Optical Properties of Gold Nanospheres

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Abstract

The optical properties of spherical gold nanoparticles are calculated using classical electrodynamics. The wavelength corresponding to maximum extinction shifts to longer wavelengths as the size of the nanoparticle is increased. The influence of higher-order multipoles is evident for large nanoparticles, making the spectra more complex. When the shell thickness of a core/shell particle is decreased, the plasmon resonance shifts to longer wavelengths. This red shift is accompanied by an increase in peak intensity. A model for core/shell nanoparticles is presented to investigate surface coverage effects. This model can be used to interpret the optical properties during the growth process or to examine the effects of shell defects, uneven growth, and surface roughness. The preliminary results for low surface coverage show an increase in extinction as the number of surface particles is increased. The peak position for the array of surface particles matches the resonant wavelength for an isolated spherical nanoparticle with a radius equal to half the shell size, as expected for the uncoupled limit.

Introduction and Background

Particles with dimensions on the order of a billionth of a meter are known as nanoparticles. These particles are often composed of coinage metals such as copper, silver, or gold. When excited with an electromagnetic field, nanoparticles produce an intense absorption attributed to the collective oscillation of electrons on the particle surface, termed a plasmon resonance. The resonant frequency is highly dependent on particle size, shape, material, and environment. By altering these characteristics, the frequency can be shifted over a wide range of wavelengths, making nanoparticles attractive as functional materials for many applications. Some examples include electronic and optical devices,[1] chemical and biological sensors,[2–5] optical energy transport,[6–9] and thermal ablation.[10]

Experimentalists have been able to synthesize uniform colloidal particles for some time. New experimental techniques have recently produced core/shell nanoparticles with a consistent size and shape.[11–14] A strong plasmon resonance is observed when the layered particle is composed of silica and gold, which can be shifted by adjusting the relative thickness of the core and shell material. The concentric sphere geometry of the particles allows for control of optical properties in a highly predictive manner, making them a new class of materials that are capable of tailoring radiation throughout the visible and infrared wavelength regimes.[13,14]

While there have been numerous papers published on the optical properties of colloidal gold studies (both experimental and theoretical), the number of theoretical studies on dielectric materials coated with gold is few. This paper is an attempt to fill the void. Studies have been carried out on solid spheres as well as core/shell nanoparticles. In addition, we have formulated a model to investigate surface coverage effects. This allows us to address the gray region between extinction of solid spheres and core/shell particles.

Approach

Classical electrodynamics accurately describes the absorption and scattering of electromagnetic waves by particles in the nanometer-size regime. The equations that govern macroscopic electromagnetic fields are known as Maxwell's Equations, in honor of James Clerk Maxwell. These laws of electromagnetic theory express the behavior of the electric and magnetic portions of a field, as well as the relationship between the two. Maxwell's Equations for a field varying harmonically in time are

$$\nabla \cdot E = 0$$

$$\nabla \cdot H = 0$$

$$\nabla \times E = i\omega\mu H$$

$$\nabla \times H = -i\omega\varepsilon E, \quad (1)$$

where E is the electric field, H is the magnetic field, ω is the angular frequency, μ is the permeability, and ε is the permittivity (dielectric constant).

The optical properties of a sphere of arbitrary radius and dielectric constant can be calculated using Maxwell's Equations. The solutions have been known for approximately a century and are commonly referred to as Mie Theory.[15,16] The problem is to find the electromagnetic field at all points in the particle and medium given the particle radius and dielectric constant. The solutions are subject to the boundary condition that the fields must be continuous when crossing between the particle and the medium. All fields are expanded in vector spherical harmonics. The polarization of the incident field, boundary conditions, and orthogonality of the basis dictate the expansions. Once the fields are known, the optical properties of the particle can be calculated from the scattered field in the far field regime.

