((1)-(4)), we have

\[ i k_i H_i = + \frac{\omega}{c} \hat{\partial} E_i \quad (7) \]
\[ ik_2 H_2, = -\frac{\omega}{c} \partial_z E_2, \]  
\hspace{1cm} (8)

And

\[ k_i = \sqrt{q_i^2 - \omega^2 \frac{\epsilon_0}{c^2}} \]  
\hspace{1cm} (9)

According to the boundary conditions that the electric and magnetic fields are parallel to the surface and they must be continuous, equations (7) and (8) can be further simplified into the following:

\[ \frac{k_1}{q_1} H_{1,} + \frac{k_2}{2} H_{2,} = 0 \]  
\hspace{1cm} (10)

And

\[ H_{1,} - H_{2,} = 0 \]  
\hspace{1cm} (11)

equations (10) and (11) have a solution with surface-plasmon condition

\[ \frac{q_1}{k_1} + \frac{q_2}{k_2} = 0 \]  
\hspace{1cm} (12)

Assume \( q_1 = q_2 = q \), and substitute it into equations (9) and (12). We now can get

[170]:

\[ q(\omega) = \frac{\omega}{c} \sqrt{\frac{\epsilon_2}{\sqrt{\epsilon_2 + 2}}} \]  
\hspace{1cm} (13)

where \( \omega/c \) represents the magnitude of the light wave vector. For a metal–dielectric interface with the dielectric of \( \epsilon_2 \), the solution \( \omega(q) \) of equation (13) has a slope equal to \( c / \sqrt{\epsilon_2} \) at the point \( q = 0 \); \( \omega(q) \) is a monotonic increasing function with respect to \( q \), which is always smaller than \( c q / \sqrt{\epsilon_2} \), and for large \( q \), it is asymptotic to the value given
by the solution of
\[ \frac{d^2}{dx^2} - 2 = 0 \] (14)

### 2.1.2 Energy Dispersion

In the case of a Drude semi-infinite metal in vacuum, one has \( \epsilon_2 = 1 \) and equation (13) becomes
\[ \dot{\epsilon} = 1 - \frac{\omega_p^2}{\omega(\omega + i\eta)} \] (15)

where \( \eta \) is a positive infinitesimal. Hence, in this case equation (13) yields:
\[ q(\omega) = \frac{\omega}{c} \sqrt{\frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2}} \] (16)

where the dispersion relation of equation (16) together with \( q(\omega) = \frac{\omega}{c} \sqrt{\frac{\omega^2 - \omega_p^2}{2\omega^2 - \omega_p^2}} \) to get
\[ \omega^2(q) = \omega_p^2 / 2 + c^2 q^2 - \sqrt{\omega_p^4 / 4 + c^4 q^4} \] (17)

Here, if light hits the surface in an arbitrary direction the external radiation dispersion line will always lie somewhere between the light line \( cq \) and the vertical line, in such a way that it will not intersect the surface plasmon polariton line, i.e. light incident on an ideal surface cannot excite surface plasmons. Nevertheless, there are two mechanisms that allow external radiation to be coupled to surface plasmon polaritons: surface roughness or gratings, which can provide the requisite momentum via umklapp processes [72], and attenuated total reflection (ATR) which provides the external radiation with an imaginary wave vector in the direction perpendicular to the surface [73,74].
2.1.3 Skin Depth

Because the electric field falls off evanescently perpendicular to the metal surface, at low frequencies, the SPP penetration depth into the metal is commonly approximated using the skin depth formula.

We assumed the spatial extension of the electromagnetic field associated with the surface-plasmon polariton (see figure 4 a). Substituting the surface-plasmon condition of equation (13) into equation (9) (with $q_1 = q_2 = q$), the decay constant of surface-plasmon along the direction perpendicular to the interface $k_i$ can be written as,

$$k_i = \frac{\omega}{c} \sqrt{\frac{-\varepsilon^2}{\varepsilon_1 + \varepsilon_2}}$$  \hspace{1cm} (18)

The attenuation length ($l_i$), defined as the depth where the electromagnetic field falls to $1/e$, is thus given as $l_i = 1/\kappa_i$. From equation (18), one can see that $l_i$ is a function of the magnitude of the surface-plasmon polariton wave vector, $q$, for a Drude metal ($\varepsilon_1$ of equation (15)) in vacuum ($\varepsilon_2 = 1$). In the vacuum side of the interface, the attenuation length is over the wavelength involved ($l_2 > 1/q$), whereas the attenuation length of the metal is determined at long-wavelengths (i.e., $|q| \rightarrow 0$) by the so-called skin depth. At large $|q|$ (where the nonretarded surface-plasmon condition of equation (14) is fulfilled), the skin depth is $l_i \sim 1/q$, leading to a strong concentration of the electromagnetic surface-plasmon field near the interface.

2.1.4 SPR on the Metal Thin film

Metal thin film is also known to support surface collective oscillations. For this geometry, the electromagnetic fields of both surfaces interact in such a way that the retarded surface-plasmon condition of equation (12) splits into two new conditions (we
only consider nonradiative surface plasmons), depending on whether electrons in the two surfaces oscillate in phase or not. In the case of a thin film of thickness $a$ and dielectric function $\epsilon_1$ in a medium of dielectric function $\epsilon_2$, one finds [165]:

$$\frac{k_1}{k_1 \tan(k_1 a / 2)} + \frac{k_2}{k_2} = 0$$  \hspace{1cm} (19)

And

$$\frac{k_1}{k_1 \text{ctn}(k_1 a / 2)} + \frac{k_2}{k_2} = 0$$  \hspace{1cm} (20)

Instead, if the film is surrounded by dielectric layers of dielectric constant $\epsilon_0$ and equal thickness $t$ on either side, one finds:

$$\frac{k_1 v}{k_1 v \tan(k_1 a / 2)} + \frac{k_0}{k_0} = 0$$  \hspace{1cm} (21)

And

$$\frac{k_1 v}{k_1 v \text{ctg}(k_1 a / 2)} + \frac{k_0}{k_0} = 0$$  \hspace{1cm} (22)

Where

$$v = \frac{1 - \Delta e^{-2k_0 t}}{1 + \Delta e^{-2k_0 t}}$$  \hspace{1cm} (23)

With

$$\Delta = \frac{k_2 \epsilon_1 - k_0}{k_2 \epsilon_1 + k_0}$$  \hspace{1cm} (24)

And

$$k_0 = \sqrt{q^2 - \hat{q}_0 \frac{\omega^2}{c^2}}$$  \hspace{1cm} (25)

Electron spectrometry measurements of the dispersion of the surface-plasmon
polariton in oxidized Al films were reported by Pettit et al [172], spanning the energy range from the short-wavelength limit where \( \omega \sim \omega_p / \sqrt{2} \) all the way to the long-wavelength limit where \( \omega \sim cq \). Good agreement between the experimental measurements and the theoretical prediction by equations ((21)–(25)) (with a Drude dielectric function for the Al film surrounded by and an oxide with a dielectric constant \( \epsilon_0 = 4 \)) has been reported, as shown in figure 6).

![Figure 6](image)

**Figure 6** Dispersion \( \omega(q) \) of the surface-plasmon polariton of an Al film of thickness \( a = 120\text{Å} \) surrounded by dielectric layers of equal thickness \( t = 40\text{Å} \).

In the nonretarded regime (i.e., \( q >> \omega_s/c \)), with \( k_1 = k_2 = q \), equations (19) and (20) take the form of

\[
\frac{\sqrt{\epsilon_2}}{2} = \mp e^{-qa}
\]  

(26)

For a Drude thin film, substituting equation (15) as well as the vacuum condition \((\epsilon_2=1)\) into equation (26), we now have

\[
\omega = \frac{\omega_p}{\sqrt{2}} (1 \pm e^{-qa})^{1/2}
\]  

(27)

However, equation (27) has two limiting cases, as discussed by Ferrell [68]:

\[
\omega = \frac{\omega_p}{\sqrt{2}}
\]  

(28)
• At short wavelengths ($|q|a>>1$), the surface waves become decoupled and each of two surfaces (figure 7) has sustained independent oscillations at a reduced frequency $\omega_s = \omega_p/\sqrt{2}$.

![Figure 7](image)
The surfaces of metal thin film

• At long wavelengths ($|q|a << 1$), there are oscillations at $\omega_p$ and tangential 2D oscillations at

$$\omega_{2D} = (2\pi nq)^{1/2} \tag{28}$$

The 2D oscillations were discussed in [173], and observed in III-V semiconductors [174] and more recently, in a metallic surface-state band on a silicon surface [175].

2.1.5 Existence of Surface Plasmon

For a metal-dielectric interface as shown in figure 4 (a), surface plasmon polaritons only exist for transverse magnetic (TM) polarization, where the magnetic fields are along y direction. The fields of surface plasmon polaritons can be expressed as equations (29), (30) and (31):

$$H_y(z) = A_y e^{i B_k z} e^{-k_z z} \tag{29}$$

$$E_x(z) = iA_x \frac{1}{\omega\varepsilon_0\varepsilon_2} k_x e^{i B_k z} e^{-k_z z} \tag{30}$$

$$E_z(z) = -A_y \frac{\beta}{\omega\varepsilon_0\varepsilon_2} e^{i B_k z} e^{-k_z z} \tag{31}$$

$$H_y(z) = A_y e^{i B_k z} e^{-k_z z} \tag{32}$$

$$E_x(z) = -iA_x \frac{1}{\omega\varepsilon_0\varepsilon_2} k_x e^{i B_k z} e^{-k_z z} \tag{33}$$

$$E_z(z) = -A_y \frac{\beta}{\omega\varepsilon_0\varepsilon_2} e^{i B_k z} e^{-k_z z} \tag{34}$$
where \( k_1 \) and \( k_2 \) are wave vector components perpendicular to the interface, \( \beta \) is the wave vector component parallel to the interface, and \( A_1 \) is a constant determined by the excitation. Substituting the boundary condition given in equation (35) into equations (29) through (34), we can arrive at equations (36) and (37):

\[
\frac{k_2}{k_1} = \frac{-\varepsilon_2}{\varepsilon_1}
\]

(35)

\[
k_1^2 = \beta^2 - k_0^2 \varepsilon_1
\]

(36)

\[
k_2^2 = \beta^2 - k_0^2 \varepsilon_2
\]

(37)

From equations (36) and (37), the dispersion of SPPs can be obtained as:

\[
\beta = k_0 \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}}
\]

(38)

Equation 38 indicates that resonance maximizes at the condition of \( \varepsilon_1 = -\varepsilon_2 \). The field distribution of surface plasmon polaritons is shown in figure 4 (a) [10].

2.1.6 Exciting surface plasmons

The excitation of surface plasmons can be achieved by introducing optical energy to the system by establishing a match between the wave vector of the incident light (\( K_{sp} \)) and the wave vector of the surface plasmon to be generated in the direction of surface plasmon propagation (\( K_{light} \)). That is,

\[
k_{light} = k_{sp}
\]

(39)

The wave vector of the incident light is obtained from equation (39) while \( k_{sp} \) comes from equation (38). With free electron model of metals (Drude theory) [169], the dielectric constant, \( \varepsilon_m \) of a metal is given by
\[ \varepsilon_m = \varepsilon_m(\omega) = 1 - \left( \frac{\omega_p}{\omega} \right)^2 \]  

(40)

Where \( \omega \) is the incident optical frequency and \( \omega_p \) is the plasmon frequency of the metal used. Substituting this into equation (36) gives equation (41) for the surface plasmon and equation (42) for the light:

\[ \omega_{sp}^2 = (ck_{sp})^2 + \frac{\omega_p^4}{4} \left[ \frac{\omega_p^4}{4} + (ck_{sp})^4 \right]^{\frac{1}{2}} \]  

(41)

\[ \omega_{light}^2 = \frac{(ck)^2}{\mu_r \varepsilon_r} \]  

(42)

Figure 8  Dispersion relations of light and surface plasmons

Figure 8 shows plots of equations (41) and (42) essentially as a function of wave vector, \( k \), since the speed of light, \( c \), is constant, and where it has been assumed \( \mu_r = 1 \), \( \mu_d = 1 \), and \( \mu_m = 1 \). This is appropriate since dielectrics and noble metals are typically non-magnetic. Also, \( \varepsilon_d = 1.00 \) for vacuum or air and \( \varepsilon_d = 2.25 \) for glass are used.

