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The Designer Optical Resonances of Metal Nanoshells

by

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Abstract

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Metal nanoshells consist of a dielectric or semiconducting core coated with a metallic layer of nanometer scale dimensions. Gold nanoshells with silica cores were fabricated by first attaching gold colloid to the surface of the silica spheres and then developing the attached gold into a complete shell. This technique formed continuous gold shells approximately 10 nm thick. By varying the relative dimensions of the core and the shell, the optical resonance of these nanoparticles can be varied over hundreds of nanometers in wavelength, extending from the visible into the infrared region of the spectrum. For a gold nanoshell with a 340 nm core, at shell thicknesses exceeding 15 nm, additional peaks appeared in the UV-visible spectrum. Calculations based on a vector basis solution to Maxwell’s equations matched both the position and relative magnitude of these secondary peaks.
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Chapter 1

Introduction

The assembly of inorganic elements using wet chemistry has some advantages over the planar techniques used in the semiconductor industry. A single drop of a colloidal solution can have more than $10^{16}$ nanoparticles with a reactive surface area up to a square meter. If densely packed on a surface, more than 100 nanoparticles would occupy the equivalent area of the state of the art transistor. The assembly of composite nanoparticles is done in parallel so that an assembly step can be completed in just a few seconds. However, the many orders of magnitude increase in particle density is only useful if we can endow these new building blocks with either an individual or collective functionality that can then be incorporated into macroscopic devices.

With dimensions approaching those of molecules, metal and semiconductor nanoparticles have interesting material properties which can be exploited for new functionality. Metals only a few thousand atoms in size show remarkable properties attributed to the dramatic reduction of freely mobile electrons. The electron gas in metallic particles responds in phase to an electromagnetic field. This collective electron excitation, known as a plasmon resonance, is responsible for the ruby red color of gold particles in solution. However, most of the functionality of the nanoparticles studied to date are
due to the properties of a homogenous material. One way to extend the functionality of inorganic colloidal particles is to work with composite structures.

The simplest composite nanoparticles consist of spheres with nanometer dimensions which have been chemically functionalized with a molecular layer. For instance, when gold colloid is terminated with a monolayer of alkanethiolates, the gold can be precipitated and redissolved without changing its properties [1]. In addition, it has been shown that chemically varying the organic shell layer may enhance the optical properties of these composites [2] or facilitate their assembly into ordered films [3]. Metal colloids can also be functionalized with a terminal layer which has an affinity for a particular molecular compound. These colloids are useful as colored markers for electron and visible microscopy [4].

The next logical progression is the coating of particles with shells that are more than a few molecular layers thick. Bimetallic nanoparticles using metals such as Ag, Au, Hg, Pb, and Cd can be grown [5, 6, 7]. The Au-Ag system is of interest in surface-enhanced Raman scattering (SERS) studies, in which a surface can be constructed that combines the benefits of monodispersity of colloidal gold with the electromagnetic enhancement of silver. Silica coatings have been used to encapsulate iron and gold particles. Iron/silica particles can be aligned by an external magnetic field and grown together to form anisotropic silica particles [8]. Gold/silica particles self-organize into a two dimensional grid with an interparticle spacing determined by the thickness of the silica shell [9].
Much of the current interest in nanoparticles is due to their optical properties. The plasmon absorptions of spherical noble metal particles are intense but essentially fixed at a particular wavelength by the properties of the material. For instance, the peak absorbance of Ag and Au 10 nm radii sphere is at $\sim 355$ nm and $\sim 520$ nm respectively, and these peak absorbance positions have only a small sensitivity ($< 30$ nm) to changes in particle size (between 10 and 100 nm) [10]. Dielectric coatings, such as the silica coating of the gold nanoparticles[9], do not significantly shift the plasmon peak. A very much larger shift in the peak absorbance is predicted for the reverse case, where a dielectric core is surrounded by a metal nanoshell. Plasmon shifts of hundreds of nanometers are predicted when the shell thickness is varied by just a few percent of the core radius [11, 12, 13]. A naturally occurring gold-terminated/gold sulfide system shows the shifting optical resonances associated with metal nanoshells and has been extensively studied by our group and others [14, 15, 16]. However, the controllable deposition of uniform metallic shells with nanometer dimensions onto other core materials has been elusive [17, 18].

To artificially produce a system of dielectric spheres coated with thin metal shells, the methods of molecular self-assembly are employed. The preparation of metal nanoshells is split into two steps: first, gold colloid is attached to the dielectric core, and secondly, the gold seed is developed into a complete shell. This is necessary since metallic ions will not to directly reduce onto a dielectric core. The gold colloid is attached to the core by using an organosilane coupling agent
that has been previously used to assemble gold colloid monolayers on planar surfaces [19, 20]. The monodisperse silica cores are coated with the coupling agent, (3-aminopropyl)trimethoxysilane. The silane-coated silica are then immersed into a gold colloid solution. This promotes the attachment of gold (1-2 nm in diameter) to larger silica particles (100-550 nm in diameter). The attached gold clusters act as nucleation sites on which to grow a continuous, ultrathin film with a controllable thickness between 5 and 50 nm. The Coulomb repulsion between neighboring silica cores keeps the nanoparticles stabilized during this growth step, thereby minimizing particle coalescence. By varying the ratio between the core diameter and the thickness of the gold shell, the plasmon absorption maximum can be tuned from 520 nm into the near-infrared. This is a range of tunability not available in any other material system.

This thesis describes the synthesis, characterization, and optical properties of silica-core, gold-shell metal nanoshells. Chapter 2 begins with a review of light scattering from a spherical object. Then, a method of extending this basic theory to cover the composite core/shell system is presented. Next, the origins and effects of two additional peak broadening mechanisms are discussed. The detailed recipe of the metal nanoshell construction is found in Chapter 3. Although the core is essentially optically inert, its physical properties are critical to the assembly of metal nanoshells. Chapter 4 begins with a review of the Stöber method of growing monodispersed silica colloid. The role of the coupling agent is discussed and examples of gold colloid
attachment are presented. The chapter concludes by addressing the issue of interparticle forces. The force between the silica cores has to be strong enough to keep the cores separated but weak enough that the much smaller gold colloid can still attach to the silica and form the foundations of a shell. The growth of the shell and the resulting optical properties are discussed in Chapter 5. Chapter 6 summarizes the present results and the future directions of this work.
Chapter 2

Theory

2.1 Introduction

This chapter outlines the theoretical foundation of the interaction between light and colloidal nanoparticles, known as Mie scattering theory. For metallic particles that are small compared to the wavelength of light (the quasi-static regime), the application of electrostatics can be used to gain an understanding of the curious optical response of these metal clusters. The full electromagnetic solution of the diffraction of a plane wave by a homogeneous sphere of any diameter and any composition situated in a homogeneous medium is then outlined. An extension of this approach has been used to solve the problem of scattering from a composite particle composed of concentric spheres with different dielectric functions. In the quasi-static limit, the concentric sphere solution is considerably simplified and can be used to illustrate many of the optical properties of metal nanoshells. However, for the nanoshells in the current study, the quasi-static limit is not applicable due to the large diameters of the silica cores (100 - 600 nm). A generalized vector basis function solution to Maxwell's equations is used instead to produce a series solution for the scattering of light from concentric spheres of any diameter. The low number of terms needed for a convergent solution makes this algorithm computationally efficient and enables the
quick calculation of the optical spectrum resulting from a model sample containing a
distribution of particle sizes and shell thicknesses.