Experimentalists typically measure particle extinction. Extinction is absorption plus scattering. Scattering arises when charged particles are accelerated by a field and reradiate. Absorption occurs when the particle takes energy out of the beam and converts it to other forms. Extinction is the sum of both of these processes. The Mie Theory expression for extinction efficiency is

$$Q_{ext} = \frac{2}{(kr)^2}\sum_{n=1}^{\infty}(2n+1)\mathrm{Re}\{a_n + b_n\}, \quad (2)$$

where $k = 2\pi/\lambda$ (wavenumber), r is the sphere radius, and a and b are the expansion coefficients of the scattered field.

Similar equations can also be used to calculate the extinction of core/shell nanoparticles.[17] The approach is exactly the same, except the system is now slightly more complex. There are two radii and two dielectric constants that must be included. This corresponds to one set for the core material and one set for the shell material. In addition, there are two boundary conditions imposed to account for the core, shell, and medium. The expressions for the expansion coefficients are more difficult to compute; once known, however, they can be inserted into Equation 2 to yield extinction efficiency.

The preceding paragraphs outline a way to calculate the optical properties of solid spheres and coated spheres. Little is known about the intermediate transition region between a sphere with no shell and a sphere with a complete shell. We have constructed a model to describe coverage effects. The shell volume is approximated using small spheres placed on the surface of the core. As the number of spheres is increased, the volume occupied by the spheres approaches the true shell volume.

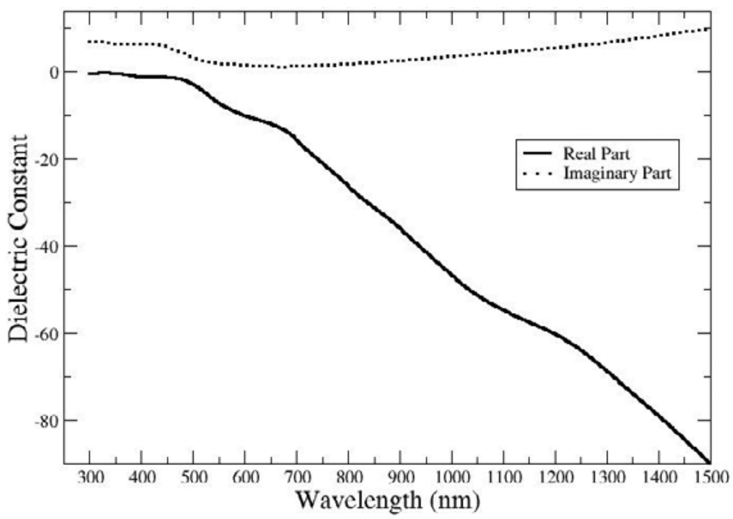

Figure 1: Dielectric constant of gold as a function of wavelength.

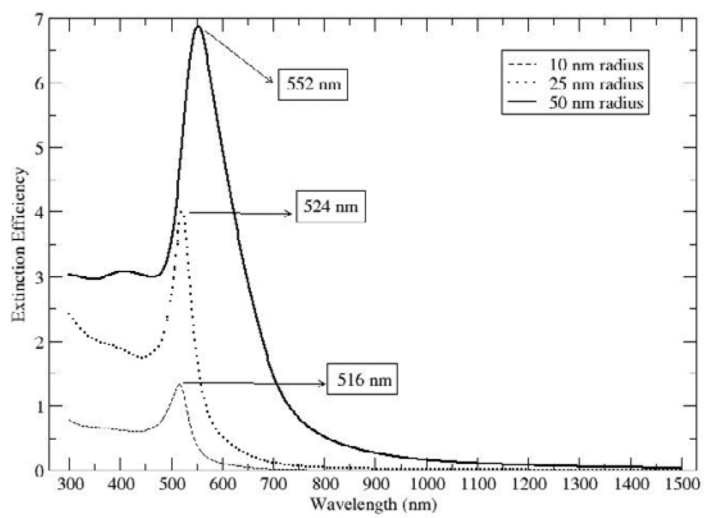

Figure 2: Extinction efficiency for spherical gold nanoparticles of varying radii. The boxed values are the wavelengths corresponding to peak extinction.