However, the wave vector of light in vacuum never matches with that of plasmon in the optical range. Hence, surface plasmons cannot be excited directly from vacuum or air.
An optically denser dielectric, like glass, has to be used to increase the wave vector of the light to achieve this excitation. Unfortunately, it is difficult to physically achieve the momentum match discussed thus far, since only scalar wave number matches are considered in figure 5. A method of realizing the wave vector match was provided by Kretschmann [3] and a diagram showcasing this method is given in figure 9.

![Diagram of Kretschmann coupling prism](image)

Figure 9  Excitation of surface plasmons using the Kretschmann coupling prism.

2.2 Localized Surface Plasmon Resonance (LSPR)

In contrast to propagating SPR, the phenomenon of LSPR from metal nanoparticles (MNPs) was observed long time ago, much longer before it was fully understood.

![Image of Lycurgus Cup](image)

Figure 10  The Lycurgus Cup in reflected (a) and transmitted (b) modes (courtesy of Celly M.S. Izumi, Brazil).
Figure 10 shows an example of the application of the LSPR effect of MNPs in early civilizations. It is the famous Lycurgus Cup made in ancient Roman time, somewhere in the fourth century A.D. The most remarkable property of this cup is that it presents the color of jade under direct light (figure 10 a). However, the color of the cup changes dramatically into a ruby color once light is shining through the cup (figure 10 b).

This behavior puzzled people for centuries. In 1959, researchers at General Electric Company Ltd found trace amounts of gold, silver and other elements in the glass. Although they believed that these trace elements were responsible for the so called “dichroic effect”, they still didn’t fully understand the mechanism [35]. The idea that the presence of Au:Ag alloy NPs, 50~100 nm in diameter, is responsible for the dichroic effect became well accepted in the late 1980s. These alloy NPs present LSPR frequencies around 400~520 nm. Hence, when the Lycurgus cup is under direct illumination, it will scatter more in that frequency range, leading to the jade color appearance. Once the illumination is through the cup, light at the same frequency range will be scattered/absorbed, and the ruby color will appear due to the complementary color effect.

With recent advances that allow the controlled fabrication and manipulation of metallic structures on the nanoscale, such of this structure was called nanoantenna, plasmonic nanoantenna, or plasmonic nanoantenna, which takes advantage of the localized surface plasmon resonance (LSPR).

Normally, nanoantennas formed by coupled noble metal particles enable the plasmon resonance and strong enhancement of the local electromagnetic field in the gap that can be tuned to different frequencies (figure 11) [2]. The localized surface plasmon resonances and highly confined electromagnetic fields produced by nanoantennas make
many applications like we discussed in chapter 1 possible. Gold and silver are appropriate plasmonic materials for the visible range due to their low electron relaxation rates, high plasma frequency, and high-frequency interband transitions.

![Nanoantennas and the resonance mechanism.](image)

**Figure 11** Nanoantennas and the resonance mechanism.[7, 8]

### 2.2.1 Conditions for the Existence of LSPR

Similar to the SPR, the LSPR is sensitive to changes in the local dielectric environment [43, 45, 46]. Localized surface plasmons are collective oscillations of electrons at the interface between small domains of metal and dielectric materials. In other words, localized surface plasmons can be viewed as surface plasmons that are on a non-flat surface and do not have unlimited interaction distances; in this case, light interacts with particles much smaller than the incident wavelength (figure 4 b). This plasmon that oscillates locally around the nanoparticle with a frequency is what we call the LSPR [41, 43]. The propagation of localized surface plasmons is limited to the small domains in which they exist, which results in an oscillation of the displaced electrons. A localized surface plasmon can therefore be modeled as an oscillatory dipole (figure 12).
In order for a localized surface plasmon to exist, certain requirements must be met. Before these conditions are mentioned, it would be appropriate to review some aspects of electromagnetic wave propagation.

To analyze localized surface plasmons, let us consider a simple case: where a metallic sphere embedded in a dielectric host under plane wave illumination (figure 13). Under electrostatic approximation we can obtain the electric fields inside the sphere:

\[ E_0 = \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} E_0 \]  \hfill (43)

From equation (43), the metal and the dielectric satisfy the condition \( \varepsilon_1 = -\varepsilon_2 \), then
resonances will happen, and strong electric fields will be generated. (see in figure 14)

2.2.2 The mechanism for excitation of LSPR

The mechanism for excitation of LSPR, or particles plasmon/Mie plasmons [10], is quite different from that of propagating SPR. For an isolated MNP under resonance conditions, when the size of the NPs is close to the penetration depth of light (e.g., ~20 nm for silver in the visible range), the free electrons in the whole MNP will oscillate together with the applied electromagnetic field. In other words, the MNP can be basically treated as a “molecule”. In response to applied field, for the simplest case, the free electrons will be shifted to one end, while the other end will be positively charged. Thus, the MNP behaves like a oscillating dipole caused by applied field. In theory, this oscillator will rely on both the electron density and the geometry of the MNP [33]. As a result, the amplitude of the induced electromagnetic field (LSP field) around the surface of the MNPs can be 1 or 2 orders [33] of magnitude higher than the field otherwise when the MNP is absent. Note that this is the simplest approximation for the excitation of
LSPR. The MNPs can have more than one single oscillation mode (i.e. multiple higher order oscillation modes exist), which means that the charge and field distribution can be quite different from what is seen in figure 3.

2.2.3 Tunable Radiative Properties

The Mie solution is a widely accepted classical description of the excitation of LSPR on MNPs. When only the dipole oscillation contributes to the extinction cross-section, the Mie solution can be reduced to the following equation [1, 3, 36-39]:

\[
\sigma_{ext}(\omega) = \frac{9V\varepsilon_d^{3/2}}{c} \cdot \frac{\omega \varepsilon_m(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_d]^2 + \varepsilon_2(\omega)^2}
\]

(44)

where \( \sigma_{ext}(\omega) \) is the extinction cross-section, \( V \) is the volume of the MNPs, \( \omega \) is the angular frequency of the exciting light, \( c \) is the speed of light in vacuum, \( \varepsilon_d \) and \( \varepsilon_m \) are the dielectric functions of the surrounding medium and the metal, respectively. It is clear from equation (44) that when \( \varepsilon_1 = -2 \varepsilon_d \) and \( \varepsilon_2 \) is small or weakly dependent on \( \omega \), the surface plasmon resonance absorption band appears.

Equation (44) shows no size-dependent effects for the LSPR frequency and bandwidth in MNPs, which disagrees with the experimental results [20, 23, and 37]. As shown in figure 15, both parameters, the resonance position and the bandwidth, change with the size. Even for MNPs smaller than 20 nm, size-dependent effects can still be noticed. For MNPs in the size range between 2 and 20 nm, a 1/r-dependency is observed for the LSPR bandwidth. However, the equation (44) fails to recognize the size-dependent effect due to the assumption that the optical properties of the MNPs are the same as they are in bulk forms [36-37]. Hence, a more complicated form of the dielectric function of the MNPs, which is both frequency- and particle-size-dependent (\( \varepsilon(\omega, r) \)), is
introduced to better match the experimental results [36].

![Figure 15](image)

Figure 15  Size, Shape, and composition tunability of the plasmon resonance in noble metal nanostructures. (a) Tuning the LSPR frequency of the gold nanorod long-axis mode by synthetically controlling aspect ratio. (b) Increase in the plasmon scattering to absorption ratio by increase in particle volume in gold nanosphere.

For larger MNPs with the size comparable to the wavelength of light, the MNPs can no longer be homogenously polarized. Higher order oscillation modes become more important in this scale and these higher order modes locate at the lower energy position [36].

2.2.4 Effects of Geometries

2.2.4.1 Effects of MNPs size

The size of a particle relates directly to its extinction ratio, which is a measure of the transmission and absorption of a particle. As shown in equation (44), the size of a particle
has a direct impact on the amplitude of the localized surface plasmon, or how well the electrons in the particle resonate at the material’s resonant frequency. The electrons in larger particles tend to resonate less as compared to those of smaller particles for several reasons: (i) the loss of the en masse displacement of electrons in the nanoparticle, and (ii) the sheer bulk of a larger particle, which dampens the tunneling across it. Red shifts due to the plasmon resonance occur with particles of increasing size.

2.2.4.2 Effects of MNPs shape

Shape also affects its resonance properties. When particles have nonsymmetrical shapes, the electrons begin to demonstrate resonances associated with each of the dimensions. For instance, while a spherical nanoparticle may have a single resonant frequency related to its singular dimension (i.e. its radius), an ellipsoidal particle may have two or three resonance frequencies corresponding to its two or three axes [6]. These differences arise from different orientations and magnitudes of the dipoles on the ellipsoidal particles [6, 15].

In this dissertation, the FEM simulation method is employed to study the nanoantenna’s resonance–geometry relationship and the optical near-field distribution, as shown in figures 16 and 17.

Figure 16  Schematic of a nanoantenna unit cell
2.2.5 Effects of Metal Nanoshell

A metal nano core-shell can be used to tune the LSPR [27]. Simulation result of such a core-shell is shown in figure 18 [40].

Starting from a solid spherical particle, as we decrease shell thickness, the LSPR red-shifts from the visible to the NIR due to increased coupling between the inner and outer shell surface plasmons [34-35]. We recently showed that the LSPR frequency decreases near-exponentially with the decrease of the shell thickness-to-core radius ratio[34]; this trend is universal and independent of the nanoshell size, core material, shell metal, or the surrounding medium, thus making it easy to design nanoshells with a desired optical resonance. The Halas group first realized the nanoshell structure via formation of a thin gold shell on the surface of silica nanoparticles [27]. Hollow
nanocages and nanocubes synthesized by galvanic replacement of silver nanoparticles by gold atoms show similar visible-NIR tunability by controlling the wall thickness and void size of the particle [36][37].

In order to further assess the importance of the aspect ratio of a nanostructure in determining the LSPR sensitivity to refractive index changes, an approximation method based on the quasistatic theory developed by Miller’s group and discrete dipole approximation calculations are applied [129]. Miller’s quasistatic theory is based on Mie theory [46], which states that the extinction energy of a metallic sphere, denoted as $E$, can be determined as the sum of the absorption and Rayleigh scattering:

$$E = 24 \frac{N_A \alpha^3}{\ln(10)} \frac{1}{l \ln(10)} \left[ (\epsilon + \frac{x}{\epsilon_m})^2 + \epsilon_i \right]$$

(45)

where $N_A$ is the areal density of nanoparticles, $\alpha$ is the radius of the metallic nanospheres, $\epsilon_m$ is the dielectric constant of the medium surrounding the metallic nanospheres, $l$ is the wavelength of the absorbing radiation, the nanostructure’s shape factor, and $\epsilon_i$ and $\epsilon_r$ are the respective imaginary and real parts of the nanostructure’s dielectric function. The dipolar plasmon resonance condition for the nanoparticles (equation (43)), which is also the occurrence of the LSPR maximum peak, is satisfied when

$$\epsilon_r = \chi n^2$$

(46)

where $n$ is refractive index of the surrounding medium.

