Calculations on the Optical Properties of Layered Metal Nanospheres

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Abstract

In this experiment, the optical properties of several spherical nanoparticles were observed. Particles were modeled using Mie theory, a set of equations that calculate the extinction coefficient of virtually any spherical particle. Initially this theory was used to model solid particles made of noble metals. As time passed, its scope was broadened to modeling coated nanospheres and other different materials. We attempted to observe many trends among the particles while changing their composition, core size, and shell size. We found that by subtly changing the attributes of the particles, we could significantly modify their extinction spectra. Finally, we attempted to model so-called "whispering-gallery modes" using Mie theory. The theory was able to predict their absorption and scattering effectively, but the programs employed were unable to model large, highly absorbing spheres.

Introduction

The optical properties of nanoparticles, both spherical and otherwise, are of great interest to the scientific community. Recently, nanoparticles have been employed as highly sensitive probes for DNA array detection. This is due to the sharp optical resonances and very low detection limits achievable with such techniques.[1] It is necessary to have some way to predict how they will absorb and scatter light. Fortunately, using Mie theory (developed in 1908 by Gustav Mie), one can calculate the extinction spectra of an incredibly wide variety of particles. The optical properties of most spherical nanoparticles are fairly well understood, but by adding a coating of a different material, one can alter how they absorb, often with interesting results.[2] Changing other factors, such as varying the thickness of both the core and shell, yields an even more diverse range of effects.[3] Here, the optical properties of both solid and coated nanospheres were observed using various applications of Mie theory.

Background

As already stated, the optical properties of noble metal nanospheres such as gold and silver have been extensively studied.[4] The intense resonances in the optical spectra of these particles are due to the collective oscillation of conduction band electrons, known as a localized surface plasmon.[5] Generally, when referring to the interaction of light with particles, one is concerned with two factors: scattering and absorption. The latter refers to the light that is taken in by the particle, while the former refers to diversion from its course via deflection. When considering a particle situated between a light source and detector, the difference between the light emitted by the source and received by the detector is the sum of these two processes. This overall phenomenon is referred to as extinction. The results presented by programs dealing with such phenomena are generally a plot of the nanoparticle's extinction as a function of the wavelength of the incident electromagnetic field.

Approach

Nanoparticles Composed of One Material
At the beginning, solid, uniform spheres in the size range of 10–200 nm were studied. These spheres were initially composed of metals such as gold and silver and later were made of less well-known materials such as nickel and aluminum. To study these particles, the well-known "bhmie" program was employed. This code is merely a functional implementation of Mie theory.[6] The program calculates the solution to Maxwell's equations for a spherical particle, thus yielding the electromagnetic field at all points around and inside the sphere. A boundary condition is necessary for these calculations, as it must be assumed that the field is continuous at the edge of the particle. When a particle is interacting with light whose wavelength is similar to the particle's size, the interaction takes place over an area known as the extinction cross-section that is larger than the particle itself. When this area is divided by the area of the geometric cross-section of the particle itself, the result is the extinction efficiency. The calculated field is used to determine the extinction efficiency of the particle at the wavelength of the incident light. Thus, after inputting the refractive indices of the materials studied, refractive index of the surrounding medium, and size of the particle, the program outputs a data table of extinction efficiency versus wavelength. Most of the particles studied had a strong peak somewhere in the visible or infrared range. Increasing the size of the particles, regardless of material, tended to broaden the peaks and shift them toward the infrared.

