The Influence of Particle-Particle Interactions, Shape, and Size on the Optical Properties of Silver Nanoparticles

Undergraduate Researcher
Anne Hawkinson, North Park University, Chicago, Illinois

Faculty Mentor
George Schatz
Department of Chemistry, Northwestern University

Postdoctoral Mentor
Shengli Zou
Department of Chemistry, Northwestern University

Abstract

Chemists and physicists have been interested in the optical properties of metal nanoparticles since the time of Michael Faraday.[1] New approximation techniques for different sizes and geometries have created renewed interest in and investigation of these particles. Many different arrays of particle extinctions of various shapes and sizes have been measured and calculated. This study focused on the optical properties of one, two, and three spheres and spheroids. The optical properties produced by most of the particles during the course of this research were exactly as is the case of three-particle interactions — the particles were not large enough or great enough in number to produce the desired effect.

Introduction

Wouldn't it be nice if we didn't need to see a doctor to find out what was wrong with us? What if we could do away with painful blood tests for disease and genetic testing? All that may be possible. The interaction of light with nanoparticles produces various optical properties. These optical properties are ideal for creating new chemical and biological sensors that could have many important and practical applications, including disease detection.

For example, suppose there was a chain of nanoparticles that absorbed a specific wavelength when irradiated by light. Now, suppose this chain was missing one particular nanoparticle, resulting in no special optical property. One could reasonably imagine that a biological protein or other molecule in the system could attach to the missing nanoparticle and bring it into the chain. This would cause the newly completed chain to absorb the desired wavelength. When this wavelength was absorbed, it would indicate that the saliva or blood being studied did contain the missing biological molecule.

Background

The aforementioned phenomenon is possible because every individual nanoparticle or chain of nanoparticles absorbs a very specific wavelength of light. If you take a gold sample and cut it in half until its radius is on the order of 10^{-9} meters, will it still maintain the properties of gold metal? In 1847 Michael Faraday[2] set out to answer that question. When the size of gold is between 10 and 20 nm, it no longer appears gold but red. Faraday determined this is because of a phenomenon called plasmon resonance.

Electrons around small-particle atoms behave like a plasma. When a small metal nanoparticle, such as gold, is irradiated by light, the electron cloud begins to oscillate. This oscillating electron cloud is called a plasmon because of its plasma-like qualities.[3] The electric-field oscillation of the light causes the conduction electrons of the particle to oscillate as well. The oscillation of the particle causes it to absorb different wavelengths of light and to scatter others. The absorption plus the scattering is called the extinction.

Plasmon resonances are unique based on the shape, size, and dielectric constant of the nanoparticle. Because there are so many dependent factors, plasmon resonances can vary dramatically with slight changes in the properties of the particle. The plasmon resonance is found by measuring or calculating the extinction of a particle. Extinction is the name given to the absorption of a particle plus the scattering of the particle. The extinction can be calculated by solving Maxwell's equations.

Mie was the first to solve Maxwell's equations when, in 1908, he discovered that the dielectric properties of a particle relate to the extinction. Mie's equation was

Extinction cross section =

$$\frac{8\pi^2 (\text{radius})^3}{\partial} \qquad \frac{3\epsilon_2}{(\epsilon_1 + 2)^2 + \epsilon_2^2}$$

The lambda represents the incident wavelength and the dielectric constant of a metal is

$\epsilon = \epsilon_1 + i\epsilon_2$

When graphed, the peak that results corresponds to the extinction of electrons in nanoparticles. The applied field gives quivering oscillations in the electron cloud that lead to an electromagnetic field.[3] Because Mie's theory only works for spherical particles, however, it is necessary to approximate solutions to find extinction.

In this paper, the factors that govern plasmon resonance will be explained, as will the Discrete Dipole Approximation (DDA) and why it is used. Finally, applications of this technique will be presented. In particular, differing optical properties derived from interactions between a sphere

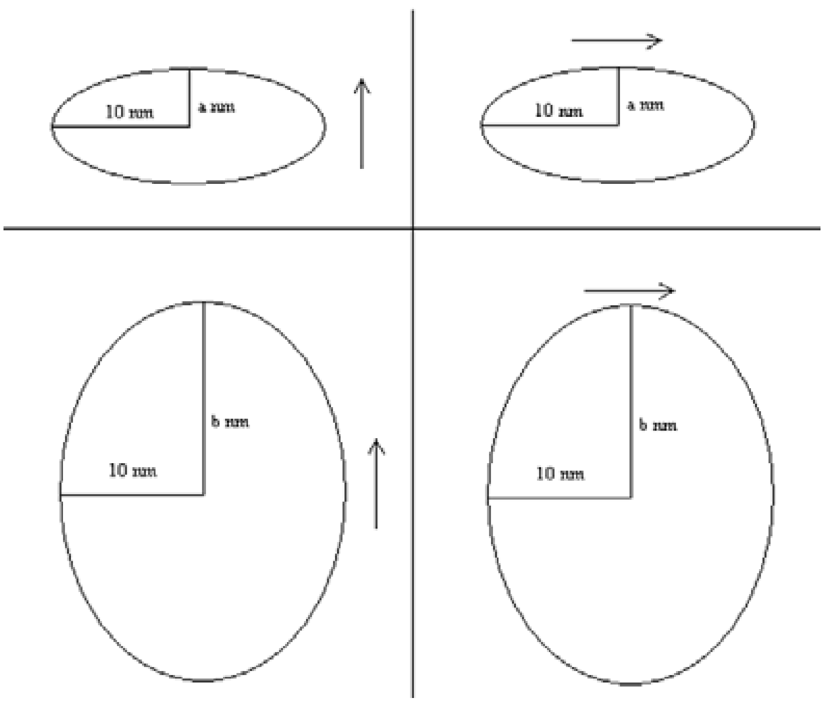

Figure 1: The images on the left show the different configurations of particles when the electric field was applied parallel to the variable axis of the particle. The images on the right show the different particle configurations when the electric field was applied perpendicularly to the variable axis of the particle. The variable a can be either 3 or 7 nm while the variable b is 20 or 30 nm.

and a spheroid, as well as interactions between three spheroids, will be shown.