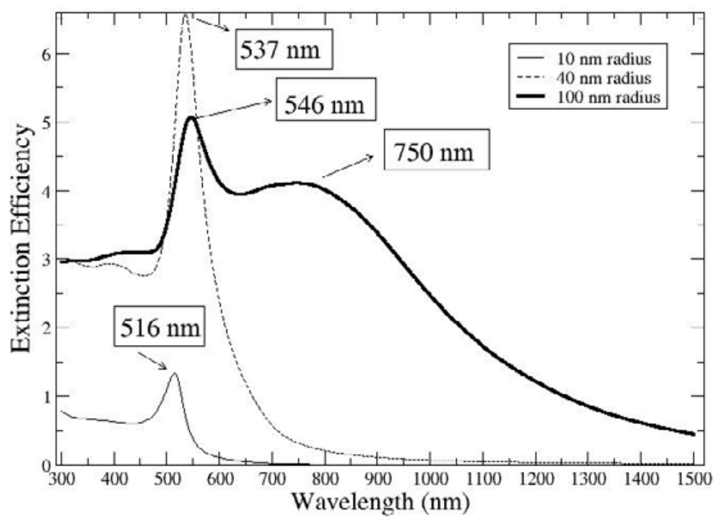

Figure 3: Extinction efficiency for spherical gold nanoparticles of varying radii. The boxed values are the wavelengths corresponding to peak extinction.

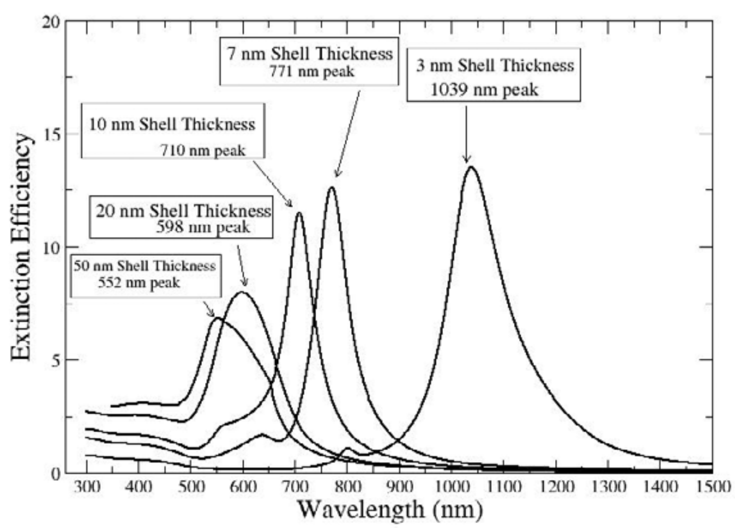

Figure 4: Extinction efficiency of core/shell nanoparticles. The core is silica and the shell is gold. Total nanoparticle radius is 50 nm.

Spheres were chosen to represent the shell volume because the extinction from an array of nonoverlapping spheres can be calculated exactly.

The method used is called the T-matrix scattering formalism.[18] The scattered field of the entire cluster is expressed as a superposition of the fields from each individual sphere, which is calculated using Mie Theory. Additional theorems are applied to the expansion harmonics at each center, yielding the scattered field of the entire cluster in a single coordinate system. The T-matrix elements are then calculated from the expansion coefficients of the scattered field from the cluster. Optical properties, such as extinction, are computed from the T-matrix elements.

All of the calculated spectra represent nanoparticles in solution ($\varepsilon_{med} = 1.769$). Experimental values for the refractive index of gold[19] have been smoothed and interpolated. The dielectric constant has been calculated from the refractive index using the known relationships[20] and can be seen in Figure 1. The refractive index used for silica in the core/shell studies is 1.43.