2.2 Quasi-static Response of a Metal Sphere to an Electric Field

The Drude model of a metal assumes that the positively charged metal atoms are
fixed in place while the valence electrons become detached and can roam freely within
the metal. A metal nanoparticle can then be modeled as an electron gas dispersed
throughout a solid sphere of positive charge. In the quasi-static regime, where the
wavelength of light is much larger than the size of the metal particle, we can assume
that the force exerted by the electromagnetic field of the incoming light moves all of
the electrons collectively. The electrons are then subjected to a force that has a time
dependence but no spatial variation. Using the boundary condition that the electric
field is continuous across the surface of the sphere, the static polarizability is found
to be

\[ \alpha = 4\pi\varepsilon_0 R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}. \]

(2.1)

where \( R \) is the sphere radius, \( \varepsilon = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) is the complex dielectric function of
the metal nanoparticle, and \( \varepsilon_m \) is the dielectric function of the embedding medium.
This polarizability shows resonant behavior whenever the denominator is minimized:
\[ \text{Resonance} \rightarrow \min |\varepsilon + \varepsilon_m| = \min [(\varepsilon_1(\omega) + 2\varepsilon_m)^2 + (\varepsilon_2(\omega))^2]. \quad (2.2) \]

At a frequency where the value of the real part of the dielectric constant \( \varepsilon_1(\omega) \) nears \(-2\varepsilon_m\), both the polarizability and the absorbance of the particle dramatically increase. This condition is called the plasmon resonance.

2.3 Mie Scattering Theory

The full electromagnetic solution of the diffraction of light from a single sphere of arbitrary material was first given by Mie in 1908 [21]. The method consists of solving Maxwell's equations with the appropriate boundary conditions in spherical polar coordinates to yield a set of ordinary differential equations. These differential equations can then be solved to yield a solution in the form of an infinite series.

The calculated optical properties are commonly expressed in terms of the absorption, scattering, and extinction cross sections: \( \sigma_{abs}, \sigma_{scat}, \text{ and } \sigma_{ext} \). Absorption describes the loss of light due to the generation of heat and scattering the loss of light due to the change in propagation direction. Extinction is the sum of these two effects.

Quantitatively, the change in intensity of a parallel beam of incident light passing through a diffracting medium can be expressed with the Lambert-Beer law.

\[ \Delta I(z) = I_0(1 - e^{-Nz(\sigma_{abs} + \sigma_{scat})}). \quad (2.3) \]
where \( N \) is the number density of clusters, \( I_0 \) is the incident intensity, and \( z \) is the path length through the diffracting medium. This expression is valid only in the low concentration limit where multiple scattering paths are neglected.

The extinction, scattering, and absorption cross sections can be extracted from Mie’s solution by series expansion of the involved fields into partial waves of different spherical symmetries

\[
\sigma_{xrt} = \frac{2\pi}{|k|^2} \sum_{L=1}^{\infty} (2L + 1) R L \{ a_L + b_L \}
\]

\[
\sigma_{xsc} = \frac{2\pi}{|k|^2} \sum_{L=1}^{\infty} (2L + 1)(|a_L|^2 + |b_L|^2)
\]

\[
\sigma_{abs} = \sigma_{xrt} - \sigma_{xsc}.
\]

(2.4)

where \( k \) is the wave number \((2\pi/\lambda)\). The coefficients are given by

\[
a_L = \frac{m \nu'_L(mx) \nu'_L(x) - \nu'_L(mx) \nu_L(x)}{m \nu'_L(mx) \eta'_L(x) - \nu'_L(mx) \eta_L(x)}
\]

\[
b_L = \frac{\nu'_L(mx) \nu'_L(x) - m \nu'_L(mx) \nu_L(x)}{\nu'_L(mx) \eta'_L(x) - m \nu'_L(mx) \eta_L(x)}.
\]

(2.5)

In the above expression, \( m = n/n_m \), where \( n \) denotes the complex index of refraction of the particle and \( n_m \) the real index of refraction of the surrounding medium. The ratio of the particle radius to the wavelength of light is called the size parameter and is given by \( x = |k| R \). \( \nu_L(a) \) and \( \eta_L(z) \) are the Riccati-Bessel cylindrical functions. The prime indicates differentiation with respect to the argument in parentheses.

The summation index \( L \) gives the order of the partial wave, described by vector spherical harmonic functions. Far from the cluster, the \( L = 1 \) term corresponds to
an electromagnetic intensity equivalent to radiation from an oscillating dipole and is referred to as the dipole term. Higher order terms in the summation correspond to the higher order multipoles: \( L = 2 \) corresponds to the quadrupole term, \( L = 3 \) to the octupole fields, etc.

For the case of gold clusters less than 20 nm in diameter, the optical properties are dominated by the \( L = 1 \) term and the theory is considerably simplified. The extinction cross section reduces to

\[
\sigma_{ext}(\omega) = 9 \frac{\omega^2}{c^2} \frac{V_0}{\varepsilon_m} \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2},
\]

(2.6)

where \( V_0 = (4\pi/3)R^3 \) denotes the particle volume and \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are the real and imaginary parts of the dielectric function of the metal nanoparticle. This is the extinction cross section for absorption only since the scattering cross section and higher order multipoles are negligible in the limit where the size of the particle is small compared to the wavelength of light. The resonance condition is satisfied when the denominator of Equation 2.6 is minimized (\( \varepsilon_1(\omega) = -2\varepsilon_m \)). For gold, this occurs at \( \sim 520 \) nm which accounts for the distinct red color of gold particles in solution.

It is important to note that while the electromagnetic calculation for Mie scattering has been derived from first principles, many of the materials issues have been incorporated into the phenomenological dielectric function. This includes electron-electron, electron-phonon, and electron-impurity interaction in the bulk. Also, for gold clusters, interband transitions of core electrons make a large contribution to the
experimentally determined dielectric function[10]. This will be important when the
effect of size dependent broadening terms are examined later in this chapter.

2.4 Quasi-static Scattering From Concentric Spheres

The Mie scattering formalism for the diffraction of light from a spherical particle
has been extended to include a composite particle that consists of concentric spheres
of different materials [11]. For particles with a shell of dielectric function \( \varepsilon_s \), thickness
\( R_s - R_l \), encapsulating a core (\( \varepsilon_c \)) and dispersed in a medium (\( \varepsilon_m \)), as shown in Figure
2.1, an analytical solution to the scattering problem can be derived. As with the
spherical scattering problem, it is useful to work in the quasi-static limit (\( |r_{port, b}| \ll \lambda| \)) to derive some of the basic optical properties [10, 12]. Although considerably
simplified, the expression for the extinction is still a complicated convolution of the
dielectric function of the three materials [12].