Since the development of various approximation methods, numerous experiments and calculations have been done to find extinction for different sizes and shapes of nanoparticles. Many different sizes and shapes have been tested.[3,4] These approximations were calculated for large arrays of nanoparticles, however, and there could be different optical properties when fewer particles are present.

Based on past experiments on the optical properties of metal nanoparticles, it is known that extinction spectra tend to show more than one plasmon resonance. These additional plasmon resonances occur when there are multiple particles. Standing alone, each particle has its own individual plasmon resonance. As two particles are brought together, the interactions between them change the resonances. The attempt of this study was to learn how close the resonances could be to each other before the coupling effect becomes so strong that it alters the resonances.

Past experiments also displayed interest in the shifts of the wavelengths. One study showed that increasing the number of spheroids in a chain will blue-shift the wavelength.[5] Once a certain number of nanoparticles is reached, there will be the predicted blue shift, but there will also be a second peak or more peaks that are red-shifted. This has only been seen in larger particles with a great number of nanoparticles. The question remains, how large do the particles have to be, and how few in number, to still produce this red-shifting effect?

Approach

When there is a target with arbitrary particle geometry (in this case, metal nanoparticles), it is common to calculate the different optical properties (such as scattering and absorption). However, as stated above, Mie's theory only works for spherical geometries, and so approximation methods are required to calculate the extinction of the particles. Different approximation methods include the Discrete Dipole Approximation (DDA), the multipole method, and the finite difference time domain method.[3]

The DDA approximates the particular target by replacing the target with a finite array of polarizable points. That is, the geometrical shape is replaced by a fixed cubic lattice of these points. The points acquire dipole moments due to the applied electric field. Since dipoles interact with each other through their electric fields, the DDA is often called coupled dipole approximation.[6]

The DDA was actually inspired by natural phenomena. In 1909 Lorentz showed that the dielectric properties of a substance are directly related to the polarizability of the individual atoms of which the substance is composed — if the atoms are located on a cubic lattice. For a finite array of point dipoles, the problem can be solved exactly. Therefore, the only approximation present in the DDA is that of the replacement of the target with the array of dipoles.

DDA works particularly well with a small number of particles that are close together. If the particles are too large or too far apart, the approximation will not work because the number of point dipoles in the lattice becomes too large for a computer to process practically.

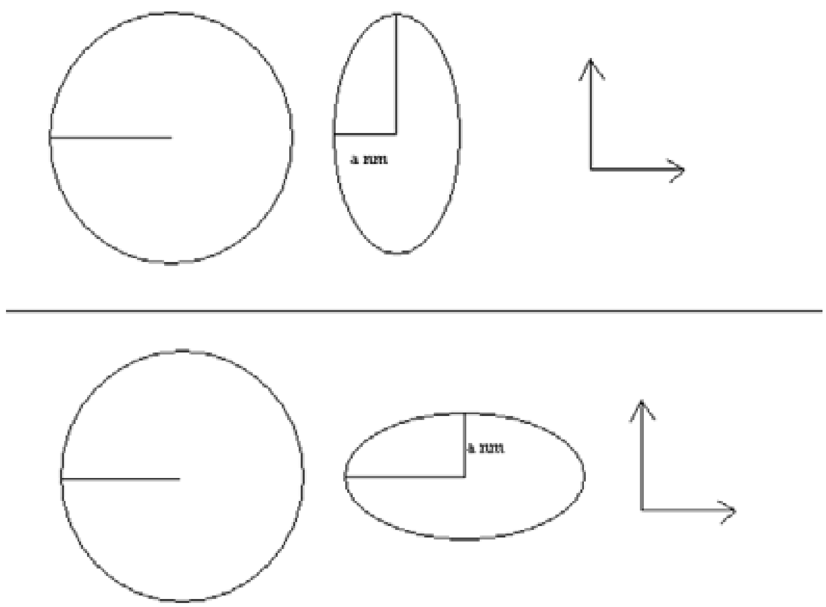

Figure 2: At top is the configuration of particles arranged with the variable axis aligned with the chain. The bottom configuration shows the variable axis of the spheroid perpendicular to the chain. The arrows indicate the different possibilities of the direction of the electric field.

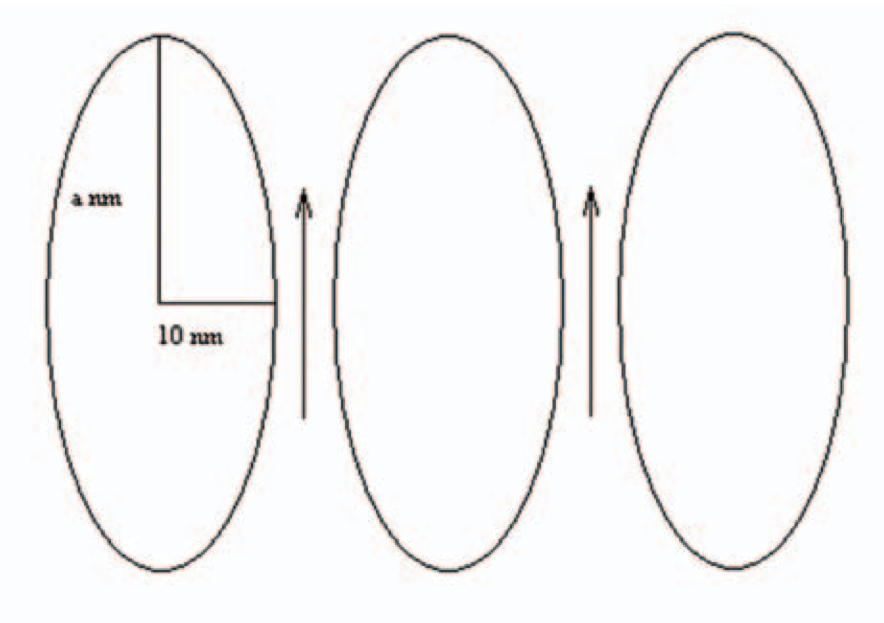

Figure 3: This is the configuration of three spheroid particles tested. The arrow indicates the direction of the electric field. The variable a changes from 3, 7, 10, 20 and 30 nm.