2.2.6 Periodic Structures

For many years, theoretical studies of the normal modes of complex composite systems were generally restricted to mean-field theories of the Maxwell–Garnett type, which gives an approximation to the behavior of localized dipole plasmons [129].
Recently, a number of methods have been developed for solving Maxwell’s equations in periodic structures [196–201]. The transfer matrix method has been used to determine the normal-mode frequencies of a lattice of metallic cylinders [202] and rods [203], a so-called on-shell method has been employed by Yannopapas et al to investigate the plasmon modes of a lattice of metallic spheres in the low filling fraction regime [204] and a finite difference time domain (FDTD) scheme has been adapted to extract the effective response of metallic structures [201].

Most recently, an embedding method [199] has been employed to solve Maxwell’s equations, which has allowed calculating the photonic band structure of three- and twodimensional lattices of nanoscale metal spheres and cylinders in the frequency range of the Mie plasmons [143]. For small filling fractions, there is a surface-plasmon polarization which in the nonretarded region yields the nondispersive Mie plasmon with a frequency of \( \frac{\omega_p}{\sqrt{D}} \). As the filling fraction increases, a continuum of plasmon modes is found to exist between zero frequency and the bulk metal plasmon frequency [143], which yields strong absorption of incident light and whose energy can be tuned according to the particle–particle separation [205].

2.2.7 Sum Rules

Sum rules have played a key role in providing insight in the investigation of a variety of physical situations. A useful sum rule for the surface modes in complementary media with arbitrary geometry was introduced by Apell et al [206], which in the special case of a metal/vacuum interface implies that [207]

\[ \omega_{s1}^2 + \omega_{s2}^2 = \omega_p^2 \]  \hspace{1cm} (47)

where \( \omega_{s1} \) is the surface-mode frequency of a given system and \( \omega_{s2} \) represents the surface
mode of a second complementary system in which the regions of plasma and vacuum are interchanged (see figure 19).

Figure 19  Complementary systems in which the regions of plasma and vacuum are interchanged. Figure 19 a shows the general situation. Figure 19 b represents a half-space filled with metal and interfaced with vacuum. The surface-mode frequencies $\omega_{s1}$ and $\omega_{s2}$ of these systems fulfill the sum rule of equation (47).

For example, a half-space filled with a metal that has a bulk plasma frequency of $\omega_p$ and is merged with vacuum filled in the other half of the space (see figure 19 b), equation (47) becomes

$$\omega_{s1} = \omega_{s2} = \omega_p / \sqrt{2}$$

which is referred as Ritchie’s frequency of plasma oscillations at a metal/vacuum planar interface.

For a Drude metal film with equal and abrupt planar surfaces, the actual values of the nonretarded $\omega_{s1}$ and $\omega_{s2}$ are those given by equation (25), which fulfills the sum rule dictated by equation (47). For a spherical fullerene molecule described by assigning a Drude dielectric function to every point between the inner surface (with a radius of $r_1$) and outer surface (with a radius of $r_2$), one finds the frequencies for the in-phase and out-of-phase surface modes [208] given below, which also fulfills the sum rule (equation...
2.3 The Coupling between LSPR and SPR Modes

Plasmonics relies on the excitation of electromagnetic modes associated to collective oscillations of the electronic charge density in the metal. These electromagnetic modes manifest differently depending whether the metallic system is localized or delocalized. Localized surface plasmon (LSP) modes are associated with a small metallic particle of subwavelength dimensions and are non dispersive. They depend on the particle geometry, material and environment [6]. LSP are often associated with a large enhancement of the electric field, generally localized at sharp corners of the particle. Delocalized surface plasmon modes, or surface plasmon polariton (SPP) modes are surface waves confined near a metal-dielectric interface, which can propagate over large distances (around 5 to 10 μm for gold in visible). SPP can be laterally confined using a metallic stripe, a band-gap structure [7, 8], a nanowire of subwavelength section [9, 10, 11], or a channel dug inside a metal film [12].

In this dissertation we investigate the coupling and the interplay between LSP and SPP by studying the interaction between a three-dimensional gold nanoparticle and a thin gold film deposited on a silica substrate (figure 20). This system supports a delocalized and a localized surface plasmon mode. Furthermore, the localized resonance associated to the particle strongly depends on the distance between the particle and the layer [13].

It is a well-known fact that the resonance wavelength of such a particle depends on its shape, volume and environment [6, 13]. In particular, it is red-shifted when the dielectric constant of the surrounding dielectric increases. When approached towards a
dielectric substrate, the plasmon resonance corresponding to the side parallel to the interface is shifted to the red [13]. This effect is even increased when the particle is approached towards a metallic interface.

Here, we consider instead the use of very thin metal films embedded in a symmetric dielectric environment (and again positioned in the near-field of a NP array), where the NP-LSPs can simultaneously be coupled to SPP modes associated with charge-density waves on both surfaces, leading to a particularly rich dispersion behavior. By placing two or more plasmonic nanoparticles arrays close to metal film, it is possible to observe the interaction between the modes of each individual nanostructure, leading to the formation of New Hybrid Modes [4]. (see in figure 20)

Figure 20  System under study: metallic nanoparticles chain depositd on a stratified Au-SiO2-Si substrate. The interaction between delocalized SPR propagating on the film with LSPR chain modes leads to an enhancement of the electromagnetic field.

2.3.1 Mechanism of SPR and LSPR Coupling Enhancement Detection

While SPR has been the predominant plasmonic sensing technique, a second emerging sensing modality is that of the localized surface plasmon resonance (LSPR) of a single metallic NP or an array of metallic nanostructures [17–24]. As with SPR, analyte
binding to the NP surface increases the local refractive index, and thus the plasmon resonance is shifted. In contrast to the SPR of films, the LSPR of a NP has the distinction that the local fields are much more tightly confined, effectively reducing the surface area that needs to be exposed to the reaction medium and the number of molecules required to achieve a measurable resonance shift.

For example, in the case of a sharp tip or a gap between two NPs, strongly enhanced fields (orders of magnitude larger than the illumination field) can be confined to just a few cubic nanometers or less [25–27]. Molecules that enter these high-field regions can produce relatively large spectral shifts in the LSPR. A disadvantage of the LSPR sensing technique is that the active volume corresponding to the local field enhancement regions of NPs is typically miniscule as opposed to the overall assay volume, so that the probability of detection by this method can be low, especially for low-concentration assays.

A schematic cross-sectional view of the investigated geometry is shown in figure 18, where both the metal (Au) film and the overlaying gold nanoparticles have nanoscale geometry. In this structure, the SPPs on the top and bottom surfaces of the Au film are strongly coupled to each other, resulting in a large splitting of their dispersion curves and in the formation of even and odd hybrid modes. Examples of the intensity profiles of these SPP modes are plotted at a free-space wavelength of 500 nm using a transfer-matrix approach [7]. The odd modes extend spatially across the entire structure including the Ag nanoparticles array, where they can be further coupled to the nanoparticles LSPs, leading to an additional anticrossing in the plasmonic dispersion spectrum. At the same time, they also feature substantial (and geometrically tunable) penetration into the substrate, where a
waveguide or optoelectronic active layer designed to operate at similar wavelengths may be located. The latter property provides an important advantage of the present structure over a coupled LSP-SPP structure involving a single metal-dielectric interface.

In order to study the plasmonic dispersion properties of these structures, normally, several square-periodic nanoparticles arrays of different period have to be fabricated on the same nanoparticles/Metal film combination deposited on a silicon wafer, and then tested via broadband transmission measurements at normal incidence. Each array can provide the additional in-plane wave vector $K_{\text{array}} = \frac{2\pi}{\Lambda} \sqrt{p^2 + q^2}$ to the incident light, where $p$ and $q$ are integers determining the diffraction order. As a result, incident photons of suitable energy (depending on $\Lambda$) can be diffractively coupled into even and odd SPP modes guided by the metal film, leading to well defined minima in the sample transmission spectrum. At the same time, the incident light can also be directly attenuated by the NPs via absorption and scattering in spectral vicinity of their LSP resonance. By plotting the energies of the measured transmission minima as a function of the array wave vector $K_{\text{array}}$, the full dispersion behaviors of the coupled nanoparticle-film coupling system can then be reconstructed. The optical transmission measurements were conducted for each NP-film structures of geometry using broadband illumination at normal incidence with unpolarized light from a deuterium tungsten halogen source. In these measurements, the samples are mounted on a piezo-controlled stage, allowing each array to be probed individually. Finally, the structure is excited by a broadband total-field scattered-field source propagating in the direction perpendicular to the substrate surface (from the air side) and encompassing the entire nanoparticle grating and metal film. This source allows the scattering and absorption contributions to the system response to be
evaluated independently. The calculated absorption spectra are then utilized to determine the LSP resonance of the nanoparticle array and the absorption wavelengths associated with grating-coupled excitation of SPP modes propagating along the film surface.

To understand the reason for the observed spectral variations, the optical excitation of a single nanoparticle and the coupling of adjacent particles through the surrounding metal film have to be considered. As recently discussed in [27], electrodynamics simulations show that the single-hole resonance can be assigned to a localized surface plasmon (LSP) of electric dipole character. Thus, the incident optical field polarizes the nanoparticle and induces an electric dipole moment \( P = \alpha(\omega) E_0 \) with a direction parallel to the incident polarization vector \( E_0 \). The frequency-dependent polarizability of a nanoparticle can be derived from the Clausius–Mossotti relation (equations (50)-(52)):

\[
\alpha = r^3 (\varepsilon_s - \varepsilon_m) / (\varepsilon_s + 2\varepsilon_m) \tag{50}
\]

For a small spherical vacuum void (\( \varepsilon_S = 1 \)) of radius \( r \) in a metal characterized by a Drude dielectric response

\[
\varepsilon_M(\omega) = 1 - \omega_p^2(\omega(\omega + i\gamma))^{-1} \tag{51}
\]

Where \( \omega_p \) is the plasma frequency and \( \gamma^{-1} \) is the dephasing rate of the free electrons. This yields a Lorentzian polarizability:

\[
\alpha(\omega) = \alpha_0 \omega_0^2 / (\omega_0^2 - \omega^2 - i\omega\gamma) \tag{52}
\]

where \( \alpha_0 = -r^3/2 < 0 \) and \( \omega_0 = \sqrt{2/3\omega_p} \) comparable to the case of a small metal particle in vacuum; and when the \( \alpha_0 = r^3 > 0 \) and \( \omega_0 = \sqrt{1/3\omega_p} \) comparable the case of a larger metal particle.

Analogous to the case of Au nanoparticles, the particles considered here exhibit a
red-shifted LSP resonance $\omega_b = \sqrt{2/3} \omega_p$, corresponding to charge oscillations in the plane of the metal film, and a larger linewidth $\Gamma > r$ due to radiative losses [28,29].
Chapter 3
PLASMANIC NANOANTENNAS: DESIGN AND FABRICATION

3.1 Introduction

An plasmonic nanoantenna is a novel metal nanostructure that can sustain electron plasma oscillations leading to a resonant frequency that is proportional to its characteristic size \( L \), and index of surrounding medium \( n \). Similar to a microwave dipole, the resonant wavelength is given by \( \lambda_{\text{res}} = 2\pi n L \). Novotny [5] and others [6] have carried out rigorous calculations to derive a simple scaling law for gold nanorods to show that the resonant wavelength \( \lambda_{\text{res}} \) is dependent on type of metal (through \( \lambda_p \), the plasmon frequency), antenna geometry, and the dielectric properties of the surrounding medium. Another way to “engineer” the antenna properties is by using a dimer antenna [54] and varying the gap between the particles [31-32, 34]. The dimers are strongly polarization dependent [3, 33], with a red-shifted peak for polarization along the dimer axis and a weak but slightly blue-shifted peak for normal polarization (figure 21).