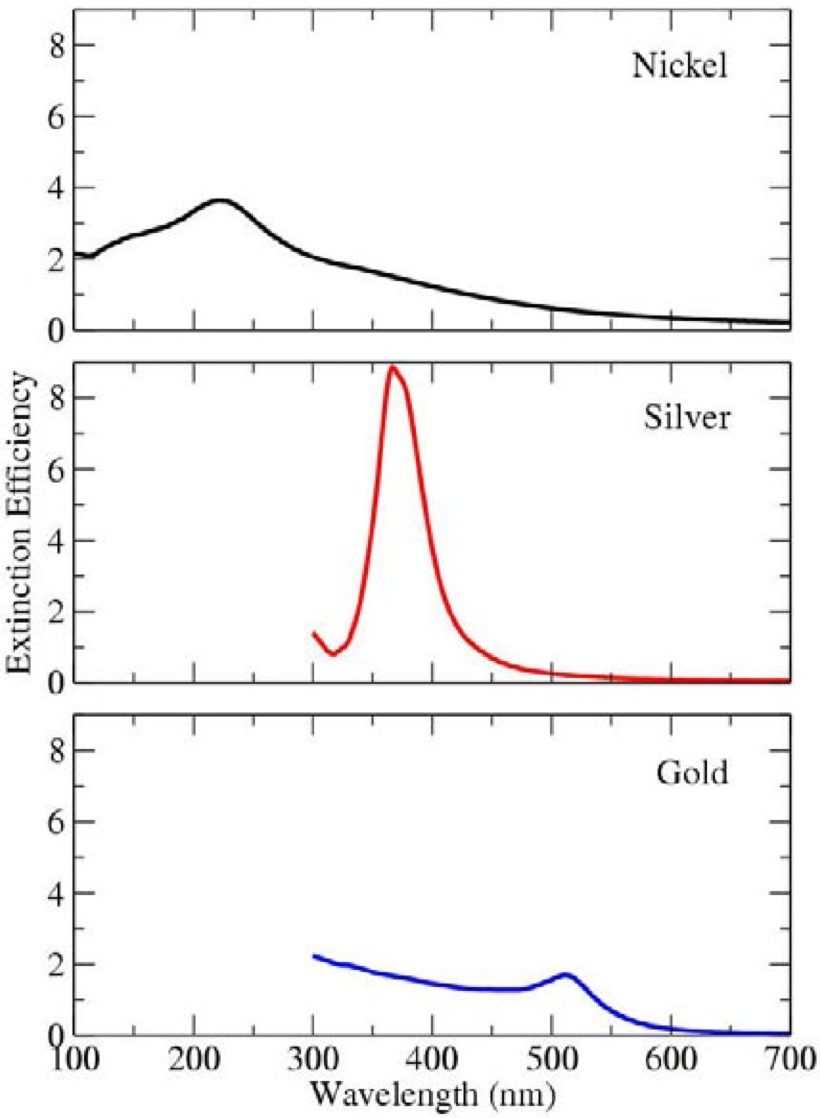

Figure 1: Extinction efficiency for 60 nm particles composed of various metals

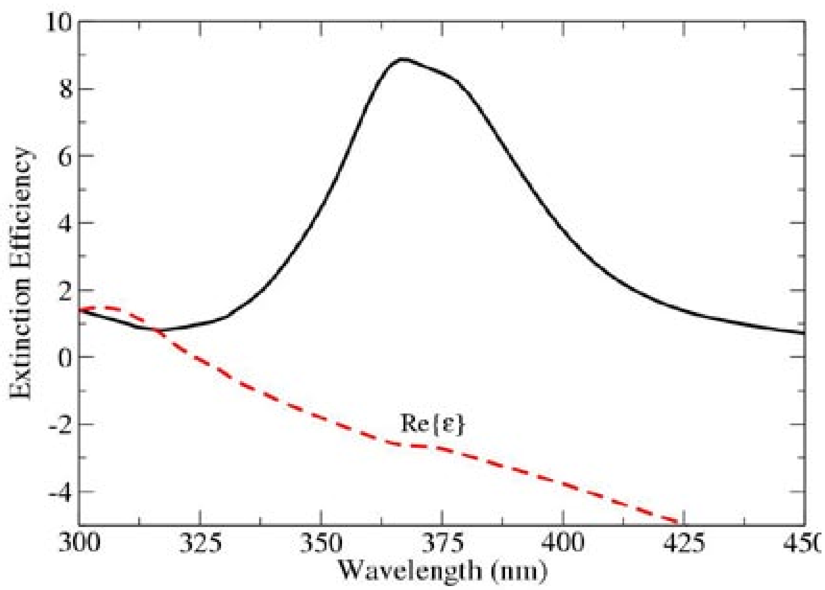

Figure 2: Extinction efficiency versus incident wavelength for a 60 nm silver sphere in a vacuum. Note that the strongest extinction (solid line) occurs when the real part of the dielectric constant is approximately -2.