The DDA can be applied to an endless list of different types of particles. In this study, various arrangements of particles were tested, along with various sizes. Next, a third particle was added and the particles were tested with multiple spheroids with the electric field perpendicular to the chain of particles. The distance between particles was varied, too.

Single Spheroid
Before studying the effects of interactions between particles, it was necessary to find the plasmon resonances of single particles. Extinction spectra were found for single spheroids with constant axes of 10 nm and variable axes ranging from 3, 7, 10, 20, and 30 nm. First, the calculation with the electric field parallel to the variable axis was performed and then repeated with the electric field perpendicular to the variable axis. Figure 1 shows an example of the setup.

A Sphere with a Spheroid
In this section, the DDA was used to calculate the extinction spectra for a sphere and a spheroid placed 2 nm apart. The length of the variable axis of the spheroid was changed as well as the directions of the spheroid and the applied electric field. The length of the radius of the variable axis of the spheroid was run at 3, 7, 10, 20 and 30 nm, while the radii of the constant axes were always 10 nm long. The particles were tested with the variable axis lined up perpendicular to the sphere as well as parallel to the sphere. Finally, the extinctions were calculated with the applied electric field parallel and perpendicular to each chain. Figure 2 shows examples of these setups.

After finding the extinctions for each arrangement, the extinction wavelength was graphed versus the variable-to-constant axis ratio. This helped determine how close together the resonances can get before interacting with one another. Based on these results, it was decided to test one arrangement at 1 nm apart. This arrangement had the two particles aligned parallel to the electric field, and the variable axis parallel to the chain of particles.

Three Spheroids
Because previous calculations have shown a red-shifted wavelength with large chains of spheres, three spheroids were used to

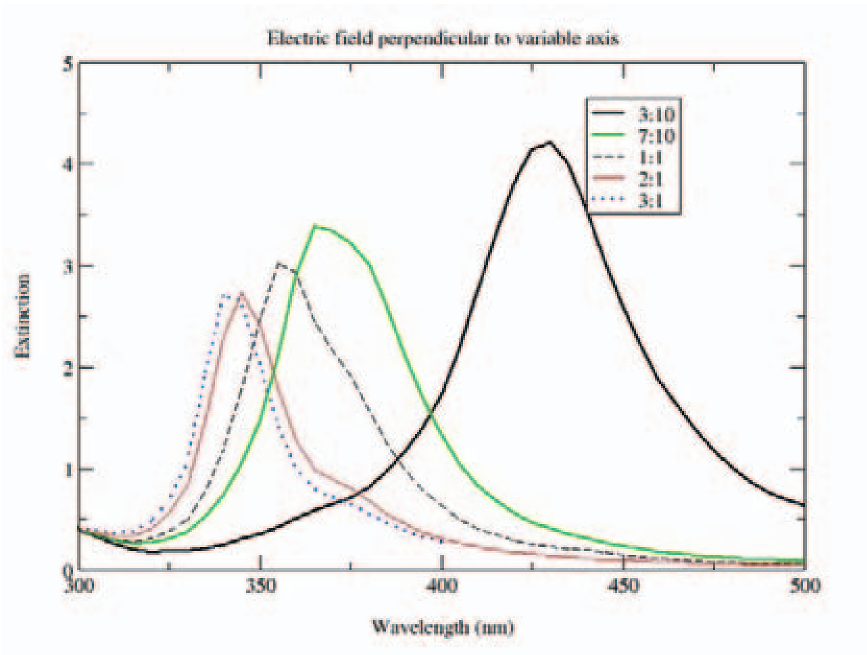

Figure 4: Extinction spectra for a single particle with the electric field perpendicular to variable axis. The legend shows the variable-to-constant axis ratio.

see if the same red-shifted plasmon resonance could be found. Three spheroids were arranged with parallel variable axes 2 nm apart. The electric field was applied perpendicular to the chain of particles. The radii of the constant axes of the particles were always 10 nm. The radius of the variable axis was varied from 3 to 30 nm, as in the case of the sphere with the spheroid. When done with more particles and larger particles, this arrangement gave a blue- and red-shifted peak. After this experiment ran, the particles were moved to 1 nm apart and the extinction spectra was calculated. In another test, the particles were kept 2 nm apart, but the size of the particles were increased to have the radii of the constant axes 12 nm, while the radius of the variable axis was 36 nm. Figure 3 shows examples of these setups.

Results and Discussion

Single Spheroid

Figure 4 shows the extinction versus the wavelength of single particles with the applied electric field perpendicular to the variable axis. When the variable-to-constant axis ratio is less than 1:1, the plasmon resonance is red-shifted from the control sphere. Also, the extinction peak is slightly more intense. When the variable-to-constant axis of the particle is greater than 1:1, the plasmon resonance is blue-shifted and the extinction peak becomes less intense. The changes in these plasmon resonances are not very dramatic because the electric field is always applied over the same cross-section of the particle.

Figure 5 shows the extinction versus the wavelength of single particles with the applied electric field perpendicular to the variable axis. When the variable-to-constant axis ratio is less than 1:1, the plasmon resonance is blue-shifted. The peaks of these extinctions are much less intense than the control sphere. When the variable-to-constant axis is greater than 1:1, the plasmon resonance is significantly red-shifted. The peaks are also up to four times more intense than the control sphere. The shifts when the electric field is parallel to the variable axis are much more dramatic than when the electric