![Figure 21](image_url)

Figure 21 (a) Topographic image of a 120 nm Au bowtie antenna with 20 nm gap fabricated using electron-beam lithography; (b) DDA simulated extinction efficiency showing polarization dependence and splitting of triangle resonance mode into two orthogonal modes for the bowtie dimer (\( L = 120 \) nm).[47]
Directly adjacent nanoparticle pairs, also known as “dimers”, give rise to very large field enhancement in their junctions, which was attracted because they allow enhancement of input signal (by $>10^3$) with extremely high intensities in the gaps [3, 33]. The high fields are important for several applications including sensing [21-24], high harmonic generation [20, 30], sub diffraction lithography [25], imaging [19] and several other novel applications [19, 28-29, 36-37]. However, precise control over fabrication of the antenna gaps is critical for field enhancement [8, 14, 34, 37].

Current manufacturing techniques, e.g., electron-beam lithography, have the capability to fabricate sub-20 nm features; unfortunately, good control of feature size as well as repeatability over large areas is essential for studying the antennas for possible applications. Additionally, the challenges of low throughput and high cost of the electron-beam lithography need to be addressed. Keeping these goals in mind, three different approaches for fabrication of Nanoantenna were taken. In the first approach, top-down methods including E-beam lithography, Focus Ion beam and etc. In second approach, bottom-up method using self-assembly to pattern nanoantenna structures. The last is a novel technique recently developed in our group [192], called “nano pipette writing system” was explored.

3.1.1 Electron-Beam lithography

Electron-beam lithography is one of the most common techniques to fabricate sub-100 nm features. Since this technique is highly matured and has been extensively used, only a general overview of fabrication steps is provided [49, 56]. For samples fabricated for optical measurements, gold and silver nanoantennas were fabricated on 0.4 mm thick glass substrates with 25 nm thick ITO coating. Samples for cathodoluminescence
measurements were fabricated on 2 inch prime grade Si (100) substrates (from www.Universitywafers.com). The pre-cleaned substrates were first sonicated in an acetone bath for 5 min and dried at 200°C for 2 min. Afterwards, Poly(methyl methacrylate) (PMMA) photoresist (2% solution of 95k mol. wt. in anisoline, from sigma alrich.) was spin deposited at 2000 RPM for 60 sec. The polymer was baked for 2 minutes at 200°C resulting into ~ 90 nm thick resist layer. The e-beam lithography exposure was carried out at 20 nA beam current at various dose values. After exposure, the samples were developed for 180 sec in 3:1 solution of IPA:MIBK. All the silver samples were fabricated using e-beam evaporation (Cooke Evaporator) in the Micro and Nano Technology Lab at pressures below 8E-7 torr, with a 3 nm Cr adhesion layer underneath. The gold samples were fabricated with e-beam evaporators (Temescal) in the Materials Research Lab at pressures ~ 5E-6 torr, with 3 nm Ti adhesion layer. Finally, acetone was used for lift-off, followed by sonication in steps of 30 sec (but only when found necessary). Figure 15 shows images of bowties fabricated using this approach.

Using the first technique, plasmon waveguides have been successfully fabricated, and electromagnetic energy transport below the diffraction limit has been detected [10]. This method suffers from serious size-limitations, however. For efficient dipole coupling of the plasmons the interparticle distance must be small: in case of 50 nm diameter particles an interparticle distance of 25 nm is preferred. Such structures are very difficult to fabricate using conventional electron-beam lithography and lift-off techniques.

3.1.2 Focus electron/ion Beam

Hsu et al. [47-50] have previously reported a novel method of direct metal patterning using electrochemical etching with a superionic conductor “stamp.” An FIB milled stamp
was brought in contact with metal film and small external potential (~0.3 V) and low pressure (< 10 MPa) were applied. Etching of the metal film at the contact region resulted in a metal pattern complimentary to the original stamp. The procedure and representative images during the various steps are shown in figure 22.

![Diagram of steps in FIB process]

Figure 22 Various steps of the embossing based FIB process and representative images taken during these steps.

In focused ion/electron beam, metal nanoparticles are formed by electron-beam induced decomposition of a metallo-organic gas. Using this technique, nanoparticles can be deposited with lateral sizes of 20-30 nm and an interparticle distance of ~10nm [13]. Drawbacks of this technique are the high equipment costs and slow fabrication. At same time, this approach has to fabricate large arrays of antennas with very narrow gaps required for various applications of nano-antennas.

3.1.3 Colloidal Self-assembly

Colloidal self-assembly offers some great advantages over these techniques in terms of particle dimensions, fabrication time and costs, although the process is less controllable. Using this method, plasmon waveguides are formed by controlled drying of a colloidal dispersion over an electron-beam patterned substrate. By coating the metal
particles with a dielectric material like silica, the interparticle distance in the particle array can be accurately tuned via the thickness of the shell. Figure 23 shows an schematic example of a self-assembled plasmon waveguide, consisting of Au-core/silica-shell nanoparticles.

![Image of a plasmon nanoantenna formed by self-assembly of Au core/silica-shell colloids in electro-beam defined trenched in silica. The insert shows a cross-section of two nanoshells in the waveguide[33].]

**Figure 23** Illustration of a plasmon nanoantenna formed by self-assembly of Au core/silica-shell colloids in electro-beam defined trenched in silica. The insert shows a cross-section of two nanoshells in the waveguide[33].

### 3.2 Plasmonic Nanoantenna Design

#### 3.2.1 Nanoantenna pattern structure and size

To manipulate the radiative damping, one can exploit the concept of plasmon hybridization [21] to study coherent coupling between closely spaced nanostructures. For example, it has been predicted theoretically that concentric ring/disk cavities (CRDC) will exhibit sub and superradiant modes due to hybridization of the fundamental dipolar modes of the two constituents [22] and that Fano resonances can arise due to the interaction with higher order modes, when the structural symmetry is broken [23].

In this thesis we focus on sub- and superradiant plasmonic modes, as well as Fano resonances, in different structures as a dolmen-style slab arrangement, a ring/disk dimer, a ring/disk cavity and a colloid dimer.
Electromagnetic modeling was performed using the FDTD method. The dielectric response of the metal was fitted to the experimentally determined dielectric permittivity using a combination of Drude and Lorentz oscillator terms [40]. This fit has excellent agreement with the dielectric permittivity of the particular Au films obtained in our fabrication process from 600 nm onward, as confirmed via SEM. The effect of the glass substrate (refractive index \( n = 1.5 \)) on the resonances has been taken into account in the simulations and leads to a red-shift with respect to extinction calculations in vacuum. Also the slanted sidewalls are taken into account; the effect of the capping resist layer is not. All the charge plots are calculated at the top surface of the structures.

We define the effective mode volume \( V_{\text{eff}} \) by analogy with the effective mode lengths discussed in [36]. To do so, we use \( u_E \), the electromagnetic energy density at the point of coordinate \( \mathbf{r} \). For lossy metals,

\[
    u_E = \frac{\varepsilon_0}{2} \left( \varepsilon_1 + \frac{2\omega\varepsilon_2}{\gamma} \right) |E|^2
\]

(53)

where \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) is the complex dielectric function of a Drude model with damping \( \gamma \). Then:

\[
    V_{\text{eff}}(\gamma_0)u_E(\gamma_0) = \int u_E(\gamma)d\gamma
\]

(54)

where \( \gamma_0 \) is the position of an analyte. In the case of a ring or a disk, \( \gamma_0 \) is two mesh cells (4 nm) away from the structure, in the direction giving the highest field. In the case of CRDC, \( \gamma_0 \) is in the gap, 4 nm away from the disk, in the direction of the incident polarization.

The experimental has a very good agreement, which shed light on the nature of the underlying resonances.
3.2.2 Number of concentric rings

3.2.2.1 Coffee ring

In physics, a coffee ring is a pattern left by a puddle of particle-laden liquid after it evaporates. The phenomenon is named for the characteristic ring-like deposit along the perimeter of a spill of coffee. Robert D. Deegan of The University of Chicago and coworkers show that the pattern is due to capillary flow induced by the differential evaporation rates across the drop: liquid evaporating from the edge is replenished by liquid from the interior.[1] The resulting edgeward flow can carry nearly all the dispersed material to the edge. The coffee ring effect is utilized in convective deposition by researchers wanting to order particles on a substrate using capillary-driven assembly. Utilized by various groups including Vele [9] at North Carolina State University and Gilchrist [10] at Lehigh University using principles developed by Dimitrov and Nagayama,[11] replacing a stationary droplet with an advancing meniscus drawn across the substrate. This process differs from dip-coating in that evaporation drives flow along the substrate as opposed to gravity. Dongmao Zhang et al have utilized coffee ring drying pattern to pre-concentrate the protein solutions prior to Raman analysis in so called Drop Coating Deposition Raman (DCDR) technique. Constricting long range interaction in the confined space, whose geometry approaches the interacting length in short range and the assembled units, is advantageous for assembly of ordered nanoparticle arrays. Solvent evaporation and nanoparticle convections at micron-scale can assist the fabrication of “coffee ring” at the edge of liquid droplet. Solvent evaporations below the indenter can confine the process of convective assembly, resulting in the parallel nanoparticle strip with sub-micron separation. Another successful attempt is that gravity can trap
nanoparticles into the valley of the wrinkled substrate during the solvent evaporation. Hitherto, constrictions are not localized enough in comparison with nanoparticle size, and it is still a challenge to assemble sub-10 nm nanoparticles into the monolayered arrays. In this article, one technique based on “pipette writing” improves to steadily dispense solvent throughout artificial groove and allow convective assemblies to be confined at nm scale space, which has a potential chance to linearly assemble nanoparticles with the sizes of 5~50 nm in monolayer.

3.2.2.2 The nanoparticles concentric rings

From the figure 24, we can easily find the coffee ring effect is still in concentric circles pattern. That means each circle channel can be generated two nanoparticles circles. The final circles amount is two times the etching circles.

![The SEM images of Coffee rings and self-assembly nanoparticles](image)

Figure 24 The SEM images of Coffee rings and self-assembly nanoparticles

3.3 Nanoparticle Selection

Size is a critical parameter for designing nanoantenna experiments. However, what is not often emphasized is the dynamic nature of particle size due to agglomeration. Primary size is defined to be the dimension of an individual nanoparticles in a suspension. The primary size is important for calculating surface area per unit mass, dissolution rates,
melting point, and for defining the smallest dimension for diffusion, uptake, and biodistribution studies. When nanoparticles aggregate, they form clusters of 10's, 100's, or even 1000's of nanoparticles that have a much larger effective size than the individual nanoparticles. The hydrodynamic diameter of the aggregates can be measured using a dynamic light scattering instrument or centrifugal particle size and yields valuable information on the aggregation state at different time points in the experiment. For important parameters such as settling rate and biodistribution, it is the hydrodynamic size not the primary size that is the critical dimension.