The geometrical dependence of the plasmon resonance for a typical metal nanoshell
is depicted in Figure 2.2. The model metal nanoshell has a silica core (\( n = 1.48, k = 0 \))
and is coated with a gold shell with experimentally determined dielectric values [23].
For a core diameter to shell thickness ratio of 20:1 the plasmon absorption maximum
is shifted out to 870 nm. As the shell thickness is increased, the peak is shifted back
towards the standard gold plasmon peak at 520 nm. This property is unique to the
metal nanoshell: if the core and shell materials were reversed, the peak shift over this
range of core-shell ratios would be less than 30 nm.
Figure 2.1 Model nanoshell particle. The core has dielectric constant \( \varepsilon_c \), the shell has dielectric constant \( \varepsilon_s \), and the exterior medium has dielectric constant \( \varepsilon_m \).

Figure 2.2 Theoretical plasmon absorption maximum of a gold/silica nanoshell in water with a range of core diameter:shell thickness ratios.
The equation for the quasi-static polarizability can be used to predict the plasmon resonance of core/shell particles. The polarizability is given by

\[
\alpha = \frac{\epsilon - \epsilon_m}{\epsilon (\epsilon + 2\epsilon_m)(\epsilon + 2\epsilon_s) + (R_c/R_s)^3(\epsilon - \epsilon_s)(\epsilon_m + 2\epsilon_s)} - \frac{4\pi R_s^3}{1}.
\] (2.7)

In the limit of \( R_c = R_s \) and \( \epsilon_c = \epsilon_s \), the above polarizability reduces to that of a spherical core particle.

The theoretical value for the quasi-static polarizability can be used to predict the tunability of the peak plasmon absorbance. Resonance is established when the real part of the denominator in Equation 2.7 is minimized. To satisfy the resonance condition at a particular wavelength, the dielectric values of the core, shell, and medium can be used to determine the necessary shell ratio. Figure 2.3 plots the peak absorbance position for a range of core radius/shell thickness ratios and predicts that the resonance can be tuned over a large range of the electromagnetic spectrum.

### 2.5 Beyond the Quasi-static Limit

Due to experimental constraints on the minimum thickness of the metallic shell, in order to obtain very large core/shell ratios we must use large dielectric cores (100-500 nm). Phase-retardation effects and higher order resonances start to play an important role in the optical properties as one moves beyond the quasi-static regime. An elegant solution that utilizes a vector basis function solution of Maxwell’s equations has been developed that provides a method of calculating the optical properties of these larger
Figure 2.3 Quasi-static calculation of peak absorbance vs. core to shell ratio.

particles [24, 25]. For the problem of a plane wave scattering from a composite particle, this method efficiently yields the exact three dimensional electromagnetic solution. A summary of this method is provided in Appendix A.

Using this formalism, the extinction cross section is expressed as an infinite series. The power of this method is the low number of terms in the basis function expansion needed to obtain convergence of the solution. The first term in the expansion yields the quasi-static approximation and can be computed in just a few seconds. An error of less than 1% is achieved by taking terms up to index \( n \sim 1.4|k r| \), where \( k \) is the wave number of the wavelength of interest and \( r \) is the radius of the particle. Figure 2.4
shows the importance of including higher order terms when the quasi-static condition has been violated. Following the rule above, $|kr| \sim 3$. Clearly, the quasi-static approximation ($L = 1$) does not represent the convergent solution. Additional terms after $L = 3$ make only small perturbations to the calculated spectrum.

The higher order modes in the series expansion of the scattering solution manifest themselves as secondary peaks that are blue shifted with respect to the primary plasmon peak. This is exactly the opposite of the higher order modes of spherical gold colloid which are red shifted with respect to the primary plasmon peak [10]. The relative positions and heights of the respective peaks provide a unique optical signature for a nanoshell with a particular core/shell geometry. The ability to match the secondary peaks is a useful metric when comparing the theoretical and experimental spectra of these composite nanoparticles.

### 2.6 Broadening Mechanisms

The predicted absorption peaks the metal nanoshells are dramatically narrower than are seen experimentally. There are two peak broadening mechanisms that affect the peak widths and need to be included in our analysis [15]. The first, inhomogeneous broadening, is simply due to the distributions of the particle core sizes and shell thicknesses. For the Stöber method of core growth, which will be discussed in Chapter 3, a gaussian distribution with a standard deviation obtained from TEM is used to estimate the core polydispersity. TEM micrographs of metal nanoshells at early stages
Figure 2.4 Effect of using higher order terms (1, 2, 3, and 20) of the series solution on the absorbance peak. The spectra are for a 300 nm diameter core of silica surrounded by a 10 nm shell of gold dispersed in water.

of growth can be used to estimate the distribution of the metal shell thicknesses.

Figure 2.5 shows the predicted effect of the shell distribution on the optical spectrum of a typical metal nanoshell. As the distribution in shell thicknesses becomes larger, the peak intensity drops and the peak broadens. There are two reasons for the peak shift associated with an increase in the shell distribution. The first is that the thicker shells (which have a peak that is blue shifted with respect to the median value) have a larger extinction cross section and thus weight the distribution towards the blue. The second is that a shell of 7 nm (5 nm median + 2 nm deviation) will be blue shifted from the median value less than a shell of 3 nm (5 nm median - 2 nm deviation) will be red shifted. Thus, the thinner shells have absorptions which are averaged out over a larger range of the spectrum.
Figure 2.5  Effect of changes in the standard deviation of the shell thickness. The dotted plot is monodispersed while the solid plot has a shell distribution of $5 \pm 2.0$ nm.

The second broadening mechanism is related to the reduced mean free path of the electrons in the metallic shell. In the case of gold nanoshells, the thickness of the shell is less than the mean free path of an electron in bulk gold ($\sim 42$ nm) at room temperature [26]. This results in a size dependent modification of the collisional frequency which in turn modifies the dielectric constant of the metal.

The experimentally determined values for the dielectric function can be modeled as having effects due to Drude conduction electrons as well as effects due to the interband transitions of electrons from gold core electrons ($5d$ band):

$$
\varepsilon(\omega)_{xp} = \left( 1 - \frac{\gamma^2}{\omega^2 + i\omega\gamma_{bulk}} \right) + \varepsilon(\omega)_{inter} \tag{2.8}
$$
where $\omega_p$ is the bulk plasma frequency and $\gamma_{bulk}$ is the bulk collisional frequency. The bulk collisional frequency embodies a number of physical processes such as electron-electron, electron-phonon, and electron-impurity interactions. To accommodate the reduced mean free path of electrons in a thin metallic shell we introduce a modification to the bulk collisional frequency of an additional scattering term related to the geometry of our system:

$$\Gamma = \gamma_{bulk} + A \cdot V_F/a.$$  \hspace{1cm} (2.9)

where $\gamma_{bulk}$ is the bulk collisional frequency described above, $V_F$ is the Fermi velocity ($1.4 \times 10^8$ cm/s) [26], and $a$ is the reduced electron mean free path. In our model we take $a$ equal to the shell thickness. Additional scattering due to the microstructure of the gold shell was not taken into account in this model. The parameter $A$ has been calculated by a number of different methods to be of the order of unity and was set $A = 1$ for our calculations [27].