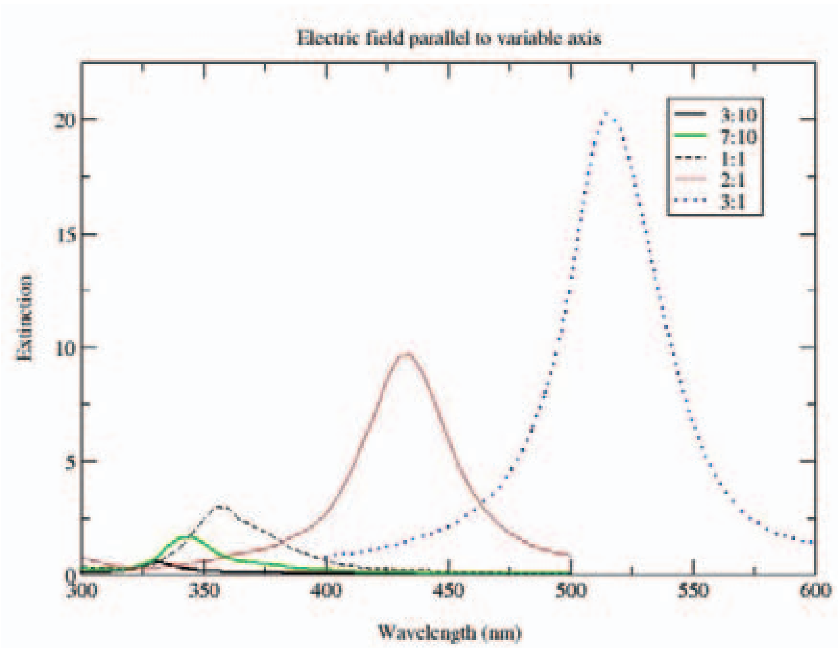

Figure 5: Extinction spectra for a single particle with the electric field parallel to variable axis. The legend shows the variable-to-constant axis ratio.

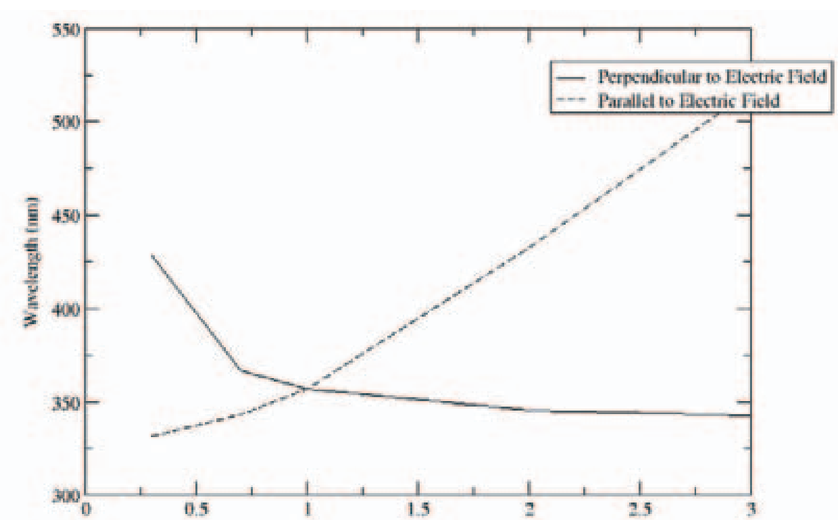

Figure 6: This is the wavelength versus the variable-to-constant axis ratio of single particles aligned both parallel to and perpendicular to the applied electric field.

field is perpendicular. Here, the cross-sections of the particles vary by almost 60 nm. The largest cross-section is 10 times larger than the smallest cross-section, which explains the more dramatic change. For this reason, more dramatic changes are expected when the electric field is parallel to the variable axis in multiple particle tests. Figure 6 shows the plasmon resonances versus variable-to-constant axis ratios. It will be important to compare these lines to the graphs obtained once a sphere is added into the system.

A Sphere with a Spheroid

After all the combinations of experiments were run, three types of shifts were seen. Figure 7a shows the setup of the particles that gave off the first extinction spectrum. Figure 7b shows that very little shift occurs, and the multiple plasmon resonances are barely visible. The multiple plasmon resonances were found and plotted against the variable-to-constant axis ratio of the system. The results can be seen in Figure 8. The bottom line on the graph indicates the resonance of the sphere, while the top line comes from the spheroid. The coupling effect is very strong once, and the wavelengths stay within 40 nm of each other once the particles reach a 7:10 variable-to-constant axis ratio. This less-than-dramatic effect is consistent with the results obtained in the single spheroid experiment. The electric field is applied over the same cross-section of the different sized particles.

Figure 9a shows the setup that led to the second type of shift, and Figure 9b shows the extinction spectra that resulted. These spectra clearly show multiple plasmon resonances. The shifts are as negligible as in the previous extinction spectra, but the peaks are more intense. The electric field was applied over basically the same cross-