To design experiments that probe the effects of size we considered,

1. If possible, use nanoparticle suspensions that are initially unagglomerated.

2. Select particles with a surface that is consistent across the range of sizes that you are interested.

3. Understand the aggregation rate upon exposure to fluids similar to those used in your experiments. For example, before introducing your nanoparticles into a cell culture experiment, determine how the particles behave in the cell culture medium alone. For many nanoparticles there is a shift in the optical properties of the particles when they agglomerate and the color of the solution can be used as an indicator for particle stability.

4. If possible, obtain the same particle size with different surfaces. For example, many of our particles are available in tannic/citrate/PVP surfaces. For nanoparticles with easily displaced stabilizing agents such as citrate, other molecules can be exchanged onto the surface simply by exposing the particles to a high concentration of the new stabilant.

5. Adjust the protocols to accommodate for the rate of agglomeration. For some systems, agglomeration occurs instantly, for others it may take days. Timing becomes
critical to maintain reproducibility since a low level of agglomerated particles may behave completely differently than particles that have agglomerated into large clusters.

3.4 Nanoparticles Synthesis

3.4.1 Gold Nanoparticles (GNPs)

GNPs are the colloidal suspension of gold particles of nanometer sizes. GNPs have been synthesized by an array of methods which mainly are based on the reduction of chloroauric acid in the presence of a stabilizing agent. The most commonly used method, the citrate synthesis method, includes reduction of chloroauric acid using trisodium citrate resulting into the formation of GNPs [2,9]. The size of GNPs is determined mainly by the salt concentration, temperature and rate of addition of reactants resulting in size range of 10–25 nm. However, the size range of 1–100 nm or more can also be achieved by varying the salt concentration and temperature. Another widely used method employs toluene using the tetra-octanyl ammonium bromide as a phase transfer reagent [10]. Several modifications of the basic methods have resulted into an array of techniques to synthesize and manipulate these nanoparticles satiating the needs of a specific research objective [11–13]. Chemical reduction using L-Tryptophane as a reducing agent for ionic gold and polyethylene glycol was used to produce AuCl4− ions to provide higher stability and uniformity in size, shape, and particle distribution [14]. Another method used methanol extract of medicinal plants as reducing agent to produce the “GREEN” or environmental friendly GNPs [15]. In another procedure, an amino acid derivative of serrapeptase has been used as stabilizing and reducing agent to synthesize stable “eco-friendly” GNPs [16]. Besides the usual spherical shape, GNPs have been synthesized in various other shapes affecting their physical and biochemical properties. For example,
hexagon and boot shaped GNPs show different surface enhanced Raman scattering (SERs) which in turn can be used to detect molecules conjugated to GNPs such as avidin, thereby making these functionalized GNPs (fGNPs) useful for biolabelling, bioassay, clinical diagnosis and therapy [17]. Gold nanocages of six and eight facets have also been synthesized [18]. Similarly, gold nanorods have been synthesized which find usage in biomedical applications for cancer imaging and photothermal therapy [19].

In our experiment, we take Gold nanoparticles (Au NPs) were obtained by reducing chloroauric acid, HAuCl4. The reducing agent, sodium citrate, also acts as a surfactant and assists, to some extent, with size control of the particles. Stock solutions of 6.0mM HAuCl4 and 11.0mM sodium citrate were initially made by dissolving the required masses of acid and salt in deionized water appropriately. The DI water had a resistance of 18.6 MΩ. An important requirement for nanoparticles for plasmonic waveguiding applications is a narrow particle size distribution. To investigate narrow size distribution, an experiment to identify the optimal reactant concentrations to obtain the narrowest size distribution of the gold nanoparticles was devised. The experimental matrix consisted of sodium citrate solutions at concentrations of 2.5, 2.0, 1.5, and 1.0mM and of HAuCl4 solutions at concentrations of 2.50, 2.00, 1.50, 1.25, and 1.00mM. The volume ratio of HAuCl4 solution to sodium citrate solution was held constant at 10%. This is the parameter referred to as volume ratio throughout this project. UV/Vis spectra of these samples were collected and analyzed. Consequent experiments were performed on only the samples with the two highest absorption peaks from this experiment.

Next was an investigation of the effect of volume ratio. The two reactions from the experimental matrix described above were repeated at the following volume ratios: 1%,
5%, 10%, 15%, 20%, 25%, 30%, 40% and 50%. Again, two colloids were selected from this pool and used when investigating the effect of thiol capping.

A 1.0mM solution of 16-mercaptohexadecanoic acid in ethanol was used as the thiol source. Various amounts of thiol were added to the colloids and UV/Vis measurements were recorded as a function of time. At this point, it was deemed that all the parameters associated with the gold nanoparticle required before conducting the experiments on the self-assembly into thin films by the proposed methods had been obtained. Attention was thus turned to the self-assembly of thin films.

3.4.2 Au@Ag Nano Coreshell

Gold (Au) and silver (Ag) nanoparticles have received considerable attention for many years because of their fascinating optical properties known as localized surface plasmon resonance (LSPR) [24,27,33], and their widespread use in applications related to photonics, catalysis, information storage, chemical/biological sensing, and surface-enhanced Raman scattering (SERS) [15,30]. In an effort to tailor their properties and thus improve their performance in various applications, people have developed a myriad of chemical methods for generating Au and Ag nanoparticles with a rich variety of shapes, including sphere, cube, decahedron, icosahedron, bipyramids, thin plate, rod, and wire [11-20]. Parallel to these developments, people have also looked into the possibility of combining Au and Ag into one single system to provide a new handle for controlling optical and catalytic properties. To this end, Au&Ag alloy and coreshell nanoparticles have been prepared and investigated in the context of catalysis, plasmonics, sensing, imaging, and biomedicine [21-35]. Particularly, by combining Au and Ag into a coreshell configuration, their LSPR properties can be potentially tailored and finely tuned by
varying the size/shape of the core and the thickness of the shell as well as the coupling between the core and the shell.

For core-shell nanoparticles, it is relatively easy and straightforward to generate Au (or an alloy of Au and Ag) shells on Ag cores (i.e., in the form of Ag@Au) because of a spontaneous galvanic replacement reaction between Ag Nanoparticles and a salt precursor to elemental Au such as AuCl$_4^-$ or AuCl$_2^-$ [36]. By controlling the volume of the salt precursor titrated into an aqueous suspension of Ag nanoparticles, one can readily control the thickness of the shells and thus the optical properties of the products. It might also be possible to directly generate Au coatings on Ag nanoparticles through the use of a salt precursor and a very strong reducing agent, although it would be hard to exclude the involvement of a galvanic replacement mechanism. In comparison, the coreshell nanoparticles with an inverted structure (i.e., Au@Ag consisting of a Au core and a Ag shell) can only be prepared via the conformal coating of Ag on Au nanocrystals in a solution phase.

In general, it should not be difficult to generate a conformal coating of Ag on the surface of an Au nanocrystal due to their close match of the lattice constant (the difference is only 0.2%) and thus the assurance of epitaxial growth. However, the deposited Ag can evolve into different shapes or morphologies depending on the experimental conditions such as the type of Au seeds (e.g., the size, shape, facets, and capping agent), the precursor to elemental Ag, the reductant, the capping agent present in the reaction solution, the solvent, and the temperature. All of these variables make this seemingly simple process hard to control and worthy of systematic investigation.

Here we use a facile route to the synthesis of Au@Ag core-shell nanocrystal with
relatively high yield (86-90%) in an aqueous solution. The edge lengths of the cubes can be finely controlled from 13.4 to 50 nm by using single-crystal spherical Au nanoparticles (11 nm, cuboctahedron) as the seeds and cetyltrimethylammonium chloride (CTAC) as a capping agent to direct the growth of Ag shells. The thickness of the Ag shells can be precisely controlled in the range of 1.2 to 20 nm due to the spherical shape and high uniformity for the Au seeds. These Au@Ag nanocubes with highly tunable and controllable sizes and shell thicknesses allowed us to systematically investigate their LSPR properties and obtain, for the first time, the critical shell thickness at which the plasmon excitation of the core will be completely screened by the shell. It is also worth pointing out that it has been very difficult to obtain Ag nanocubes with edge lengths smaller than 25 nm when a hydrophilic system based on polyol reduction in used [37].

In the experiment, the process of synthesis the Au@Ag nanoparticle using two steps, including Au nanocrystal seeds synthesis and Au@Ag nanocubes synthesis:

1) Synthesis of Au Nanocrystal Seeds capped with CTAC or CTAB

The Au nanocrystal seeds were prepared using a two-step procedure. We first made 3-nm Au nanoparticles by adding 0.6 mL of icecooled NaBH4 solution (10 mM) into a 10 mL aqueous solution containing HAuCl4 (0.25 mM) and CTAB (100 mM), generating a brownish solution. The seed solution was kept undisturbed for 3 h at 27 °C to ensure complete decomposition of NaBH4 remaining in the solution. For the synthesis of CTAC-capped Au seeds, 6 mL of aqueous HAuCl4 solution (0.5 mM), 6 mL of aqueous CTAC solution (200 mM), and 4.5 mL of aqueous AA solution (100 mM) were mixed, followed by the addition of 0.3 mL of the 3-nm Au nanoparticles. The final mixture turned from colorless into red within 1 min, indicating the formation of larger Au
nanocrystals. After 1 h, a UVvis spectrum was recorded from the Au nanocrystal suspension and the products were collected by centrifugation (14 500 rpm, 30 min) and then washed with water once. After dispersing the nanocrystals in deionized water, the concentration of elemental gold in this seed solution was found to be 0.146 g/L (the corresponding number concentration of Au nanoparticles was 1.08 10^{16}/L) as determined by ICPMS. For the synthesis of CTAB-capped Au seeds, the same method and addition sequence were used, except for the use of 6 mL of CTAB solution (200 mM) instead of CTAC solution in the growth of Au seeds. Also, the same washing conditions we used as for the CTAC-capped Au seeds. In order to generate much better uniform coreshell nanocubes, in here, two methods are employed in our experiment.

2.1) Synthesis of Au@Ag Nanocubes with CTAC@Au Seeds in the Presence of CTAC.

In a typical procedure, 0.5 mL of the CTAC Au seeds and 4.5 mL of CTAC (20 mM) aqueous solution were mixed in a 20 mL vial. After the mixture was heated at 60 °C for 20 min under magnetic stirring, a specific volume of aqueous AgNO\textsubscript{3} solution (2mM) and an aqueous solution of AA (50 mM) and CTAC (40mM) were simultaneously injected at a rate of 0.2 mL/min using a syringe pump. The volume of AA (50 mM) added into the reaction solution was kept the same as that of AgNO\textsubscript{3}. Different volumes (0.25, 0.5, 1, and 2 mL) of AgNO\textsubscript{3} were used to control the size of the resultant Au@Ag nanocrystals from 13.4 nm up to 20 nm. After injection, the concentrations of AgNO\textsubscript{3} in the final solutions were 0.09, 0.17, 0.29, and 0.44 mM, respectively. During the injection, the reaction mixture turned from red to brownish yellow. After 4 h, the vials were cooled in an ice-bath. The products were collected by centrifugation (14 500 rpm for 15 min)
and then washed with water once.

To control the size of Au@Ag nanocubes in the range of 20-50 nm, we used different volumes (0.5, 0.25, 0.1, and 0.05mL) of the CTACAu seeds. We kept the total volume of aqueous suspension containing the Au seeds and CTAC (20 mM) at 5mL. After mixing the two aqueous solutions and heating them at 60 °C for 20 min under magnetic stirring, 5 mL of AgNO₃ (2mM) aqueous solution and 5 mL of an aqueous solution containing AA (50 mM) and CTAC (40 mM) were simultaneously injected at a rate of 0.2 mL/min. Other procedures were the same as described above.