The modified collisional frequency was incorporated into the bulk dielectric values as follows:

$$\varepsilon(R, \omega) = \varepsilon(\omega)_{xp} + \frac{\omega_p^2}{\omega^2 + i\omega\gamma_{bulk}} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma}.$$ \hspace{1cm} (2.10)

$\varepsilon(R, \omega)$ is the size-dependent dielectric function where $\varepsilon(\omega)_{xp}$ is the experimental dielectric function [23], and $\omega_p$ and $\gamma_{bulk}$ have the standard values of $1.298 \times 10^{16}$ rad/s and $3.83 \times 10^{-14}$ s$^{-1}$ respectively [26]. Figure 2.6 shows the effect of the size dependent broadening. Inclusion of this additional scattering mechanism reduces the
predicted peak height of a 5 nm gold shell encapsulating an 80 nm silica core by nearly a factor of 3. There is also a slight red shifting of the peak as the scattering length is decreased.

**Figure 2.6** Effect of decreasing the scattering length parameter $a$ in a nanoshell particle with an 80 nm silica core and 5 nm gold shell. The dotted line uses a scattering length of 42 nm (bulk), while the solid line sets the scattering length equal to 5 nm (thickness of the shell).
Chapter 3

Experimental

3.1 Introduction

The assembly of metal nanoshell particles is a remarkably robust process. Once the Stöber grown silica has been coated with an organosilane layer, the silane-coated-silica cores can be used for many weeks. The shell growth is very repeatable once the appropriate concentrations of the reactants is determined. This chapter presents a recipe for producing metal nanoshells. A more detailed discussion of the critical aspects of the assembly appears in the next two chapters.

3.2 Growth

3.2.1 Stöber Growth of the Core

The Stöber method [28] was used to grow monodispersed silica cores. Tetraethyl orthosilicate 99.999+\% (Aldrich), ammonia hydroxide (Fluka 29.3+\% $\text{NH}_3$), and water (Millipore TotalQ Water - MilliQ$^\text{UV}$ + MilliQ$^\text{RO}$) were added to a glass beaker containing dehydrated ethanol and stirred overnight. The hydrolysis and condensation of silicon alkoxides can be described by the following chemical reactions:
≡Si-OR + H₂O ⇌ ≡Si-OH + ROH     (hydrolysis)
≡Si-OR + ≡Si-OH ⇌ ≡Si-O-Si≡ + ROH     (alcohol condensation)
≡Si-OH + ≡Si-OH ⇌ ≡Si-O-Si≡ + H₂O     (water condensation)

where R is any alkyl group (C_rH_{2r+1}).

Particles with 110 nm and 330 nm diameters were prepared using TEOS/NH₄OH/ethanol volumes of 1.5/3.0/50 and 1.5/5.0/50 mL respectively. All glassware was cleaned with chromic acid cleaning solution (5g sodium dichromate mixed with 1 mL H₂O and diluted to 100 mL in sulfuric acid), washed extensively with deionized water and rinsed with TotalQ water.

### 3.2.2 Attachment of Organosilane Molecules

Aliquots (10 and 40 µL) of 3-Aminopropyl triethoxy silane (APTES) (99% Aldrich) were added to 10 mL of the 110 nm and 330 nm colloidal solutions. Once mixed, the solutions were allowed to stand overnight. After 12 hours the change in solubility of the particles results in a separation between the milky white colloidal solution and a clear ethanol layer. The silane-coated silica was centrifuged at 200-1500 RCF for 30 minutes, followed by dispersion for 1 minute at 8 Watts in a probe ultrasound homogenizer (this will hereafter be referred to as a “wash”). The particles were then dispersed in 50 mL of 1-pentanol (99+% Aldrich). Condensation of the silane coated
silica was promoted by heating to 105°C for 1 hour. Five more wash steps in ethanol were performed to eliminate excess silane from the solution.

3.2.3 Gold Colloid

Ultrasmall gold colloid, 1-3 nm in diameter, was synthesized using a recipe reported by Duff [29]. A solution consisting of 45 mL of water, 300 μL of 1M sodium hydroxide and the reducing agent tetrakis hydroxymethyl phosphonium chloride (THPC) (1 mL of a solution of 1.2 mL of 80% aqueous solution diluted to 100 mL with water, Aldrich) was stirred in a 100 mL flat bottom beaker with a pyrex coated magnetic stir bar. After 2 minutes, 2 mL of chloroauric acid (25 mM dark-aged stock solution, hydrogen tetrachloroaurate(III) trihydrate 99.999% from Aldrich) was added and within a few seconds the solution turned a dark brown. The exact mechanism of the THPC oxidation of gold(III) is not known. Variations of the initial gold chloride concentration varied the final particle size [29].

3.2.4 Gold Colloid Attachment

Typically, a gold colloid monolayer on silane terminated substrates covers ~30% of the exposed surface area. The silane coated silica was added to a centrifuge tube containing gold colloid in a quantity that would provide a 5x excess over the amount needed to cover the silica surfaces. The centrifuge tube was gently shaken and allowed to stand for 3 hours. Rapid stirring of this solution promoted particle aggregation
and was avoided. The samples were centrifuged at 200-1000 RCF twice to remove excess gold colloid, and a final dilution was made to a silica surface area density of .04 m²/mL.

3.2.5 Gold Growth

Once the gold was covalently attached to the silica surface, it was used to provide reduction sites for the deposition of gold from solution. The particles were grown while fixed in place on the silica until they coalesced into a complete shell. Ideally, all available gold should be deposited onto the existing gold decorated silica without self-nucleation. A solution of 1.5 mL of chloroauric acid stock solution (25 mM) and 25 mg of potassium carbonate was diluted to 100 mL. This solution was aged in the dark for one day. A 2-5 mL aliquot of gold decorated silica solution was added to 1 mL of the potassium carbonate/gold solution and was rapidly stirred. The addition of 10 μL of freshly made sodium borohydride (50 mg in 20 mLs) resulted in a color change within 5 - 15 seconds. With a large core to shell ratio, after addition of the NaBH₄ reductant the solution turned red, purple, blue, green, and then faint yellow representing the farthest red shift of the absorbance peak. Then, as the shell grows thicker, the color will change to blue and then to a muddy orange. Metal nanoshell formation is indicated by differences in the absorption and scattering of the colloidal solution. For instance, a solution of nanoshells that looks blue when held to the light appears a muddy orange/red when placed in front of a black background.
3.3 Characterization

3.3.1 Transmission Electron Microscopy

Bright field images were obtained using a JEOL JEM-2010 TEM operating at 200 kV. Samples were prepared by placing a drop of solution on a carbon-coated copper grid, waiting 30 minutes, removing the excess solution and allowing the grid to dry on filter paper. Image analysis was performed with Image Tool for Windows from the University of Texas Health Science Center in San Antonio.

3.3.2 UV-Visible Spectroscopy

UV-Visible absorption spectra were obtained with a Hitachi U2000 UV-Visible scanning spectrophotometer in the wavelength range from 400 to 1050 nm. Solution spectra were obtained by measuring the absorption of dilute solution in a methacrylate cell with a path length of 1 cm.