Results and Discussion

Solid Gold Sphere

The extinction spectrum of a solid gold sphere has been calculated using Mie Theory. This consists of calculating extinction from Equation 2 at many different wavelengths. The extinction spectrum for several nanoparticle radii can be seen in Figure 2. The wavelength corresponding to maximum extinction shifts to longer wavelengths (red shift) as the particle radius increases. The peak seen at 516 nanometers (nm) corresponds to the resonance condition for small spheres —

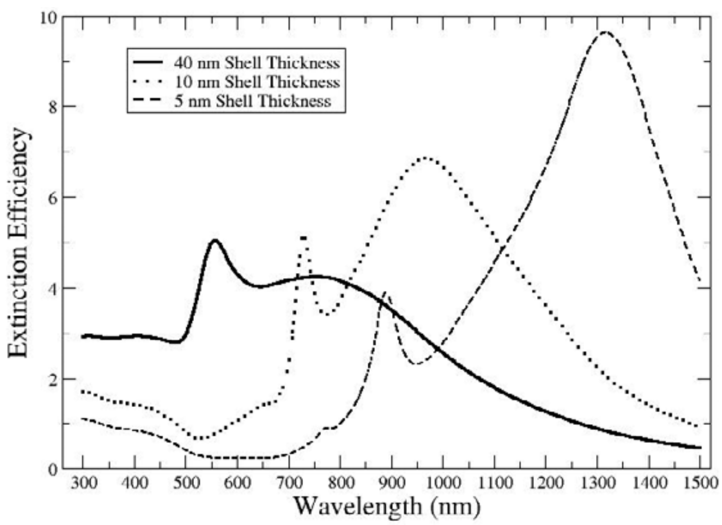

Figure 5: Extinction efficiency of core/shell nanoparticles. The core is silica and the shell is gold. The total nanoparticle radius is 100 nm.

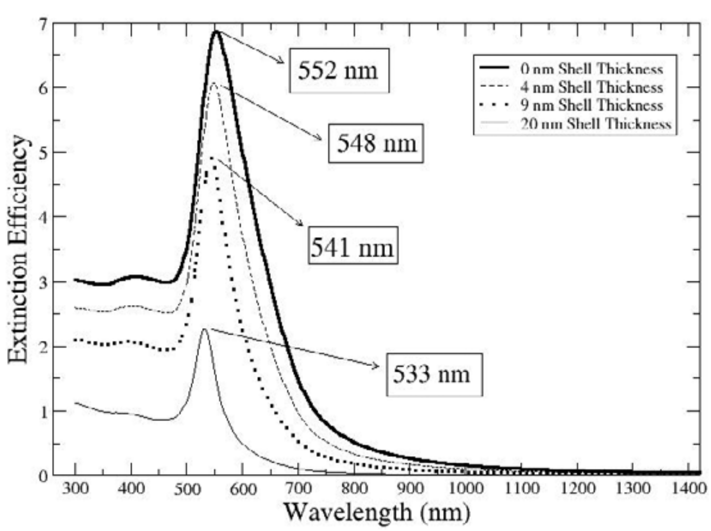

Figure 6: Extinction efficiency of core/shell nanoparticles. The core is gold and the shell is silica. The total nanoparticle radius is 50 nm.

specifically, when $\mathrm{Re}\{\varepsilon\} = -2\varepsilon_{med}$ (see Figure 1). A large red shift of the dipole peak and a much more complex spectrum occur when the particle radius is increased further, as seen in Figure 3. A 100 nm gold sphere displays a broadened dipole peak at 750 nm. Also evident is the appearance of a quadrupole peak at 546 nm. The higher-order modes in the field expansion become important as the nanoparticle becomes larger. This results in the appearance of quadrupole resonances and possibly octopole peaks for very large particles.