2.2) Synthesis of Au@Ag Nanocubes with CTAB-Au Seeds

The experiments were conducted in the same way as those with CTAC-Au seeds described in the previous sections, except for the use of different seeds.

3.5 The Growth of Thin Metal Film

Gold is currently the most important plasmonic material for optical devices including optical antennas. Due to its lower bulk electrical resistivity (2.44×10⁻⁸ at room temperature) and resistance to electromigration in metal interconnects, gold is also a potential material for achieving higher current densities and faster switching speeds. Despite several decades of efforts, there exists a lack of control over film growth of gold films, due to its high mobility and island-like growth. Therefore, improving device performance by growing high quality films is of enormous interest. A new approach of improving the gold film roughness by depositing a very thin Cr buffer layer has been shown earlier, which changes the thermodynamics of film growth [61]. Here, a new approach using Pd buffer layer (around 5nm), which has very small lattice mismatch with gold, is used that allows epitaxial growth of very thin metal films with extremely low
Both of these thin films were deposited using the same e-beam evaporator (figure 25). But before the deposition the chamber was cleaned thoroughly using alcohol to eliminate any possible contaminations. The built-in deposition thickness indicator (QCM) was re-calibrated using the surface profilometer which was first calibrated with a standard. The vacuum level of the deposition chamber [36] was kept at $10^{-7}$ Torr.

To get the less roughness thin metal film, the deposition rate of both metal films was kept at 0.1 Å/sec to manufacture the highest deposition uniformity. The Pd film thickness of 5 nm was deposited. Following the Pd film deposition gold nanofilms were immediately in situ deposited. The gold film thicknesses is about 50 nm were deposited.

### 3.6 Hybrid Plasmonic Nanoantenna Assembly

#### 3.6.1 Nano pipette writing system

In order to fabricate this hybrid This system was developed by our group using three high accuracy nano-step actuators (Physik Instrumente (PI) GmbH & Co. KG) and three nanostepping controllers to achieve nano scale etching requirements by automated programing.(figure 26)
The whole system can be fabricated nanoantenna at 0.01\(\mu\)m step (x axis), 0.1\(\mu\)m step (Y axis), and 10\(^{-6}\) degree step (rotate movement). This system can be driven by
programming C language, Labview or its own controlling system. In this dissertation, we used its own controlling system to pattern our plasmonic nanoantennas.

In the pipette writing system, two different size steel needles (6mm length, 8mm length), shown in the figure 27, were used in the experiment (Based on previous results, 6mm needle is a better choice for us, because the longer needles were easily bent during the processing.

![Steel needles used in the nanopipette system](image)

**Figure 27** Steel needles used in the nanopipette system

3.6.2 System programming

Detail information sees in the appendix.

3.6.3 Nanoparticles assembly

Phosphorous-doped silicon (100) wafers with the resistivity of ~10 ohm•cm polished on single side were utilized as the substrates for convective assemblies. Commercial pipettes were made from polypropylene, and their tips with the cone shapes had the inner diameter of ~0.4 mm and the outer diameter of 0.6 mm. The taper angle of the apex was
~8°. These pipette tips were gently polished by using silicon carbide paper in one direction (600 mesh), and the parallel grooves were created below the tips, which can serve as the leaking channels for the distribution of Au colloid. To determine the size of the grooves, stainless steel plates were polished in the same condition and characterized by SEM. All the steps of the assembly processes were conducted in ambient environment with room temperature (20°C), atmospheric pressure, and the humidity of ~50%. During the self-assembly process, the symmetrical axis of pipette tip was held to be perfectly vertical to the surface of silicon wafer, and moved towards the silicon wafer until gentle touch. Before loading Au colloid, the empty pipette did the translational sweep on the horizontal plane, making sure the motion was smooth enough to avoid pipette bending. The sweeping rate of pipette tip is around 2~3 microns per second. After being dried, microstructures of assembled arrays were characterized by SEM. The whole process was shown in figure 28.
Figure 28  Schematic illustration of colloidal particles assebling at the menisus of a colloidal suspenson droplet. In the early stage, the colloidal particles assemble into a monolayer: a) side view of the monolayer and b) top view of the monolayer. c) As time elapse, colloidal particles assemble into a multilayer (side view)

3.7 Summary

In this chapter, we firstly synthesis two kinds of metal nanoparticles: gold nanoparticle and Au@Ag coreshell nanocube, especially for Au@Ag we try to use two methods to synthesis. Secondly, the e-beam evaporation is employed to deposit metal thin film above the silicon wafer and microscope glass slides. In order to construct the hybrid plasmonic nanoantenna structure, we invented and build up a novel fabrication platform; meantime, this platform can be fabricated nanoantenna structure through the precisely programming. At last, the colloidal self-assembly fabrication approach is used to generate the nanostructure pattens.
Chapter 4

CHARACTERIZATION OF FABRICATED NANOANTENNAS

4.1 Characterized Nanoparticles

The colloids created were investigated by means of UV/Vis absorption spectroscopy (JASCO V670) in which features of the surface plasmon resonance (SPR) peak were measured and by scanning electron microscopy (SEM) in which the physical dimensions of the nanoparticles were measured. (See in figure 29) While the SPR measurements yielded information on the frequency response of the colloids to electromagnetic excitation, the SEM measurements provided data on the exact dimensions of the particles.

![SEM imaging of 50nm Gold Nanoparticles](image)

Figure 29  SEM imaging of 50nm Gold Nanoparticles

The spectra of surface plasmon resonance peaks obtained from the reactions of several different concentrations of HAuCl4 (denoted by a specific number) and sodium citrate (henceforth referred to as NaCitrate) (denoted by a specific letter) are given below table 2. The NaCitrate solution concentrations used were 2.5, 2.0, 1.5, and 1.0mM while the HAuCl4 solution concentrations used were 2.50, 2.00, 1.50, 1.25, and 1.00mM.
Table 2  Key for HAuCl4:NaCitrate Reaction Matrix

<table>
<thead>
<tr>
<th>HAuCl4 Concentration</th>
<th>NaCitrate Concentration</th>
<th>2.5mM</th>
<th>2.0mM</th>
<th>1.5mM</th>
<th>1.0mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50m</td>
<td>a1</td>
<td>b1</td>
<td>c1</td>
<td>d1</td>
<td></td>
</tr>
<tr>
<td>2.00m</td>
<td>a2</td>
<td>b2</td>
<td>c2</td>
<td>d2</td>
<td></td>
</tr>
<tr>
<td>1.50m</td>
<td>a3</td>
<td>b3</td>
<td>c3</td>
<td>d3</td>
<td></td>
</tr>
<tr>
<td>1.25m</td>
<td>a4</td>
<td>b4</td>
<td>c4</td>
<td>d4</td>
<td></td>
</tr>
<tr>
<td>1.00m</td>
<td>a5</td>
<td>b5</td>
<td>c5</td>
<td>d5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 30  Absorption spectra of the SPR peak from gold nanoparticles illustrating effect of varying HAuCl4 concentrations at constant NaCitrate concentrations
As can be seen in figure 30, increasing the chloroauric acid concentration resulted in larger gold particles, confirmed by the slight red shift in the SPR peak wavelength at higher HAuCl4 concentrations. From the figures 30 and 31, colloids b1 and c1, corresponding to reactions between 2.5mM HAuCl4 and 1.5 and 2.0mM NaCitrate, respectively, were chosen for further experimentation since the absorption curves
associated with the gold nanoparticles produced via these reactions produced the highest peak-to-FWHM (full-width-half-maximum) ratios of all the reactions. The FWHM was calculated by assuming that the only responses in the absorption spectra were due to surface plasmon peaks between 520 and 540 nm and were of Gaussian distributions. The end points were therefore assumed to satisfy the Rayleigh scattering criterion, therefore assumed to satisfy the Rayleigh scattering criterion,

\[ \lambda \propto I \frac{1}{\lambda^4} \]  

(55)

and the endpoints of the spectra were therefore fitted to

\[ I = \alpha \frac{1}{\lambda^4} + b \]  

(56)

By way of a Matlab program, the constants a and b are assumed to be arbitrary for each absorption spectrum and only assisted with obtaining the FWHM. While a served to scale the absorption spectra appropriately, b aided with adjusting the baseline offset, which is introduced by the electronics associated with the spectrometer. The maxima for the absorption curves were read off the plots and the peak-to-FWHM ratios were determined and plotted to obtain figure 32.

![Figure 32 Absorption curve of Nanoparticles using FWHM](image)
4.2 Characterized Core-shell Nanocrystals

The core-shell nanocrystals created were investigated by means of UV/Vis absorption spectroscopy. Their features of the surface plasmon resonance (SPR) peak were measured and by scanning electron microscopy (SEM) in which the physical dimensions were measured. Same as the Nanoparticles characterization, the SPR measurements yielded information on the frequency response of the colloids to electromagnetic excitation, the SEM measurements provided data on the exact dimensions of the particles.

The spectra of surface plasmon resonance peaks obtained from the reactions of several different Ag shell thickness. The Ag shell thickness used was 4.5nm, 3.1nm, 2.1nm, and 1.2nm.

4.2.1 The definition of the Ag shell thickness is calculated as figure 33

![Figure 33 Definition of the Ag shell thickness](image)

The spectra of surface plasmon resonance peaks obtained from the reactions of several different Ag shell thickness. The Ag shell thickness used was 4.5nm, 3.1nm, 2.1nm, and 1.2nm.

4.2.1.1 The definition of the Ag shell thickness is calculated as figure 33

$$ t = \frac{(a - d_{\text{core}})}{2} $$

and $d_{\text{core}}=10$ nm for the CTAC-Au seeds in our experiments.

4.2.1.1 Radius (r) of virtual sphere used in the description of truncation:
When a model of a spherical Au core and cubic Ag shell (without truncation) was used, we found that the extinction peak position around 500 nm stayed almost unchanged when the thickness increased, showing discrepancy with the experimental data. Considering the possible slight truncation for the cubic structure, we modified the model to a spherical Au core and cubic Ag shell with a certain degree of truncation at corners. We used a virtual sphere of radius \( r \) to describe such a truncation. When \( r = a/2 \) (where \( a \) is the edge length of the cube), the sphere touches the 6 faces of the cube; when \( r = 1.41(a/2) \), the sphere touches the 12 edges of the cube; when \( r = 1.73(a/2) \), the sphere touches the 8 corners of the cube. For \( r = 1.25(a/2) \), the UV-vis spectra for different Ag shell thicknesses agreed well with the experimental data (see figure 35).

Figure 35  Absorption spectra of the SPR peak for Au@Ag nanospheres using different Ag thickness
4.3 Antenna extinction cross section

For any optical studies, the first step in characterization of antennas involves excitation of the nanostructures using a broadband source. The transmitted signal shows a dip in the spectrum corresponding to the antenna resonance. At this wavelength, the incoming radiation has the highest coupling with the structures. To quantify the quality of this interaction, the most common method is to measure the scattering cross section [4,73], which is related to the ability of the antenna to scatter, absorb and reradiate the incoming radiation. A large cross section means high interaction volume of the nanostructure, providing better sensitivity to the nearby molecules and other species used for sensing. During optical measurements (inset, figure 36), the transmitted intensity $I$ at the spectrometer is a function of the incident beam power, and absorption and scattering by the antenna at each wavelength, which can be expressed as [4, 39, 73]

$$I(\lambda) = I_{\text{inc}}(\lambda) - I_{\text{abs}}(\lambda) - I_s(\lambda)$$  \hspace{1cm} (58)

Where $I_{\text{inc}}$ is the intensity of the incident beam (the intensity measured without samples), $I_{\text{abs}}$ is the intensity loss due to absorption in the antenna, and $I_s$ is the intensity loss due to scattering in all directions.