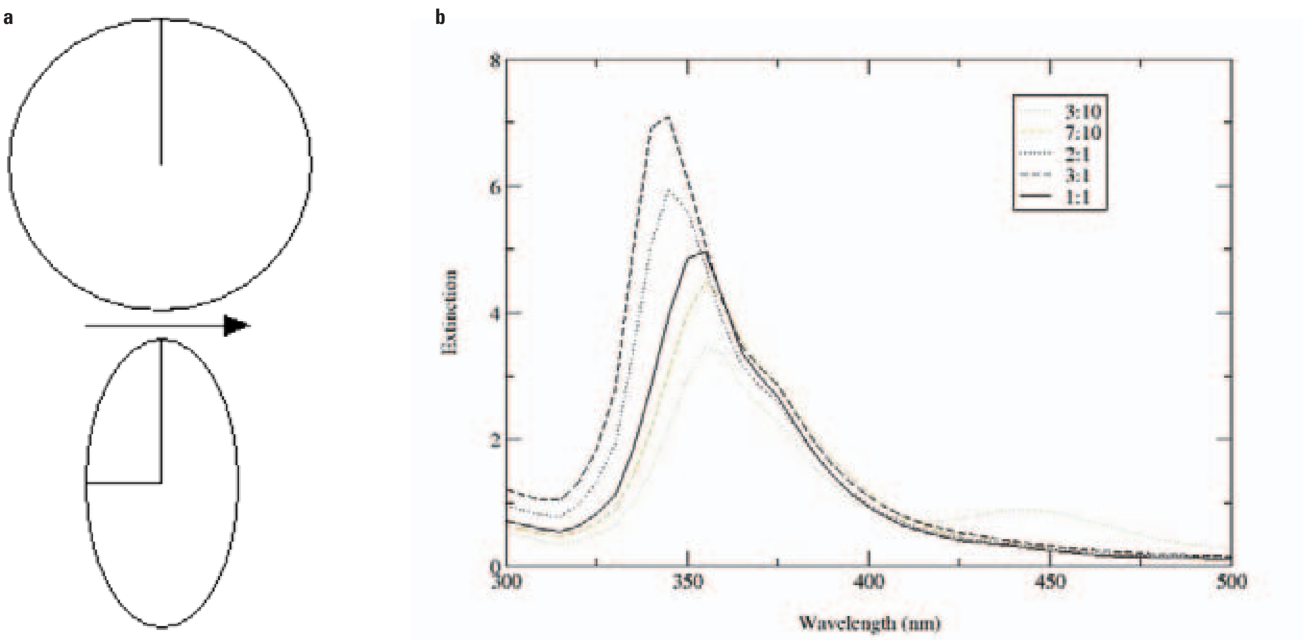

Figure 7: a shows the configuration of particles that lead to the extinction spectra in b. The solid line in the center is the control sphere. The legend is the variable-to-constant axis of the spheroid.

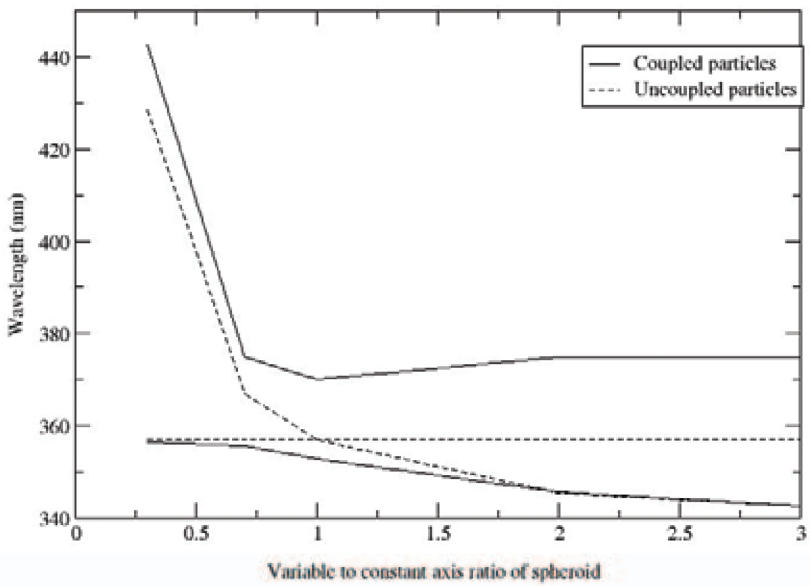

Figure 8: The wavelengths of the plasmon resonances versus the variable-to-constant axis of the configuration seen in Figure 7a. The dashed line represents the extinction for the uncoupled sphere and spheroid.

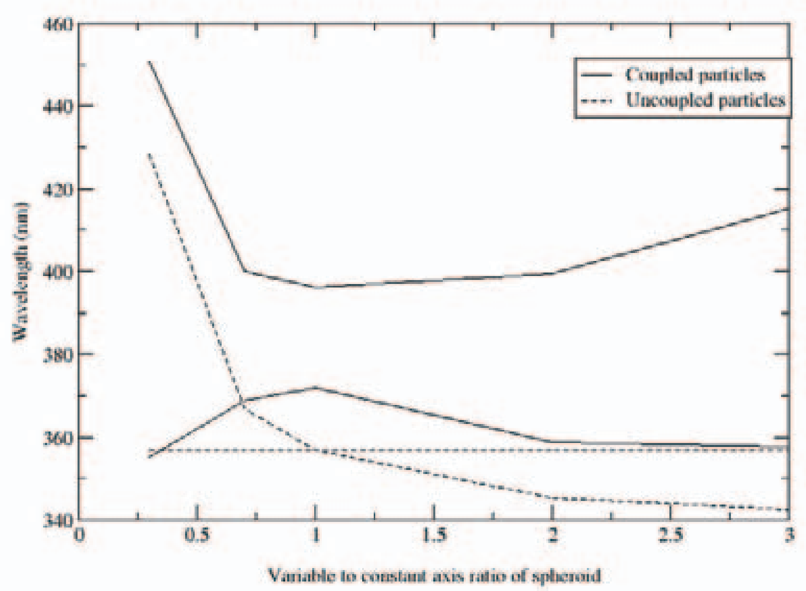

Figure 10: The wavelengths of the plasmon resonances versus the variable-to-constant axis of the configuration seen in Figure 9a. The dashed line represents the extinction for the uncoupled sphere and spheroid.

section of particles, which explains the lack of shifting. However, the electric field was applied along the particles rather than through the chain of the particles. The multiple plasmon resonances were plotted against the variable-to-constant axis ratio in Figure 10. The top and bottom line indicate the different parts of the sphere. The top line comes from the spheroid and is comparable to Figure 6a. Once the wavelengths are less than 30 nm apart, the coupling effect is so strong that it changes the course of the resonances.

Figure 11b shows a much larger shift and a greater intensity in the red-shifted peaks. This is consistent with the results obtained in the single sphere experiment because, as shown in Figure 11a, the electric field runs along the variable axis of the sphere. Figure 12 shows the resonances versus the variable-to-constant axis ratio. Because of the strength of the resonances, the coupling effect does not affect the spectra until the particles are about 10 nm apart. Based on these results, this arrangement was moved closer together and tested again. Figure 13 shows the extinction spectra for this arrangement. Because the particles are so close together, the interaction between the two is much greater. This pushes the plasmon resonances apart into more distinct peaks. Figure 14 shows the plasmon resonances versus the variable-to-constant axis ratio with the particles 1 nm apart. The particle plasmon resonances are almost 40 nm apart when coupling takes effect.