3.3.3 Dynamic Light Scattering Measurements

Particle densities and the degree of aggregation were measured using a N1 Plus Photon Correlation Spectroscopy analyzer from Coulter Corp., Hialeah, FL. The analyzer was used to measure particle sizes, track particle coalescence, and to estimate particle concentrations after filtering and centrifuging steps.
Chapter 4

Inorganic Colloidal Assembly of Gold-Decorated Silica Particles

There are a number of challenges in the construction of monodisperse metal nanoshells. First, the chosen core must have the desired physical and optical properties. Then, the core must be functionalized with a coating that allows for the attachment of metal seed particles. Finally, the seed must be attached and grown in place until coalescence into a complete shell takes place. At every stage of the growth, steps must be taken to keep the particles from aggregating. In most cases, by simply keeping the external forces on the particles to a minimum, the inherent electrostatic repulsion between two particles is enough to prevent permanent flocculation.

4.1 Growth of Monodisperse Silica Cores: The Stöber Method

The wavelength of the peak plasmon absorbance of metal nanoshells depends on the ratio of the size of the core to the thickness of the shell; thus, our ability to control these two parameters determines the tunability of the system. However, due to experimental restrictions on the minimum thickness of a complete shell, it is the core size that determines how far the peak absorbance wavelength can be red shifted.

An ideal core material is monodisperse, spherical, easily synthesized over a wide range of sizes, and has a surface that can be functionalized. Monodisperse colloidal
silica produced by the base catalyzed reaction of tetraalkoxysilanes in alcohol solutions satisfies the above conditions. Silica in narrow size distributions can be synthesized in sizes ranging from 50 nm to > 1 μm. In addition, the growth is self narrowing so that large particles (needed for large shifts in our plasmon frequency) have a polydispersity of just a few percent. Since the seminal work by Stöber [28] in 1968, there has been considerable debate on the exact mechanism of particle formation. Due to the importance of the physical properties of the core and the chemical structure of the surface, the growth mechanism of colloidal silica will be reviewed.

Stöber and others [28, 30, 31, 32] have shown that variations in water, ammonia, and tetraethylorthosilicate (TEOS) concentration produce monodisperse silica spheres of various sizes. Temperature and electrolyte concentration also affect the final diameter of the particles. Monodispersity is found for concentrations in the ranges of 0.1-0.5 M TEOS, 0.5-17.0 M H₂O and 0.5-3 M NH₃. Different alcohols can be used as solvents although ethanol is the most common. However, even within these ranges, certain combinations can produce irregularly shaped colloids, floculated solutions, and bimodal or polydisperse solutions.

The hydrolysis and condensation of silicon alkoxides can be described by the following chemical reactions:
\[ \equiv\text{Si-OR} + \text{H}_2\text{O} \leftrightarrow \equiv\text{Si-OH} + \text{ROH} \quad \text{(hydrolysis)} \]
\[ \equiv\text{Si-OR} + \equiv\text{Si-OH} \leftrightarrow \equiv\text{Si-O-Si} \equiv + \text{ROH} \quad \text{(alcohol condensation)} \]
\[ \equiv\text{Si-OH} + \equiv\text{Si-OH} \leftrightarrow \equiv\text{Si-O-Si} \equiv + \text{H}_2\text{O} \quad \text{(water condensation)} \]

where R is any alkyl group (C\(_r\)H\(_{2r+1}\)). Hydrolysis is generally the slowest of the three reactions and once a single alkoxy group has been hydrolyzed, the remaining alkoxy groups have a greater affinity for hydrolyzation.

Particle formation is a function of colloidal stability. When TEOS is added to a basic alcohol solution at concentrations above 10\(^{-3}\) M, the solution is supersaturated and aggregation begins. Cryo-TEM studies by Bailey [33], where TEM artifacts due to the drying process are eliminated, show that, hydrolyzed monomers initially react to form microgel polymers. At a critical size and crosslink density, these low density polymers collapse to form dense seed particles approximately 10-30 nm in diameter, dependent on reactant concentration. Initially, the particles are unstable and grow by coalescence but eventually they reach a size where charge stabilization is obtained and aggregation is unlikely. At this point, the particles grow only by addition of hydrolyzed monomer or polymers to the silica surface.

The final size distribution of a base catalyzed alcosol depends on the initial reactant conditions. For instance, the final particle diameter has a strong dependence on [NH\(_3\)]. At low concentrations of NH\(_3\), particle stability is higher. Thus, nucleation stops at a relatively early point in the reaction and a large number of seed particles
form and develop. However, at less than 60 nm final diameter, the polydispersity of these solutions is greater than 10% and the colloids are irregularly shaped (Figure 4.1a). If the concentration of the NH₃ is increased, aggregation of small particles continues for a longer time and fewer seeds are formed. The ultimate uniformity of the particles is increased (Figure 4.1b).

The change of mass of a particle during the reaction depends on the probability of a collision between two particles. While smaller particles diffuse faster than larger ones, they have a smaller cross sectional area; since these two factors depend on the square of the particle radius, the probability of a collision is equal for two different particles of different size. This results in a constant rate of mass addition for all particles in solution. Since a given collision (mass transfer) will proportionally increase smaller radius particles more than larger radius particles, this leads to a self-sharpening of the size distributions of colloidal particles. Stöber grown particles greater than 300 nm can have polydispersities of less than 1% and are nearly perfectly spherical [34].

The condensation of TEOS in Stöber grown particles is not complete during room temperature growth. Typically the particles have a gravimetrically determined porosity of 11-15% [35]. This corresponds to a density of approximately 1.98 - 2.04 g/cm³ for the silica cores. ²⁹Si NMR data [36] shows further evidence of incomplete condensation with a Q4:Q3:Q2 ratio of approximately 60:30:5. Also, several percent of alkoxy groups are never hydrolyzed and end up trapped inside the particles.
Figure 4.1 TEM micrographs of small silica (left) with rough features and a large size distribution and larger silica (right) with a polydispersity of only 3% (294 ± 9 nm).

The refractive index of silica cores can be determined using the technique of index matching. A. van Blaaderen and A. Vrij reported that the silica dispersed in a mixture of ethanol and toluene allowed maximum transmission when the effective index of refraction of the solvent was 1.45 [36]. Silica has negligible absorbance in the visible and mid-infrared wavelengths.

Table 4.1 lists the different sized cores that were used for nanoshell synthesis. Multiple TEM micrographs were analyzed with software from the University of Texas Health Science Center in San Antonio. DLS measurements were taken over a period of 3 hours at a 90 deg scattering angle. The discrepancy between the TEM and DLS measurement may be due to a shrinking of the silica particles under the electron beam[32]. Also, DLS measures a hydrodynamic radius, not the true particle radius.
and may thus overestimate the particle diameter. An additional estimate of the core sizes comes through the relative positions and the heights of the secondary peak plasmon positions as the metal nanoshells are grown thicker. The two sizes were estimated to be 340 nm and 110 nm respectively which agrees with the TEM and DLS measurements within experimental error.

4.2 Functionalization of Silica Cores

The second step in the synthesis of metal nanoshells was to coat core particles with covalently attached molecules that act as bonding sites for gold colloid. Colloidal gold has an affinity for nitrile, phosphorous, and sulfur groups, and there have been several reports of metal colloid attachment to organosilane coated planar surfaces [19, 20, 37, 38]. The main application is in the control of surface roughness of substrates used in surface enhanced Raman spectroscopy studies. Additionally, the attachment of silane coupling agents to silica particles in solution is well characterized [32, 39, 40]. Changing the terminal functional group allows the particles to be studied in non-polar organic solvents. Combining these two ideas results in the aqueous attachment of metal colloids to organosilane coated particles.