Also, the transmitted intensity can be written as

$$I(\lambda) = I_{\text{inc}}(\lambda) - C_{\text{ext}} \times S_{\text{inc}}$$  \hspace{1cm} (59)

Where $S_{\text{inc}}$ is the power density at the sample and $C_{\text{ext}}$ is extinction cross section of the antenna. $C_{\text{ext}}$ can also be regarded as the area of “geometric shadow” of the antenna, since the rate at which energy would impinge upon this area equals the actual rate of energy removal from the incident beam due to scattering and absorption by the antenna.

From this measurement, extinction efficiency can be derived, which is extinction cross section...
section divided by actual geometric cross section of the nanostructure.

Figure 36  Extinction efficiency of a 240 nm nanoparticles strips spaced 3 μm gap. Inset shows sketch of the measurement setup. A resonance peak at 960 nm is observed (the peak at 1200 nm is due to change in detector in measurement setup).

Figure 36 shows the extinction efficiency, $Q_{\text{ext}}$, of a 240 nm nanoparticle strips measured for arrays that are spaced 3 μm gap in both directions for minimal interaction. At resonance peak of 960 nm, highest efficiency, $Q_{\text{ext}} \sim 11$ was observed, indicating that on the spectrometer, the antenna appears almost 11 times larger than its geometrical size. This high extinction value for the lithographically designed nanostructures suggests excellent uniformity in fabrication as well as in the ability to efficiently excite them.

4.3.1 Antenna arrays

Plasmonic nanoantennas are seldom probed individually due to low signal-to-noise ratio. However, the array behavior of antennas can be dramatically different from that of individual nanostructures due to strong interactions [75-76]. When considering ordered arrays of nanoparticles, the polarizability of nanoparticles in an array also involves their geometric arrangement factor, $S$, and is given by [77]
\[
\alpha' = \frac{1}{\frac{1}{\alpha} - S}
\]  

(60)

where \( \alpha \) is polarizability of a single particle. From this expression, when the two terms in denominator are comparable, particle polarizability in arrays can be enhanced, resulting in resonances that are strongly influenced by the spacing in arrays. Examples of such a modification of resonance behavior are shown in figures 37. As the particles are brought closer, the dominant mode shows sharper resonance [76] as well as significant blue-shift. Therefore, any studies involving arrays of nanostructures need to account for the significant shift in resonance peaks based on their arrangement.

![Image of Plasmonic nanoantenna](image)

Figure 37 The pattern of Plasmonic nanoantenna

4.4 Summary

In this chapter, the optical spectrum meter and scanning electron microscope (SEM) are employed to characterize this hybrid plasmonic nanoantenna. In the first, through the SEM imaging we confirm the geometry of nanoparticle and nanoantenna structures. Then, we use optical spectrum meter to characterize their surface plasmon polarization effects show in above.
Chapter 5
APPLICATIONS OF NANOANTENNAS

Noble-metal nanostructures including colloidal nanoparticles and nanostructured surfaces have emerged as a fundamental tool for a number of fast growing applications, with a remarkable amount of literature dedicated to localized surface plasmon resonance (LSPR) effects and surface enhanced analytical techniques [1-3]. However, there still are some limitations and disadvantages in the conventional nanoantenna based applications. Hence, the hybrid plasmonic nanoantenna, in here, is employed to explore and beyond such these limitation and disadvantages. Based on our experimental environment, three applications are delivered in this dissertation, including 1) Enhanced Bio-fluorescence, 2) Surface enhanced Raman spectroscopy (SERS), and 3) Waveguide and Resonantor for Optically Interconnetced SoC Systems

5.1 Enhanced Bio-fluorescence

Fluorescence experiments are typically performed in sample geometries that are large relative to the size of the fluorophores and relative to the absorption and emission wavelengths. In this arrangement the fluorophores radiate into free space. Most of our knowledge and intuition about fluorescence is derived from the spectral properties observed in these free-space conditions. The presence of nearby metallic surfaces or particles can alter the free-space condition and can result in dramatic spectral changes. Remarkably, metal surfaces can increase or decrease the radiative decay rates of fluorophores and can increase the extent of resonance energy transfer [1–4]. These effects result from interactions of the excited-state fluorophores with free electrons in the metal, the socalled surface plasmon electrons, which in turn produce favorable effects on the
fluorophore. The effects of metallic surfaces include fluorophore quenching at short distances (~0–5 nm), spatial variation of the incident light field (~0–15 nm), and changes in the radiative decay rates (~0–20 nm). The use of fluorophore–metal interactions in biotechnology has primarily been referred to as radiative decay engineering or metal nanoparticles-enhanced fluorescence (MNP-EF).

For excitation power below saturation, the fluorescence signal $S_o$ for an isolated emitter is proportional to $\eta_o|d E_o|^2$, where $\eta o$ is the quantum efficiency of the emitter, $d$ is its electric dipole moment, and $E_o$ is the excitation field at the position of the emitter. $[5]$ $\eta o$ is simply the ratio between the radiative decay rate $\gamma_r$ and the total decay rate $\gamma_{r0}$. The total decay rate accounts also for a non-radiative decay $\gamma_{nr}$, i.e. $\gamma_{r0} = \gamma_r + \gamma_{nr}$. When the emitter is coupled to a nanoantenna and we assume that the detection efficiency does not change, the fluorescence signal will now be proportional to $\eta|d E|^2$, where $\eta$ is the effective quantum efficiency that takes into account also the energy dissipated by the nanoantenna and $E$ is the near field of the nanoantenna at the emitter position. Recalling that the nanoantenna modifies both the radiative decay rate, $\gamma_{r0} \rightarrow \gamma_r$, and the total decay rate, $\gamma_{r0} \rightarrow \gamma_r$, the effective quantum efficiency $\eta = \gamma_r/\gamma_t$ can be written as

$$\eta = \frac{\eta_0}{(1-\eta_0)\gamma_{r0} / \gamma_r + \eta_0 / \eta_a}$$

(61)

where $\eta_a$ is defined antenna quantum efficiency and corresponds to the fraction of energy dissipated solely by the nanoantenna and not by other intrinsic non-radiative channels, i.e. $\eta = \eta_a$ when $\eta_0 = 1$. The fluorescence enhancement due to the nanoantenna is thus
\[
\frac{S}{S_0} = \frac{\eta}{\eta_0} \frac{|d.E|^2}{|d.E_0|^2}
\]  
(62)

Notice that the enhancement can be obtained either by increasing the electric field, by increasing the quantum efficiency or by both effects. The collection efficiency could also play a role, but we assume here that the system emitter-nanoantenna retains the dipole emission pattern of an isolated emitter.

It is well known that metal NPs exhibit a near field mostly radially polarized and particularly strong for excitation wavelengths close to the plasmon resonance.[19] Therefore, achieving fluorescence enhancement by exploiting metal NPs could seem quite straightforward. However, one has to consider that the quantum efficiency decreases as the emitter approaches the NP [17] so that there is a tradeoff between two competing effects. Consequently, to obtain strong fluorescence enhancements one has to design nanoantennae that do not quench the emitter.

Except for a single spherical NP, obtaining an analytical solution for the field enhancement and the decay rates can be extremely challenging. For this reason, we employ the finite-difference time-domain (FDTD) method to solve Maxwell’s equations numerically. For the field enhancement we excite the NP with a broadband plane wave and compute the near field in selected positions after Fourier transforming the electric field in frequency domain. That allows us to compute the spectral dependence of the field enhancement within a single run. The calculation of the decay rates can be also performed within classical electrodynamics thanks to the equality between the normalized decay rates and the normalized power emitted by a classical dipole at the same position and orientation of the emitter, where for normalized quantities we intend
decay rate and radiation with respect to the case without nanoantenna [20].

Figure 38  Screen capture of confocal microscope system operation

Figure 39  Plasmonic Nanoantenna enhance measurement with linescale
Figure 40  Radiation patterns and fluorescence enhancement when a=400 nm for Rhodamine 6G dyes with peak emission at 560 nm.

The radiation patterns for different values of grooves are presented in figure 37, while the number of grooves N is increased from 0 ('bare' nanoaperture) to N = 3. Rhodamine 6G emission centered at 560 nm. All fluorescence images are integrated over a ±20 nm bandwidth. For each image, the intensity is normalized by the average number of detected molecules calibrated by fluorescence correlation spectroscopy (FCS) to represent the fluorescence intensity per molecule. This procedure enables the quantification of the fluorescence enhancement for each emission angle while the number of grooves is increased. (figure 40)

Increasing the number of grooves narrows the angular divergence and improves the directivity when a = 440 nm and λ = 560 nm (sample optimized for fluorescence
beaming along \( \mu = 0 \). However, when \( a = 440 \text{ nm} \), supplementary side-lobes shown as figure 41) emerge while the number of grooves is increased above \( N = 2 \). In that case, the antenna's performance as noted by the directivity can be worse for \( N = 3 \) than for \( N = 2 \). Thus, selecting \( N = 2 \) grooves thus appears as a correct compromise between directivity, angular divergence, side lobes and fabrication complexity.

![Figure 41](image)

**Figure 41** A typical antenna radiation pattern in cartesian coordinate system representation showing side lobes.

5.2 Surface enhanced Raman spectroscopy (SERS)

SERS indicates the phenomenon that molecules absorbed on rough metal surfaces or metal nanostructures give out much stronger Raman signals than the molecules not near metal structures. The SERS is a sensitive analysis technique utilizing this phenomenon. The enhancement is sufficiently large to detect single molecules in theory [3]. It is generally agreed that two mechanisms contribute to the overall large enhancement of SERS: 1) an electromagnetic enhancement mechanism, and 2) a chemical enhancement mechanism.

The electromagnetic mechanism is based on the significantly amplified
electromagnetic fields generated by the localized surface plasmon resonance (LSPR) of metal nanostructures [5]. The incident electromagnetic radiation excites surface plasmons in the metal nanostructure, which produce an enhanced electric field (amplified light) at the surface. The amplified light is Raman-scattered by molecules near the surface. Moreover, the Raman scattered light will also resonate with surface plasmons (under the right conditions). Then, the electric field of the Raman scattered light will be enhanced. Consequently, amplification of the electric field by the metal nanostructures occurs twice, i.e. once for the incident light and once for the Raman shifted light.

To maximize both the amplifications, the surface plasmon resonance frequency of the metal nanostructure should be near that of the incident and Raman scattered light. The plasmon resonance frequency of a metal nanostructure is determined by the size, shape, and composition of the metal nanostructure and the dielectric constant of medium ($\varepsilon_m$).

Mie solved Maxwell’s equation to describe the scattering of light by a sphere.[7] Mie’s solution can explain why the electric field near metal nanoparticles is amplified resulting in the enhancement of Raman signal and tell the conditions for maximizing the enhancement. The solution has the form of an analytical infinite series. When electromagnetic radiation is incident upon a metal nanostructure, the electric field of the radiation generates collective oscillations of the conduction electrons.