Core/Shell Studies

We begin by studying a coated nanoparticle with a silica core and a gold shell. Figure 4 shows the extinction for several particles with different ratios of core to shell size. The total nanoparticle radius is kept constant at 50 nm. The spectrum with a peak at 552 nm is the extinction from a solid gold sphere with a radius of 50 nm (no silica core). As the shell thickness is decreased, the peaks shift to the red and become more intense. Increasing the ratio of core radius to total radius causes the peak to shift red. Thinning the shell layer produces a large increase in polarization at the sphere boundary, which yields the more intense extinction peaks. The same general trends are observed when the nanoparticle size is increased. Figure 5 shows the equivalent plot for a nanoparticle with a radius of 100 nm. Again, as the gold shell is decreased, the dipole resonance becomes more intense, and red shifts. Higher-order poles begin to show up in the spectrum for larger particles. Quadrupole peaks can be seen at approximately 540, 725, and 880 nm.

The result is quite different if gold is the core and silica is the shell. Figure 6 shows the effect of decreasing silica shell size for

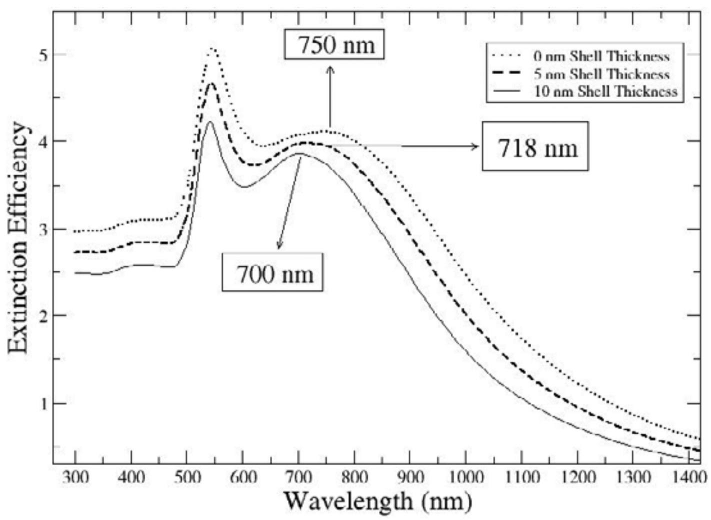

Figure 7: Extinction efficiency of core/shell nanoparticles. The core is gold and the shell is silica. The total nanoparticle radius is 100 nm.

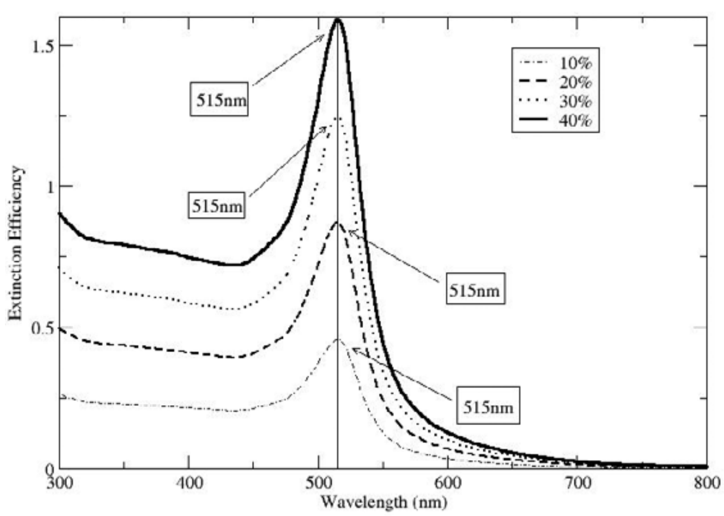

Figure 8: Extinction efficiency for the core/shell model of coverage effects. The percentages shown in the graph represent the percentage of the true shell volume that the surface particles occupy.

a 50 nm nanoparticle. Again, an increase in intensity and a red shift are observed as the shell size is decreased, but the shift is only 20 nm. The magnitude of the shift is approximately 25 times smaller than the red shift observed for the equivalent gold shell particle. This effect is based on a particle's dielectric properties as well as the relative amount present in the coated particle. Increasing particle size to 100 nm yields quadrupole peaks and shifts the dipole peaks to the red, as seen in Figure 7.