<table>
<thead>
<tr>
<th>Run Label</th>
<th>TES/NOH/H2O/EtOH (ml)</th>
<th>TEM diameter (nm)</th>
<th>DLS diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stob50</td>
<td>1.5/5.0/0.0/50</td>
<td>294 ± 9 nm</td>
<td>332 ± 22 nm</td>
</tr>
<tr>
<td>Stob110A</td>
<td>1.5/2.8/0.0/50</td>
<td>114 ± 10 nm</td>
<td>136 ± 11 nm</td>
</tr>
</tbody>
</table>

Table 4.1 Different sized stober grown particles used in this study.
Sufficient aminopropyl triethoxy silane (APTES) for a five monolayer coating of the silica particles was added directly to the Stöber aerosol and allowed to stand overnight. The attachment occurs in a 4 step process illustrated in Figure 4.2. With trihydrolyzable silanes such as APTES, three dimensional polymer matrices can form in solution and be adsorbed to the silica surface. The degree to which oligomerization takes place in solution and how it is incorporated onto the surface is not completely understood. Thus, the surface is an unordered multi-layer of partially condensed silane with any number of the available siloxane bonds binding each oligometric unit to the silica surface or to other attached silanes. Although the attached silane facilitated the adhesion of gold colloid to the silica surface without any further processing, only a condensation step (heating to 105°C in pentanol) bound the gold strongly enough to allow growth of a metal shell.

4.3 Gold Colloid Attachment

Colloidal gold attaches to the silane coated silica particles with approximately the same 30% density as seen on planar surfaces [41]. Figure 4.3 shows typical coverage densities. Once attached, the gold decorated silica particles can be centrifuged and redispersed without addition of any additional stabilizing compounds. This was surprising but also fortuitous since it allows for the separation of silica from the residual colloidal gold while the gold attached to silica remains in a chemically reactive state. The exact mechanism of this inherent stabilization is not known although it is prob-
Figure 4.2 The process of APTES condensation onto a silica particle. The resulting multi-layer is disordered and in an unknown state of condensation.
ably due to a steric barrier resulting from the ionic adsorption of solute molecules. A centrifuge cycle leaves a red pellet in the tube and the residual colloidal gold in the supernate. After three cycles of centrifuging, removing the supernate and redispersing the pellet, the supernate became clear. TEM was used to verify that there was no unattached colloidal gold in these washed solutions.

![TEM micrographs](image)

**Figure 4.3** TEM micrographs of 110 nm silica particle with 3 nm attached gold particles (left) and 340 nm silica colloid with 2 nm attached gold particles (right).

### 4.4 Routes to Flocculation

One of the main difficulties of inorganic colloidal assembly is selective attachment. In our case, we would like to completely coat silica with gold without aggregation of either the larger silica particles or the colloidal gold. When the silica is added to an excess of gold colloid, the gold is small enough that it is still unstable with
respect to the silica and it can be adsorbed to the surface. During this process, the Coulomb repulsion between the larger silica particles keeps them separated. It may be possible to further tailor the attached solution environment (electrolyte concentration, temperature, and pH) to optimize the interparticle forces for the desired balance between isolation and assembly.

Residual reactants can also cause problems. However, removing excess reactants is more difficult than in planar fabrication where a rinse step simply involves washing the surface to remove all unreacted chemicals. In the colloidal assembly environment, a "rinse" involves many iterations of centrifugation and redispersion. Typically, 5-7 wash cycles were necessary to remove a sufficient amount of the unwanted reactants.

Centrifugation also causes coalescence of the particles. High intensity probe ultrasound was useful in redispersing pellets that could not be separated by vigorous shaking. We saw no evidence that probe ultrasound at any intensity was dislodging a significant amount of the attached gold clusters. However, at higher centrifuge speeds, the flocculation of the particles was irreversible. Since higher centrifuge speeds do not aggregate APTMS silica, it is the attached gold colloids that are irreversibly linking the silica particles. As a general rule, longer centrifuge times (1 hour or more) at a lower speed reduced the degree of coalescence. Particle count rates in the DLS were used to monitor the silica concentration in the supernate.

In addition, the combination of filtration and centrifugation could be used to range filter the particle sizes in solution. All gold colloid sizes used in this study were stable
in solution at forces greater than 5000 RCF. Large silica particles coated with gold could be removed at forces < 200 RCF and particles > 300 nm in diameter would self-settle overnight. Larger conglomerates of particles could be removed using PTFE filters (Fisher) with pore sizes greater than 3 times the size of the core. However, as the filter pore size approached the size of a core triplet or doublet, the filters became clogged and their effective pore size rapidly decreased.
Chapter 5

Shell Growth and Metal Nanoshell Optical Properties

The optical properties of metal nanoshells depend on the size of the core and the thickness of the shell. For example, a silica core 300 nm in diameter with a thin, 5 nm shell has a narrow, red-shifted plasmon peak that is well approximated by a single term in the series solution (i.e. quasi-static approximation). As the shell is grown thicker, the distinct optical signature of the higher order plasmon peaks provides an excellent verification of the metal nanoshell theory. However, with large core diameters it is difficult to image the early stages of shell growth with TEM. Thus, two different core sizes for nanoshells were used to illustrate their properties: large core diameter particles (340 nm) that have a large peak plasmon shift and distinct higher order modes, and smaller core sizes (110 nm) that are easier to image and have a single absorption peak that can be followed in the visible portion of the spectrum.

5.1 Shell Growth on 340 nm Cores

Once gold clusters have been firmly attached to the silica surface, they are grown in place until the gold can coalesce into a complete shell. This requires the reduction of gold chloride without self-nucleation. Both hydroxylamine hydrochloride (HHC)\(^\text{[42]}\) and sodium borohydride reduce gold chloride ions from solution to the attached gold
clusters without self-nucleation. Due to the rapid reaction of sodium borohydride with water, fresh NaBH₄ solutions were prepared for every shell growth. Solutions of HHC were stable for hours.

The growth of the gold clusters attached to the silica is accompanied by a color change. The color change of gold nanoshell growth with a 340 nm core progresses from brown to red, then purple, blue, green, and through yellow as progressively more gold chloride is reduced. This initial red shifting of the shells can be seen in Figure 5.1. The TEM verified there all of the gold particles remained attached to the silica cores and that no new gold particles were being formed that could have been responsible for the optical shifts in the UV-visible spectrum.

The shell growth can be divided into three regimes. Initially, gold clusters attached to silica have the same UV-visible spectrum as colloidal gold. Then, as more gold chloride is reduced from solution onto the attached gold particles, the particles begin to coalesce into islands of gold on the silica surface. As these islands continue to grow and merge, their aspect ratio increases and this leads to a red shift of the absorption maximum as seen in previous studies of gold platelets in solution [43]. Finally, when the gold shell is complete its optical properties depend only on the geometry of the particle. In the example in Figure 5.1, the absorption peak has been shifted out of the range of the spectrophotometer.