In SERS, equation (64) determines the magnitude of the field at the sphere surface induced by the incident light. If $|g|$ is large, then $|E_{out}|^2$ can be expressed as

$$g = \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}$$  \hspace{1cm} (63)

$$|E_{out}|^2 = E_0^2 \cdot |g|^2 \cdot (1 + 3\cos^2 \theta)$$  \hspace{1cm} (64)
Where $E_{\text{out}}$ is the electric field outside the sphere energy; $E_0$ is the magnitude of $E_0$, $\theta$ is the angle between the applied field polarization direction and the vector $\mathbf{r}$ that locates positions on the sphere surface. Therefore, the largest electric field intensity, $4 |E_0| g |g|$, is obtained when $\theta = 0$ and $\theta = 180$.

The second amplification happens to the scattered Raman shifted light. We can determine the overall enhancement arising from incident and scattered fields, as figure 65 shown,

$$G = \frac{E_{\text{out}}^2}{E_0^2} \geq 16 |g|^2 |g|^2$$

(65)

where the primed symbols indicate the values at the scattered frequency. The best way to get large enhancement is to make both fields resonate with surface plasmons.

The basics of the field enhancement by a metal nanosphere are described above. Field enhancements for other shapes, such as nanocubes and triangular nanoprisms, are usually calculated numerically, by using methods such as finite difference time-domain (FDTD)[9] and discrete dipole approximation (DDA)[10].

Because hot spots formed near target probes confined within the interstices of the adjacent metal nanostructures can enable single-molecule detection due to near-field coupling of localized surface plasmon resonance,[3] Metal nanostructure films embedding hot spots are perfect substrates for surface enhanced Raman scattering (SERS) providing considerable Raman enhancements.[46-48]. However, their geometrical requirements for both narrow interstices to provide large near-field coupling and sufficient space to allow entrance of the analytes, are contradictory, and cannot be satisfied in current fabrication techniques dependent on surface agents. Here we report a two-step method to fabricate hybrid films consisting of self-supported metal thin film
with the absorbed probes and subsequent nanoparticle conjugates without using surface agents. Raman scattering within hot spots with 1 nm gap shows $2.9 \times 10^8$ times enhancement compared to pure gold nanoparticles. The enhancement primarily results from strong near-field coupling between metal film and nanoparticle, which is also theoretically supported by finite-difference time-domain simulation. Excellent detection limit toward $10^{-11}$ mol/l offers an opportunity to track spatial orientation of single molecule and engineer hybrid nanostructures as commercial SERS substrates.

Unfortunately, such substrates have competing geometrical requirements between the need for the narrowest interstice between neighboring units to provide maximum near-field coupling, and for sufficient space to accommodate the target probes[9-13]. Due to the exponential decay of electromagnetic fields normal to metal surface, the interstices are typically preferred to be 1~2 nm, where near-field coupling can induce significant Raman enhancement [14-15]. On the other hand, such small gaps are not favorable for the insertion of target molecules dissolved in the solvents. Numerous efforts have been made to address these issues and different nanostructures have been used as the precursors, including nanoparticles, nanowires, nanopores, and their conjugations [16-19]. Most fabrication processes utilize self-assemblies from colloidal suspensions stimulated either by mechanical motions or by modification of surface charge using surface agents [16, 18, 20-21]. While these films can provide enhanced Raman signals in certain sites, and enhancement factor strongly depends on specific parameters [22-24]. For instance, interstitial gap sensitively depends on the types and doses of surface agents rather than the probes of interest. Essentially, a primary concern is the random agglomeration of metal nanostructures due to non-specific electrostatic coalescences, an example being
discrete nanoparticle clusters. Thus precise control of the interstices with narrow gaps is crucial to guarantee reproducible Raman scatterings.

A $10^{-5}$M Rhodamine 6G solution was selected to evaluate SERS performance of coupling of metal film and nanoparticle as shown in figure 42.

![Graphs showing Raman enhancement comparison between different structures](image)

**Figure 42** The results compared between different structures

Raman enhancement on hybrid coupled nanoparticle with metal films can probably arise from two different sources: near-field couplings within the interstices SPR and LSPR. Excellent sensing abilities of hybrid NPG-nanoparticle film originate from the introductions of numerous interstices. Some of them can serve as hot spots with huge Raman enhancements, enabling single-molecule detection.
5.3 Waveguide and Resonator for Optically Interconnected SoC Systems

How to guide light along subwavelength waveguides is a challenging problem in integrated photonics (figure 43). One potential solution is to use plasmon waveguides made of periodic chains of metal nanoparticles [1] that benefit from strong lateral field confinement. Such confinement effect is caused by the electromagnetic coupling between individual localized surface plasmon (particle plasmons) supported by each of the particles.

Although significant progress has been made in understanding plasmon waveguides over the years [2, 3, 4, 5, 6, 7, 8], plasmon waveguides have not found their applications due to their inherent high propagation loss. In plasmon waveguides made of Au and Ag nanoparticles, for instance, optical signal can only travel several hundred nanometers [9] before it dies out, as opposed to signal propagation distance of several hundred micrometers to even a few millimeters needed in a SoC.

Figure 43 Conceptual 3DI of future ONoC ICs [17]

One solution to the aforementioned high propagation loss in plasmonic waveguides is by the coupling of metal nanoparticles and metal film [1–10], which relies on the complex interaction between the nanoparticle’s localized surface plasmon and the thin
film’s delocalized surface plasmon polarization to help extend the propagation distance.

As pointed out in Chapter 2, this enhancement effect becomes more significant when the nanoparticle is within a distance of \(~50\) nm to the film surface (figure 44).

![Waveguides made of coupled nanoparticles and metal film](image)

Figure 44  Waveguides made of coupled nanoparticles and metal film
Deep subwavelength nanoantennas, with sizes smaller than 100nm, have long been considered in the fabrication of nm IC chips and biological/chemical sensing at the Gene’s level. However, such small subwavelength nanoantennas suffer from severe signal attenuation problem that the signal propagation distance is within just a few hundred nanometers. In this dissertation, we proposed a feasible solution to overcome this propagation loss problem through signal enhancement that explores hybrid plasmonic effects which can effectively couple the SPR with LSPR. Normally, the SPR was only be exited above the metal film using total internal reflection under certain wavelength. And The LSPR formed by coupled noble metal particles enable the plasmon resonance and strong enhancement of the local electromagnetic field in the gap that can be tuned to different frequencies. Unfortunately, the traditional fabrication methods including Top-down and Bottom-up cannot fabricate such hybrid nanoantenna structures at once forming.

In response to this fabrication problem, we invented a hybrid plasmonic nano-printing method that combines lithography and a direct metal nanoparticle patterning technique. This metal nanoparticle patterning technique allows the metallic nanoparticles to be dropped into the nanoantenna’s grooves at the same time when this nanoantenna is being patterned. Different from the conventional top-down fabrication method, our method explores the convective assembly to achieve a desired surface morphology in well-ordered, rapid, and controllable deposition on practically relevant scales.
Using this proposed fabrication method, we successfully fabricated two hybrid plasmonic nanoantenna structures. These two structures were fully characterized through optical measurement and scanning electronic imaging.

To further demonstrate our proposed nanoantenna and develop the new applications, these fabricated plasmonic nanoantennas were applied to enhance the signals from three applications: bio-fluorescence, surface enhanced Raman spectroscopy, and next generation System on Chip (SoC). The results have showed that signal enhancement up to 100 times has been achieved compare to the ordinary device.

In summary, this study on plasmonic nanoantenna and hybrid plasmonic nanoantenna are still on-going. Now the study is concentrating majorly on three topics. The first is the study of nanoantenna principles and behaviors, and using them to design our hybrid plasmonic nanoantenna. The second is invented a novel fabrication method combined the top-down and bottom-up method. By applying this combined fabrication method to fabricate hybrid plasmonic nanoantenna to achieve performance enhancements. Then the third is to further improve three important applications performance by using this hybrid plasmonic nanoantenna. Shortly, working on such an exciting and cutting-edge research field, more complete works are expected to be published from time to time.

6.2 Outlook

Plasmonic nanoantennas are promising devices for the next generation of applications, e.g., all optical communication and threshold less nano-lasers. They are also important for understanding interaction of light with matter at the nanoscale. Therefore, recent progress made in understanding plasmonic nanoantennas over the last decade is highly encouraging. The exponential growth in the number of high-impact publications
also promises to sustain the progress.

However, future growth requires a more holistic approach involving both materials and optical aspects of the research. Better ways to manufacture various antenna designs with ever smaller features is one of the critical aspects that need to be addressed. This requires sustained effort both in terms of understanding the material properties as well as engineering of methodologies that can help pattern features at this scale.

Understanding the nature of resonance using cathodoluminescence and plasmonic characterization is only the first step in their application in critical areas of future devices. The theoretically predicted sub-Å resolution using top-down and bottom-up, even our hybrid fabrication tools are still several orders away; however, it has already helped in understanding some critical aspects of antennas.

The application of plasmonic antennas in sensing is one of the most sought-after goals of research. Except our did three applications, one of the most important milestones in application of plasmonic nanoantennas will be the arrival of Seagate’s latest hard disk drive that is expected to hit the market in 2013. It will utilize the quadrupole mode of a 70 nm gold sphere for heat-assisted magnetic recording [28].
APPENDIX A

Set the home position

*********************
SET HOME
*********************

2 MNL A
2 WAC ONT? A = 1
2 MVR A 10
2 WAC ONT? A = 1
2 MPL B
2 WAC ONT? B = 1
2 DFH

Automated Etching

*********************
Loop
*********************

2 GOH A  // go back to home position
2 WAC ONT? A = 1  // wait to keep moving the axis A, until A stops
2 MVR A 5  // set the initial radius
2 WAC ONT? A = 1
2 MPL B  // move axis B to the top ( Move to the Positive Limit position )
2 WAC ONT? B = 1  // wait to keep moving the axis B, until B stops
2 MVR B -1  // move B down by 1 mm ( MoVe Relative distance )
2 WAC ONT? B = 1
2 MVR C 0  // move C to align with 0 degree
2 WAC ONT? C = 1
0 LOOP 10
2 MVR A 0.2  // set step of radius
2 WAC ONT? A = 1
2 MVR B -0.72 // move the needle to the surface of the silicon and draw the circles
2 WAC ONT? B = 1
2 VEL C 10  // set speed of spinning
2 MVR C 360 // set angle of spinning, 360 for one circle
2 WAC ONT? C = 1
2 MVR B 0.72 // drive the needle away from the surface
2 WAC ONT? B = 1

****************
Back to home
****************
2 GOH A  // go back to home position
2 WAC ONT? A = 1  // wait to keep moving the axis A, until A stops
2 MPL B  // move axis B to the top ( Move to the Positive Limit position )
2 WAC ONT? B = 1  // wait to keep moving the axis B, until B stops
2 MVR B -1 // move B down by 1 mm ( MoVe Relative distance )
2 WAC ONT? B = 1
2 MVR C 0  // move C to align with 0 degree
2 WAC ONT? C = 1
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VITA

Graduate College
University of Nevada, Las Vegas

Shengjie Zhai

Degrees:
1) Bachelor of Science, Optics, 2004
   Nanjing University of Science and Technology, China

2) Master of Science, Biomedical Engineering, 2008
   Chongqing University, China

Special Honors and Awards:
National Outstanding Master Thesis (China National Knowledge Infrastructure), 2009

Publications:
Journal Articles

Dissertation Title:
Plasmonic Nanoantennas: Fabrication, Characterization and Applications

Dissertation Examination Committee:
   Chairperson, Das, Biswajit, Ph.D.
   Committee Member, Yingtao Jiang, Ph.D.
   Committee Member, Mei Yang, Ph.D.
   Graduate Faculty Representative, Hui Zhao, Ph.D.