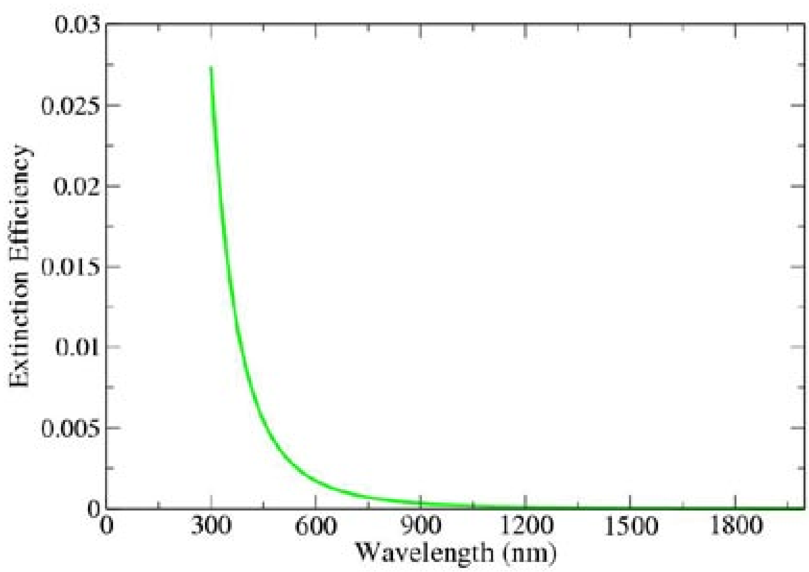

Figure 3: Extinction efficiency versus incident wavelength for a 60 nm silica sphere.