Once the shell is complete, the optical properties are determined solely by the ratio of the size of the core to the thickness of the shell. As the shell is grown
Figure 5.1 Initial growth of gold shell on 340 nm diameter silica particle. As an increasing amount of gold ions are reduced onto the seed particles, the peak shift towards longer wavelengths [curves (a) through (e)].

thicker, the peak blue shifts (Figure 5.2). The multiple peaks in both the experimental and theoretical plots are due to higher order plasmon resonances. As the Stöber grown core particles are nearly monodisperse, the shell thickness can be estimated by subtracting the TEM determined diameter of the core from the diameter of the nanoshell. The estimated shell thicknesses were used to calculate the theoretical fits which are shown as the dotted lines in Figure 5.2. The shell standard deviation was held constant at approximately 30% and the reduced scattering length parameter $a$ was set equal to the shell thickness. A constant offset of 0.14 was included for all of the fits. The source of this linear background has not been determined but may be a function of additional scattering from particle aggregates.
Figure 5.2 The solid lines in (a) through (d) represent UV-visible spectra of progressively thicker shell growth on 340 nm diameter silica particles. Theoretical peaks are plotted with dotted lines and represent shell thicknesses of 7, 15, 23, and 48 nm.

With particles of this size, higher order terms in the partial wave expansion start to become apparent in the optical spectrum. The growing shoulder at ~700 nm in curves (b) and (c) is due to the quadrupole term of expansion series ($L = 2$). The peak at ~600 nm that is just beginning to be seen in curves (b) and (c), becomes prominent as the leftmost peak in curve (d). This peak is due to the octupole term ($L = 3$). This resolution of the various plasmon peak orders has not previously been observed since it is difficult to grow monodisperse spherical gold particles > 100 nm in diameter.
5.2 Early Shell Growth on 110 nm Cores

A uniform thin metal shell is necessary for narrow peak widths and large red shifts of the plasmon peak absorbance. The size of the initial gold colloid attached to the silane coated silica determines the minimum thickness needed for complete shell formation. Although clusters as small as tens of atoms can be formed in solution [29], attaching clusters below a critical size reduces the uniformity of the resulting shell. This is due to two factors. For very small attached gold cluster sizes (< 1 nm), some of the clusters were dislodged from the silica surface during the subsequent gold reduction. This resulted in a net decrease in the number of seed particles that eventually coalesced into a complete shell. Also, a number of the ultrasmall gold clusters remained attached to the silica surface but did not grow larger. Two possible reasons are coverage with another molecular species or that the reductant lacked affinity for a cluster with only tens or hundreds of atoms[44]. The optimal size for gold seed clusters appeared to be ~2 nm. A series of images showing the early shell development is shown in Figure 5.3. The shell appears complete at approximately 10 nm thickness. A clear progression is seen between the initial seed attachment and the full shell growth. The first five spectra are shown in Figure 5.4. As more gold is reduced, the peak heights monotonically increase and shift to longer wavelengths.

The minimum usable cluster size is likely to be dependent on the quality of the silane layer. Using a silane coupling agent with three active hydroxy sites results in a complicated three dimensional silane network being formed on the silica surface. The
Figure 5.3 TEM micrographs of shell growth on 110 nm diameter silica core. (a) is attached gold only. The amount of gold chloride reduced onto 1mL of silica seed ranged from 1. 2. 3. 4. to 16mL corresponding to (b)-(f) respectively.
Figure 5.4  UV-visible spectra of early shell growth on 110 nm cores. The spectra correspond to the same relative gold to silica ratios as Figure 5.3 (0:1, 1:1, 2:1, 3:1, 4:1, and 16:1). The spectrum from the 16:1 gold to silica ratio has been reduced by a factor of 3.

molecular nature of this layer (porosity, degree of condensation, deformability, number of active amine groups, etc.) is critical to the strength of the silane-Au attachment. For example, without condensing the silane layer by heating in pentanol, the attached gold clusters grew in place but did not coalesce into a shell. The interparticle forces were enough to dislodge some of the gold seeds from the silica surface. Optimization of the silane layer may allow us to reduce the initial colloidal size and thus, reduce the minimum thickness needed for a continuous shell.
5.3 Thicker Shell Growth on 110 nm Core Nanoshells

Once the shell is complete, thicker shells on the 110 nm particles shift the peak from $\sim 900$ nm to $\sim 650$ nm. This blue shifting of the peaks is shown in Figure 5.5. The nanoshell solutions were centrifuged and 0.2$\mu$m filtered after shell growth. The centrifuge step separates the silica from residual colloid. This ensures that the secondary peak that is starting to develop at $\sim 550$ nm is due to a higher order mode of the metal nanoshell and not an artifact caused by gold colloid formation during the gold shell growth. Filtering removes larger clusters that have linked during the gold attachment to silica, the gold shell growth step, or during a wash step.

The calculated spectra are shown in Figure 5.6. The two curves were compared to the calculated spectra from core particles particles ($110 \pm 16$ nm) with shells of ($10 \pm$...
Figure 5.6  Experimental (solid line) and calculated (dotted line) spectrum for a (110 ± 16) nm core gold nanoshell. The calculated spectrum in the left figure has a shell of (10 ± 2) while the right figure has a shell of (27 ± 8).

2) and (27 ± 8) respectively. A 0.1 constant offset was included in the fit. Although the predicted absorption peak is close to the experimental value, the experimental curves shows a much slower falloff in the the long wavelength region. This is in part due to unremovable doublets that pass through the 0.2 μm filter (Figure 5.7). The doublets are anisotropic and thus increase the effective ellipticity of a nanoshell particle. This has been previously reported to cause a red shift in the plasmon peak position [17] which explains the higher wavelength contributions in the experimental spectra. In addition to doublets, the 110 nm silica cores were less spherical, rougher, and more polydisperse than the 340 nm cores. These factors could also contribute to the deviations from the calculated spectra.
Figure 5.7  TEM micrograph of a gold nanoshell doublet.
Chapter 6

Conclusion

Using the techniques of self-assembly, we have attached gold clusters (≈ 2 nm in diameter) onto larger silica particles (>100 nm). These gold decorated silica particles can be used as seeds on which to grow an ultrathin continuous shell of gold. The metal nanoshells show a peak plasmon absorbance that is tuned by varying the ratio between the size of the core and the thickness of the shell. This tunability has been shown to span the visible and the near-infrared portions of the electromagnetic spectrum.

Metal nanoshells are large enough that the quasistatic calculations are no longer a valid approximation. Higher order modes start to play an important role in the optical signature of these particles. Due to the extremely small polydispersity of the silica core, it is possible to observe these higher order resonances as the gold shell is grown thicker. The relative positions and heights of these secondary peaks can be used to predict both the core diameter and the shell thickness.

The optical tunability of nanoshells may have a number of technological applications. With their large tunable extinction, a concentrated solution of the nanoparticles could be used as a coating for absorption in the visible or infrared. Surface enhanced Raman spectroscopy is currently restricted to wavelengths near the plasmon resonance of gold and silver (<550 nm). Attaching nanoshells to a surface may provide
a tunable substrate for surface enhanced Raman spectroscopy. There is also an internal field enhancement associated with nanoshells that may result in an increase in the nonlinear optical properties of the core. The nonlinear optical properties may be even further enhanced by changing core material or by embedding an optically active species inside the silica core. Also, a controllable ultrathin shell is a good model for the study of electron dynamics in a confined system.