Three Spheroids
Figure 15 shows the extinction spectra of three spheroids with the electric field perpendicular to the chain of particles (see Figure 3). Except for the 3:1 spheroid,

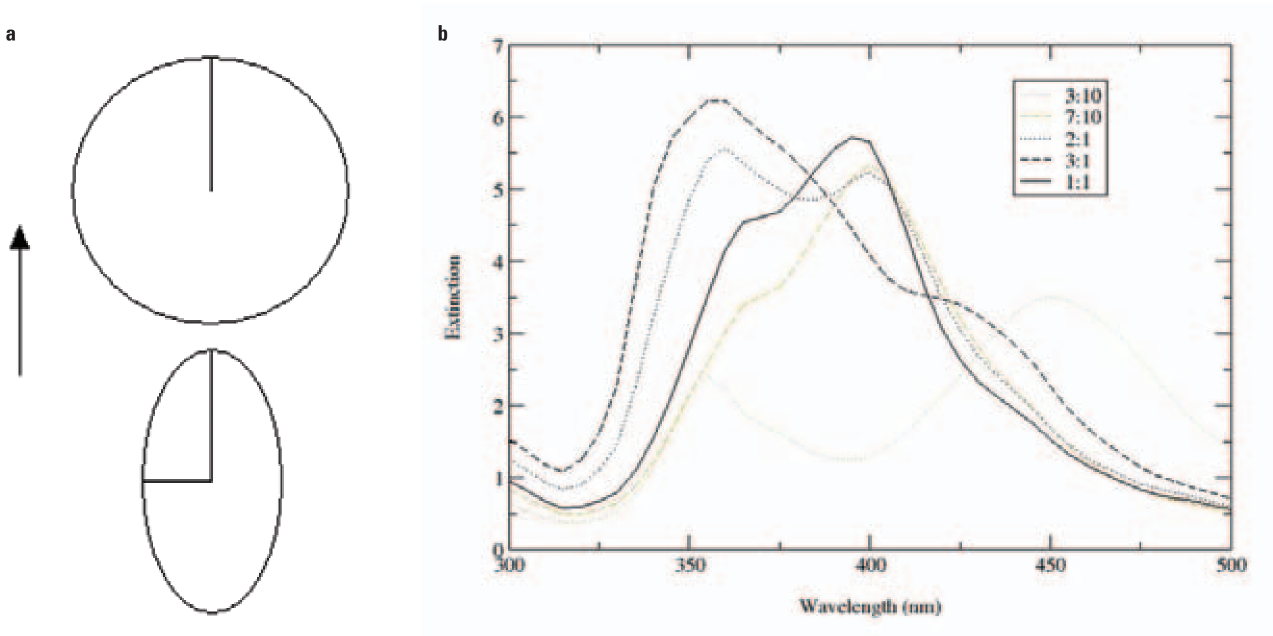

Figure 9: a shows the configuration of particles that lead to the extinction spectra in b. The solid line in the center is the control sphere. The legend is the variable-to-constant axis of the spheroid.

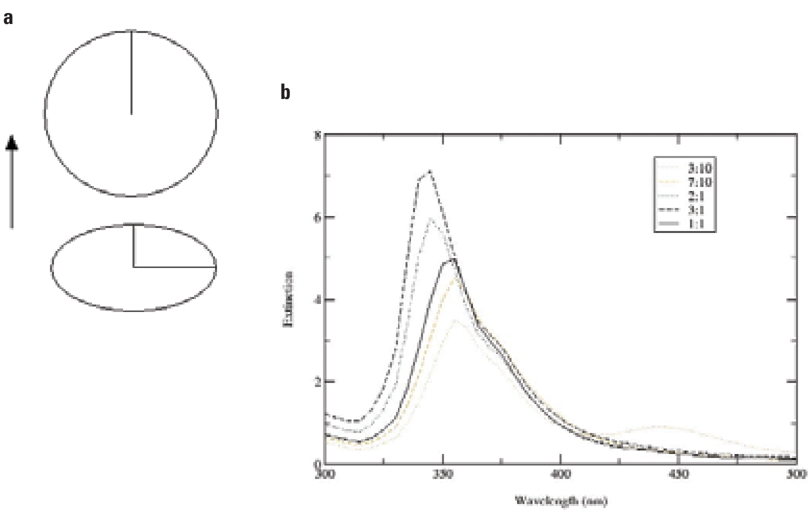

Figure 11: a shows the configuration of particles that lead to the extinction spectra in b. The solid line in the center is the control sphere. The legend is the variable-to-constant axis of the spheroid.

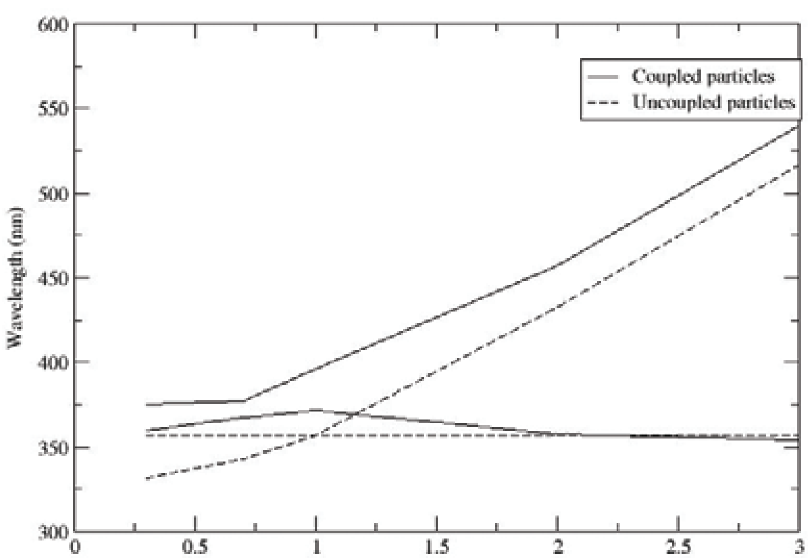

Figure 12: The wavelengths of the plasmon resonances versus the variable-to-constant axis of the configuration seen in Figure 11a.

the anticipated red shift is not visible at all, and even then it is a very small peak. Zooming in on any of the extinction lines will show that there are many negligibly small plasmon resonances. These resonances are not significant enough to have an effect on the overall system; however, they do show the beginnings of the desired effect. Due to the lack of red shift, these particles were either too small, too far apart, or too few in number to produce the desired effect. To test this hypothesis, one experiment was run where the spheroids of 30 nm radius were moved closer together. In another test, the particles were kept 2 nm apart, but the radii were increased.