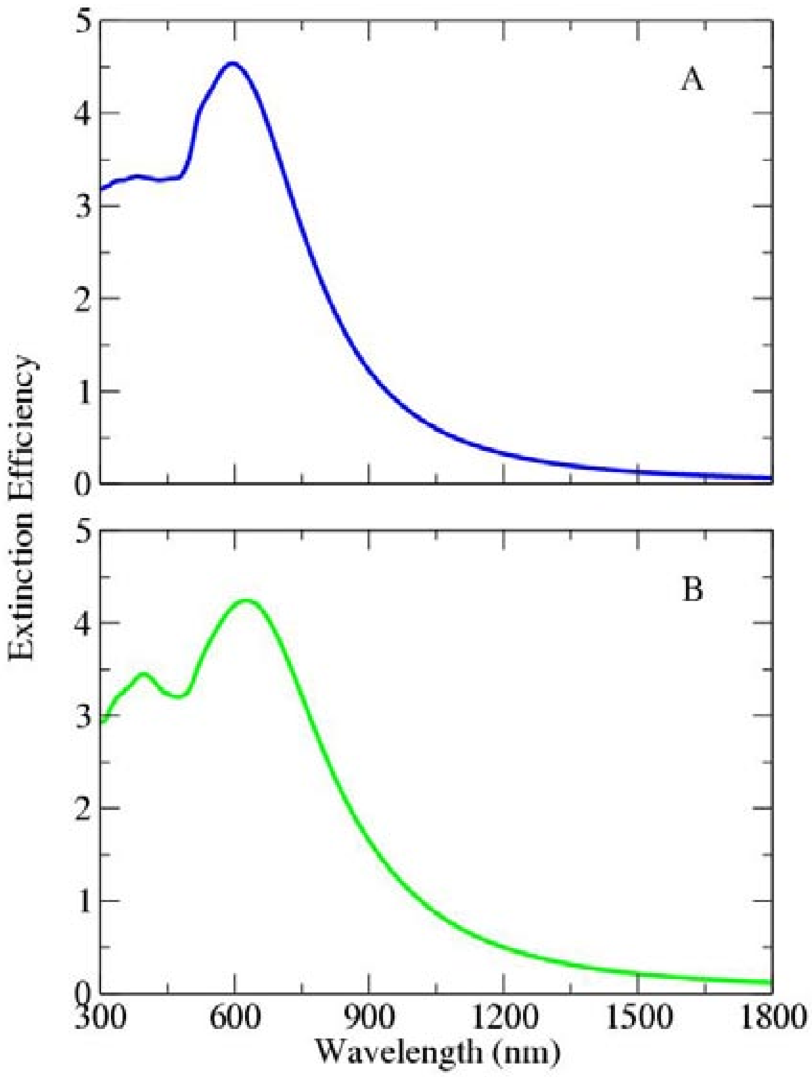

Figure 4: Extinction efficiency for both a 200 nm gold particle (Panel A) and a 180 nm gold particle with a 10 nm nickel shell (Panel B).

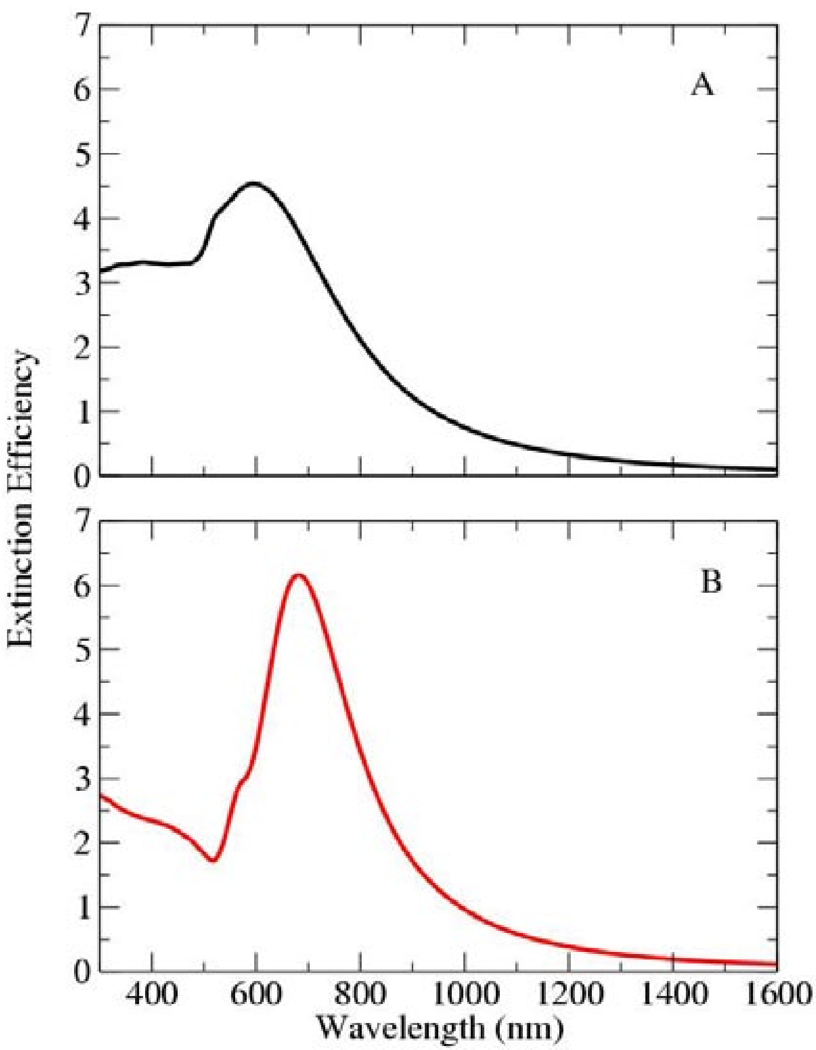

Figure 5: Extinction spectra for a 200 nm gold particle (Panel A) and a 160 nm silica particle with a 20 nm gold coating (Panel B). Note that changing the core of the particle from a metal to a dielectric material while leaving the outer layer unchanged results in a sharpening and redshifting of the major peaks.