In addition, the construction of the metal nanoshell system is interesting in itself. Using the methods of self assembly in a colloidal environment provides unique challenges over planar fabrication. The delicate balance between the binding energy of reactants and the electrostatic repulsion allows selective attachment in a three-dimensional setting. However, there are a number of difficulties with colloidal inorganic assembly. Particle coalescence is an issue at every stage of the assembly. Also, simple steps in planar technology such as a substrate rinse are much more laborious in the colloidal system. However, if the method can be perfected, colloidal inorganic assembly promises the production of devices on a scale orders of magnitude ahead of current planar technology. Metal nanoshells provide an excellent model systems in which to explore the problems and potential benefits of this method of assembly.
Appendix A

Vector Basis Function Solution of Maxwell’s Equations

A.1 The L, M, N Basis

The solution of electromagnetic scattering problems can be simplified by the judicious choice of basis functions in which to pose the problem. An obvious starting point in the selection of such functions would be to choose a basis that has components that satisfy the Helmholtz equations [24]:

\[ \nabla \cdot \nabla \cdot \mathbf{E} - \omega^2 \mu \varepsilon \mathbf{E} = 0 \]  \hspace{1cm} (A.1)

\[ \nabla \times \nabla \times \mathbf{H} - \omega^2 \varepsilon \mu \mathbf{H} = 0 \]  \hspace{1cm} (A.2)

Then, since each element within the basis satisfies the Helmholtz equations, any linear combination of such a set is also a solution. If the initial radiation and boundary conditions can be satisfied by an expansion in this basis then this constitutes a valid solution to the problem. The solution to the scalar Helmholtz equation.
\[ \nabla^2 \psi(r, t) + k^2 \psi(r, t) = 0. \] (A.4)

has the form in spherical coordinates.

\[ \psi_{mn}(r, \theta, \phi) \sim z_n(kr) P_n^m(\cos \theta) e^{im\phi} \] (A.5)

where \( z_n(kr) \) represents either the spherical Bessel functions \( j_n(kr) \) or the spherical Hankel functions of the first kind \( h_n^{(1)}(kr) \). The \( P_n^m(\cos \theta) \) are the associated Legendre functions.

Using this solution as a starting point, Sarkar [25] has shown that there exists a basis function \( \mathbf{L} \), \( \mathbf{M} \), and \( \mathbf{N} \) that both satisfies the Helmholtz equations and forms a complete set. The exact form of the functions in spherical coordinates is shown below.

\[
\mathbf{L}_{mn} = \nabla \psi_{mn} = k \left\{ \frac{dz_n(kr)}{d(kr)} P_n^m(\cos \theta) e^{im\phi} \mathbf{e}_r + \frac{z_n(kr)}{kr} \frac{dP_n^m(\cos \theta)}{d\theta} e^{im\phi} \mathbf{e}_\theta + im \frac{z_n(kr)}{kr} \frac{P_n^m(\cos \theta)}{\sin \theta} e^{im\phi} \mathbf{e}_\phi \right\}. \] (A.6)

\[
\mathbf{M}_{mn} = im z_n(kr) \frac{P_n^m(\cos \theta)}{\sin \theta} e^{im\phi} \mathbf{e}_\phi - z_n(kr) \frac{dP_n^m(\cos \theta)}{d\theta} e^{im\phi} \mathbf{e}_\phi. \] (A.7)

and

\[
\mathbf{N}_{mn} = n(n + 1) \frac{z_n(kr)}{kr} P_n^m(\cos \theta) e^{im\phi} \mathbf{e}_r + \frac{1}{kr} \frac{dz_n(kr)}{dr} \frac{dP_n^m(\cos \theta)}{d\theta} e^{im\phi} \mathbf{e}_\phi. \]
\[ + \imath m \frac{1}{kr} \frac{d(r z_n(kr))}{dr} \frac{P_n^m(\cos \theta)}{\sin \theta} \epsilon^{i m \phi} \mathbf{e}_0. \] (A.8)

A.2 Shell Problem

In addition to being a complete set, it has been shown that any arbitrary plane wave can be expanded in terms of the L, M, and N basis functions [25]. The incident plane wave can be expressed in terms of this basis function along with the intensities of the scattered fields. For instance, the scattered E field in the three regions shown in Figure A.1 is given by:

\[ \mathbf{E}_1 = \sum_{n=1}^{\infty} \left\{ a^{(1)j}_{\pm 1n} \mathbf{M}^{(1)j}_{\pm 1n} + b^{(1)j}_{\pm 1n} \mathbf{N}^{(1)j}_{\pm 1n} \right\} \] (A.9)

\[ \mathbf{E}_2 = \sum_{n=1}^{\infty} \left\{ a^{(2)j}_{\pm 1n} \mathbf{M}^{(2)j}_{\pm 1n} + b^{(2)j}_{\pm 1n} \mathbf{N}^{(2)j}_{\pm 1n} + a^{(2)h}_{\pm 1n} \mathbf{M}^{(2)h}_{\pm 1n} + b^{(2)h}_{\pm 1n} \mathbf{N}^{(2)h}_{\pm 1n} \right\} \] (A.10)

\[ \mathbf{E}_3 = \sum_{n=1}^{\infty} \left\{ a^{(3)h}_{\pm 1n} \mathbf{M}^{(3)h}_{\pm 1n} + b^{(3)h}_{\pm 1n} \mathbf{N}^{(3)h}_{\pm 1n} \right\} \] (A.11)

The ±1 indicates the two choices for the value of \( m \). The superscripts identify the region and the type of function being used. For example, the \( h \) superscript in \( \mathbf{M}^{(2)h}_{\pm 1n} \) represents the M functions that are derived from the scalar solution that uses spherical Hankel functions of the first kind for their radial part. The \( j \) superscript represents functions that have spherical Bessel functions for their radial part. The
Figure A.1 Shell-geometry with single shell. There are three spherically concentric regions indicated. The core has dielectric constant $\varepsilon_c$, the shell has dielectric constant $\varepsilon_s$ and the exterior medium has dielectric constant $\varepsilon_m$.

numeric label identifies the region and so the value of $k$ at the frequency of the incident electromagnetic wave.

By matching the continuity of the transverse components of the electric and magnetic fields at the interfaces $R_c$ and $R_s$, we obtain eight boundary conditions that yield a set of eight linearly independent equations which can be solved to obtain the coefficients in Eqn. A.9 through Eqn. A.11. These coefficients completely determine the electromagnetic field. What is exceptional about this solution is the low number of terms needed for convergence. The quasistatic approximation is given with $n = 1$ and a convergence of better than $1\%$ is achieved by taking terms up to index $n$, where $n \sim 1.4|kr|$. 
Once the field parameters have been determined, other physical quantities can be easily calculated. For instance, the scattering cross section can be expressed in terms of the incident and exterior region field coefficients:

\[ Q_r = -\frac{2\pi}{k_0^2} \text{Re} \sum_{n=1}^\infty \frac{4n^2(n + 1)^2}{2n + 1} \left\{ a_{1n}^r (a_{1n}^{(3)h})^* + b_{1n}^r (b_{1n}^{(3)h})^* \right\}. \]  \hspace{1cm} (A.12)

This is valid for distributions of scatters that are sufficiently dilute and random so that there is no mutual interaction or interference between the scattered waves from individual particles.
Bibliography