Coverage Effects

Small gold spheres are placed on a silica sphere to emulate a core/shell nanoparticle. An effective gold shell is formed on the silica surface as the number of gold spheres becomes large. The model has been developed to investigate the optical properties of the nanoparticle as the gold shell is being formed. It can also be used to study surface defects, such as surface roughness and uneven shell growth, that if restrictive, are not included in the Mie treatment of a coated sphere.

We begin by modeling a core/shell particle for which the extinction spectrum has been calculated above. Gold spheres with a radius of 5 nm are placed randomly on the surface of a silica sphere of radius 40 nm. This is meant to model a 50 nm core/shell particle with a 10 nm gold shell, which has an intense resonance at 710 nm (see Figure 4). Figure 8 shows the effect of increasing the number of spheres on the surface. Peak intensity increases as the percent volume occupied by the gold spheres increases. The wavelength corresponding to the peak intensity is 515 nm in all cases and does not shift towards the expected range of approximately 700 nm. A Mie calculation on an isolated gold sphere with a radius of 5 nm also exhibits a peak at 515 nm, as seen in Figure 9.

Therefore, the gold spheres on the surface are not interacting. There is an additive effect from each sphere, resulting in a more intense peak located at the same wavelength.

The spheres must interact to correctly model a shell film. The lack of interaction is due to the distance between the spheres. Essentially, the gold spheres are not close enough to feel each other. We speculate that this can be remedied by placing more spheres on the surface, thus decreasing the interparticle distance. One stipulation of the T-matrix method is that the spheres do not overlap. All of the random number generators tested have trouble finding positions that do not overlap for densities above 35 percent of the occupied shell volume. At this time we are investigating different lattices placed on a spherical surface to increase the density of surface particles above 40 percent of the occupied shell volume. We speculate that as the volume of the surface particles approaches that of the true shell, the model will produce results in accord with core/shell calculations. Future work will be done to test this hypothesis.

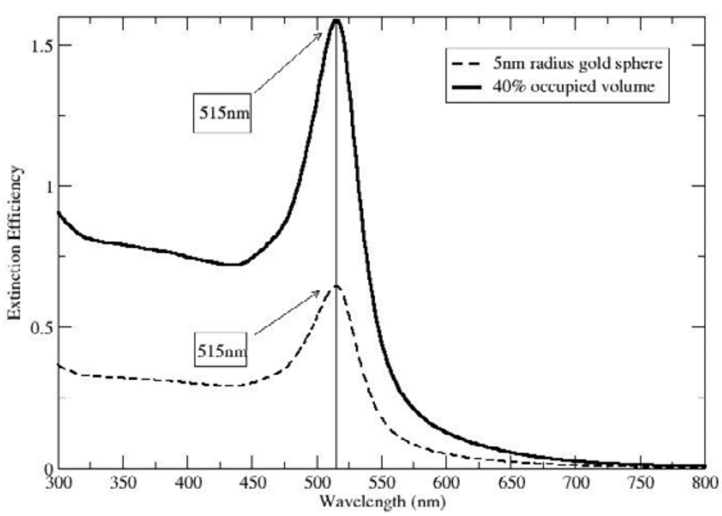

Figure 9: Extinction efficiency versus wavelength. The graph compares the resonance from many gold spheres placed on a silica core with that of a single gold sphere with the same radius.

Conclusions

The optical properties of spherical gold nanoparticles can be tuned by adjusting the physical dimensions. The dielectric properties of the material are extremely important and play a large role in the intensity and placement of the plasmon resonances. As spherical nanoparticles get larger, the peaks broaden and shift to longer wavelengths. Higher-order modes also become important, making the extinction spectrum more complex. Core/shell nanoparticles display a red shift and an increase in intensity of extinction as the shell size is decreased. The magnitude of the shift is highly dependent on the shell material. The surface coverage model shows the correct behavior in the low coverage limit. Future work will extend this to high coverages, gleaning knowledge about optical properties of core/shell nanoparticles during the growth process and about the effects of surface defects.

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