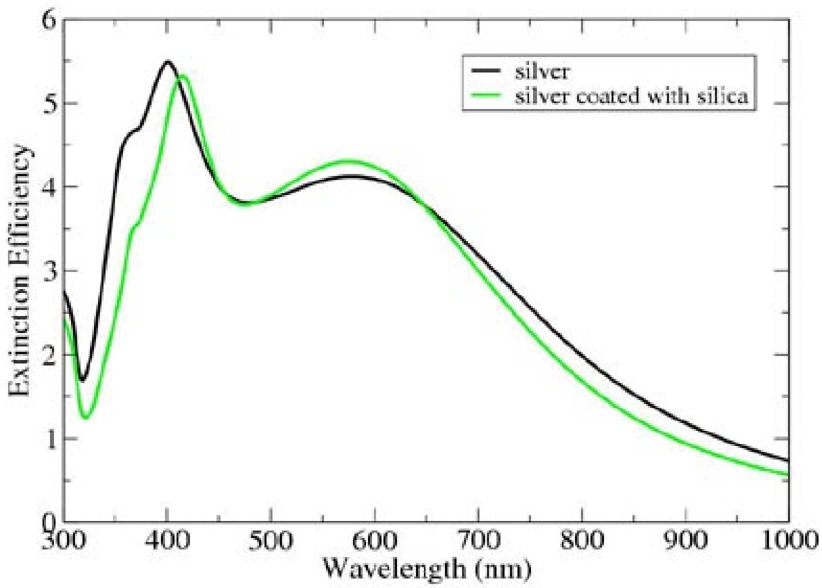

Figure 6: Extinction spectrum for a 200 nm silver particle versus that of a 180 nm silver particle with a 10 nm silica coating. Note that the peaks remain essentially unchanged between the two graphs.

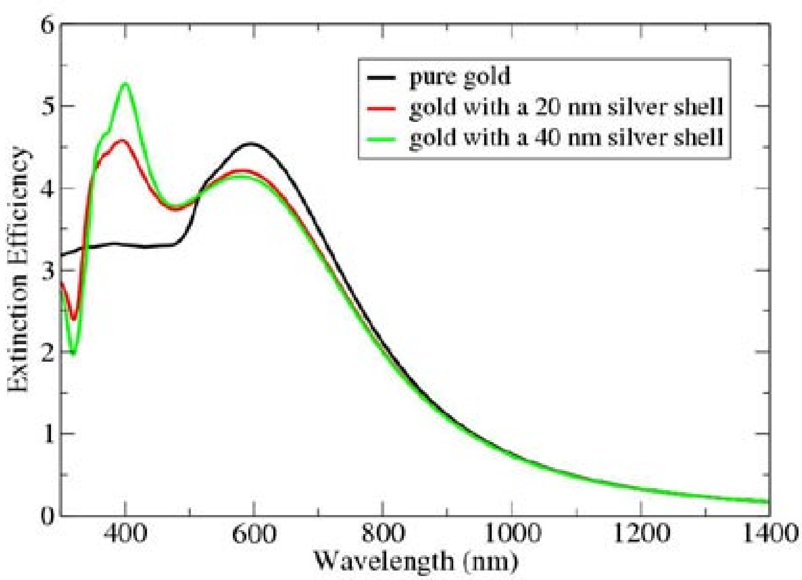

Figure 7: Extinction spectra for a 200 nm gold particle, 160 nm gold particle with a 20 nm silver shell, and 120 nm gold particle with 40 nm silver shell. Notice that adding a shell to the particle initially has a large effect on its spectrum, but subsequent thickening of the shell induces a less and less prominent change.

Nanoparticles with an Added Shell

After becoming comfortable with the general characteristics of spectra of particles with uniform composition, we added shells for the purpose of altering optical properties. The program "bhcoat" was used to simulate the absorption and scattering of particles with one shell. Highly similar to the one used for uniform particles, it merely uses an additional set of parameters and assumptions to model the shell.[7] The theory driving the calculations is identical. When shells were added to the simulation, more interesting phenomena could be observed. This motivated further changes to the simulation, such as using a variety of different materials and significantly varying the thickness of the shells. More complex conclusions and trends could be seen in this set of data as well.