Figure 16 shows the extinction spectra for the three particles when the distance was changed from 2 nm to 1 nm. The peak is not as distinct but is more red-shifted. This larger red shift is consistent with the results obtained when the two particles were moved 1 nm apart. The red shift, however, is still not an intense enough peak to affect the system very much, so the results did not match the hypothesis. It would not be useful to see if the particles would produce a more intense peak with the particles any closer together, since this would be difficult to apply.

Finally, the three particles were enlarged to have minor axes radii that were 12 nm and a major axis radius of 36 nm. DDA is not very practical for large particles, so this was the largest particle that could be tested. Figure 17 shows the results. The red-shifted peak is, as anticipated, more intense than the smaller particles. This indicates the presence of the desired wavelengths that are unable to be seen with these small particles. This effect may be seen if the particle number was increased at this size. However, DDA is impractical

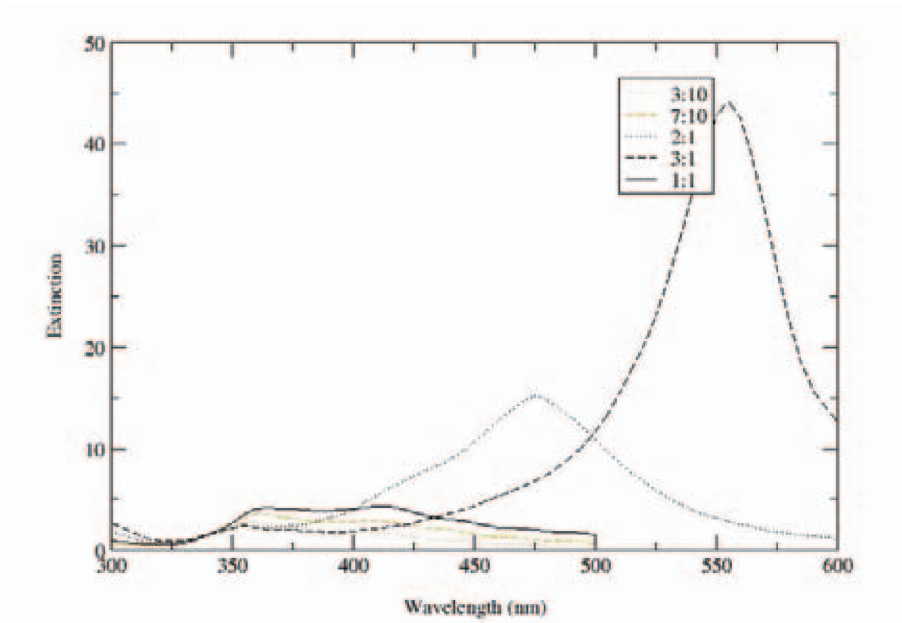

Figure 13: Extinction spectra for Figure 11a with 1 nm between particles. The legend represents the variable-to-constant axis ratio of the particles.

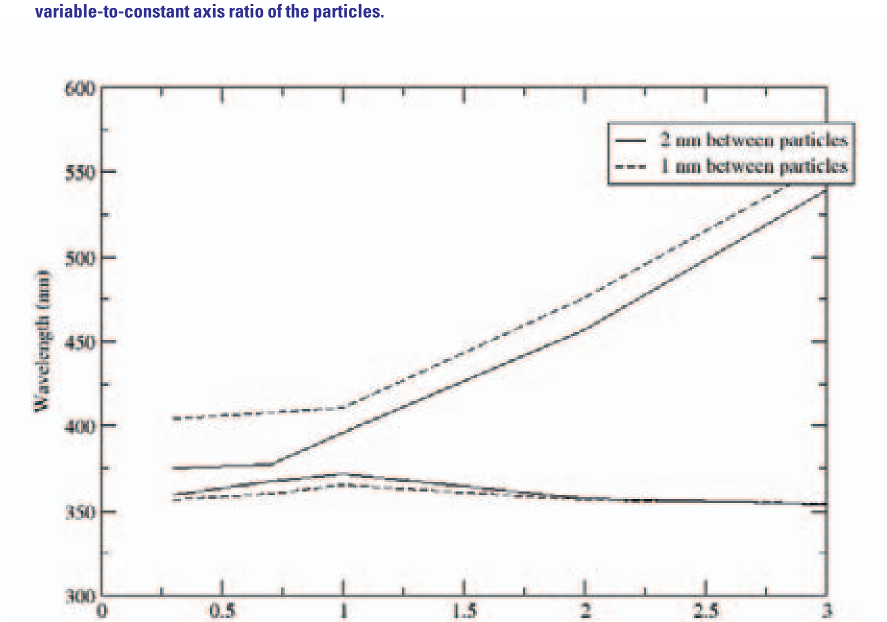

Figure 14: The wavelengths of the plasmon resonances versus the variable-to-constant axis of the configuration seen in Figure 11a with the particles both 1 and 2 nm apart.

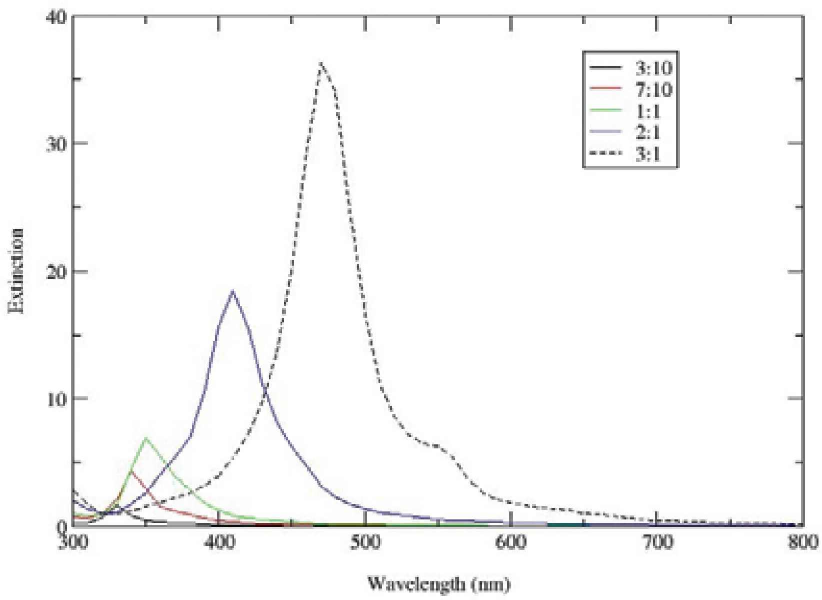

Figure 15: Extinction spectra of three spheroids shown in Figure 3.