Simulating "Whispering-Gallery" Modes

An interesting phenomenon can be observed among very large (over 1,000 nm) dielectric spheres. When the sphere becomes this large, so-called "whispering-gallery modes" arise, where incident light is reflected into the sphere and achieves total internal reflection within the walls of the particle.[8] At certain wavelengths of light one can observe very sharp, well-defined peaks in the spectrum of a given particle. These resonances are of interest because of their extreme selectivity, potential applications, and comparative lack of research on the subject. Before modeling them, it was first necessary to test Mie theory to see if it could predict such modes. The same code was used, only with larger particles and dielectric materials. Fortunately, the data matched that obtained experimentally from other sources, thus validating the effectiveness of Mie theory to predict even complex phenomena. Once established, it was easy to use the same programs from before to observe whispering-gallery modes and find methods to make them more selective and clear.

Results

Nanoparticles Composed of One Material

First, it was necessary to test the "bhmie" program on solid gold and silver nanoparticles of various sizes. As expected, the results matched experimental data. At small sizes, particles of several different materials showed high extinction at different wavelengths (Figure 1). It is easy to predict where these peaks will occur, however; during the calculation of the extinction efficiency, Q_{ext}, it becomes apparent that the strongest extinction will take place when the real part of the particle's dielectric constant is equal to -2 times the dielectric constant of the medium. In a vacuum (where the dielectric constant of the medium is 1) small particles will absorb strongly when the real part of their dielectric constant equals -2 (Figure 2). Strong absorption at a given wavelength was often precluded by shallower peaks or shoulders at lower ones. Increasing the size of particles tended to shift the peaks towards longer wavelengths and to broaden them. Also, as particles increase in size, more and more extinction peaks begin to appear. This occurs because of the approximation used to calculate the scattering and absorption of the particle. At small sizes, the particle can be effectively considered to have two centers of charge. As the size increases, more complex interactions occur, and more poles must be added for the calculation to work. Each peak in the spectrum is a result of these increasingly complex interactions. Small spheres composed of dielectric materials such as silica, though interesting optically when coated, merely yield a plot of exponentially decaying extinction as wavelength increases when modeled alone (Figure 3). However, at very large sizes, whispering-gallery modes can be observed in such particles, drastically affecting their absorption. This will be discussed in further detail below.

Core-Shell Nanoparticles

The results when shells were applied to the particles were a bit more interesting and varied. Several prominent trends could be observed that applied to nanoparticles made of all materials studied. For example, adding thin coatings of metals to metal nanospheres tended to broaden the strongest peaks as well as shift them toward the infrared portion of the spectrum (Figure 4). Changing the core of a particle can also affect its extinction spectrum; adding a small dielectric core to various metal nanospheres, for instance, causes their major peaks to be intensified and shifted towards the infrared (Figure 5). Conversely, adding a dielectric shell to a metal particle has very little effect on its spectrum; it only effectively quenches the absorption, resulting in less intense peaks at identical wavelengths (Figure 6). When coating metal spheres, the thickness of the shell had a large role in how it affected the optical properties of the particle as a whole. Adding a thin metal layer to a nanoparticle drastically affected its spectrum. The exact nature of the effect varied on the materials present in both the core and the shell. As the shells increased in thickness, however, less and less of a change could be seen from the previous spectrum (Figure 7). Overall, a very large variety of spectra could be produced by subtly altering the materials and thicknesses involved in the composition of the particles.

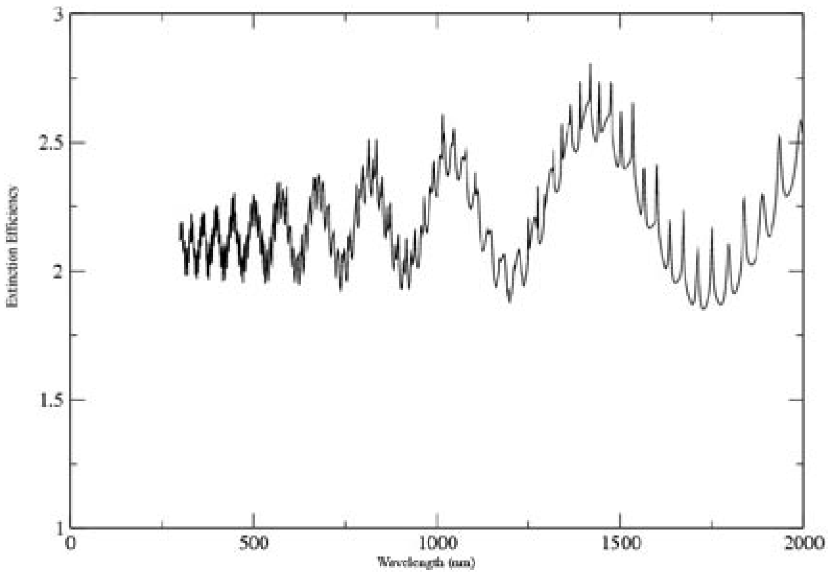

Figure 8: Extinction efficiency for a 4510 nm silica sphere. The many sharp peaks represent individual whispering-gallery modes.

Whispering-Gallery Modes

As stated earlier, small dielectric spheres are not very interesting from an optical point of view. Their absorption is comparatively strong (although very weak compared with metal particles) at short wavelengths, but as one moves into the visible and UV regions, it declines exponentially. However, if one significantly increases the size, something very different happens. At sizes around or above 1,000 nm, the absorption plot oscillates with the wavelength in a pattern loosely resembling a sine curve. Several sharp peaks accompany this pattern; these represent the whispering-gallery modes (Figure 8). After the "bhcoat" program was tested against experimental data[9] (to verify that Mie theory could predict whispering-gallery modes), it was used to try and predict the behavior of large coated dielectric spheres. Unfortunately, at large sizes the mathematical approximation used to functionally implement Mie theory in the program breaks down. It was impossible to obtain an accurate prediction of ways to quench the whispering-gallery absorptions using a metal coat. However, this does not mean that modeling such particles is theoretically impossible; it is merely a matter of adjusting the code to be able to handle such particles more accurately. In the future, it is of interest to see whether adding a metal coat could help to trap light more effectively within the particle and create absorbencies that are easier to manipulate. Also, in the future we hope to translate any sort of controlled whispering-gallery modes to nonspherical particles, such as pyramidal shells.

Discussion

Overall, the above calculations bring to light several less-explored characteristics of layered nanospheres. It is clear that very specific absorption spectra can be calculated for any desired function by using different combinations of materials at varying thicknesses. Mie theory proves so versatile, it can be used to model the absorption of particles that cannot even be synthesized yet. By modeling them ahead of time, one can predict which types of particle will yield optically interesting results and therefore deserve attention. At this point, the only weakness in the theory is its current implementation. The approximate (though highly accurate) spectra given by programs such as "bhcoat" are ineffective at large sizes for anything but dielectric materials. The fact that we were unable to model large, highly absorbing spheres limited our ability to further explore the behavior of whispering-gallery modes by adding, for instance, a metal shell to a large dielectric sphere in the hope of quenching some of the absorptions.

However, since the theory remains intact, it should be conceptually easy to modify existing programs to produce higher-quality results for large particles. Once this is complete, it will be possible to calculate spectra for virtually any spherical particle.

Conclusions

Here, Mie theory was used to model a very wide range of spectra and phenomena. It was shown that through subtle manipulation of a particle's characteristics, one could significantly alter the way it absorbs light. Future work in this field, then, would focus on changing even more variables in particles' compositions. Nonspherical particles and particles with multiple layers, for example, have already proven to be very optically interesting. With every new type of particle modeled, we will come closer and closer to complete understanding of how light is absorbed on the nanoscale.

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