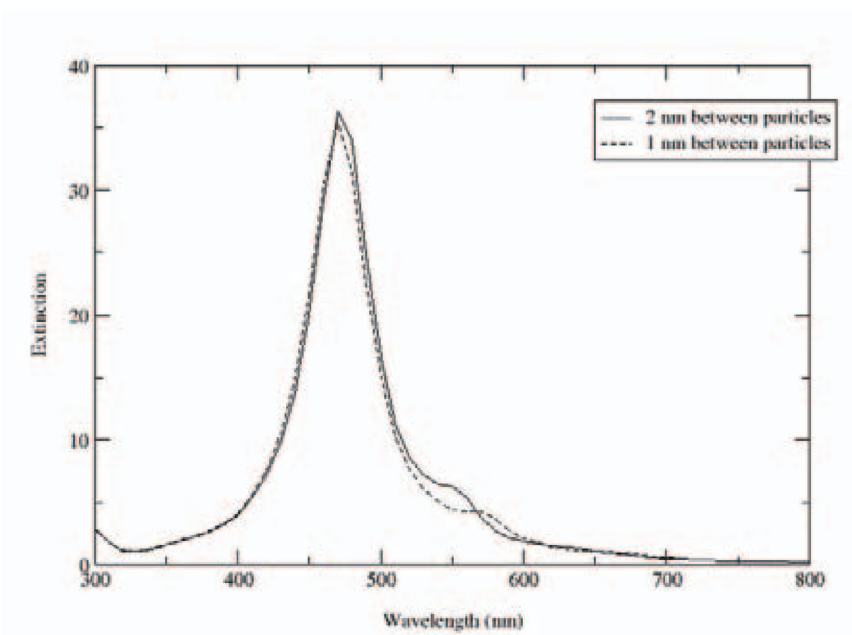

Figure 16: Extinction spectra for spheroids with constant axes radii of 10 nm and variable axis radius of 30 nm.

for a greater number of particles.

Conclusions

This research indicates that small clusters of particles show interactions that are often the same as large arrays of particles. It also shows that very small chains of nanoparticles will not always be large enough to produce the same effects of similar chains of larger size. The optical properties of these nanoparticles are already being applied in the biological and chemical worlds. The more that is understood about these particles and their optical properties, the sooner better sensors can be built. If we can learn where the largest electric fields are given off, where the induced polarizations occur, and what particles will create the best electric fields, then we will have a good chance of making useful sensors.

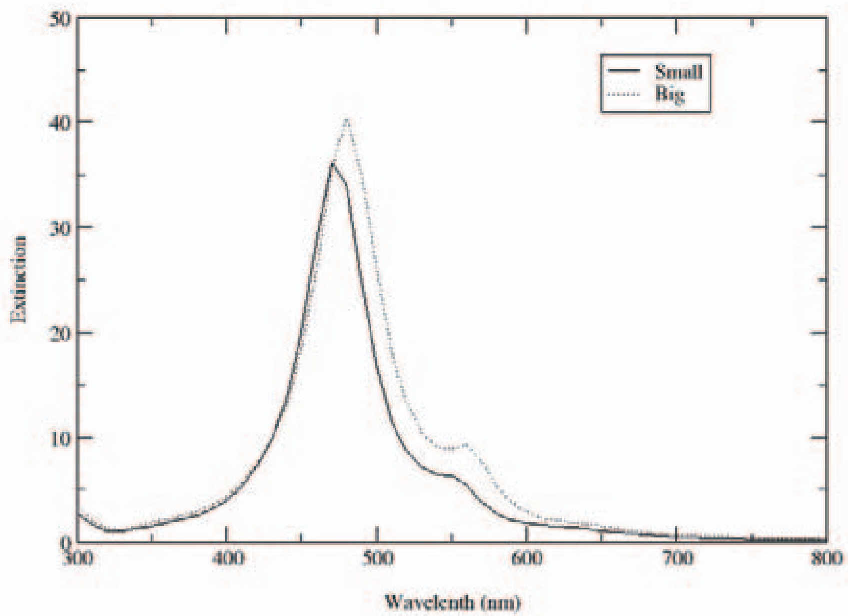

Figure 17: Extinction spectra for three spheroids as seen in Figure 3. The small particle has radii of 10 nm, 10 nm and 30 nm. The big particle has dimensions of 12 nm, 12 nm and 36 nm.

References

(1) The English chemist and physicist Michael Faraday, b. Sept. 22, 1791, d. Aug. 25, 1867, is known for his pioneering experiments in electricity and magnetism. Many consider him the greatest experimentalist who ever lived. Several concepts that he derived directly from experiments, such as lines of magnetic force, have become common ideas in modern physics.

(2) Mulvany, P. *The Beauty and Elegance of Nanocrystals*; University of Melbourne: Melbourne, 2003.

(3) Kelly, K. L.; Coronado, E.; Schatz, G. C., et al. *J. Phys. Chem.* **2003**, *107*, 668.

(4) Lazairides, A. A.; Schatz, G. C. *J. Phys. Chem. B* **2000**, *104*, 460.

(5) Laor, U.; Schatz, G. C. *Chem. Phys. Lett.* **1981**, *82*, 566.

(6) Drain, B. T.; Flatau, P. J. *J. Opt. Soc. Am. A* **1994**, *11*, 1491.