Phy293: Frontiers in Contemporary Experimental Physics

[2nd Year Undergraduates]

Absorption & Scattering/ Emission Spectra of Gold Nanoparticles

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Background Information from: Caroline Scacca & Colin Boyle
FDTD Modeling by: Erich See

Equipment used:
White light fiber lamp, Ocean Optics Spectrometers with Associated Software, Different Morphologies of Au nanoparticles in Cuvettes, lenses, iris apertures

Objectives:
1) Measure the absorption spectrum of gold nanospheres.

2) Look for plasmon enhanced scattering or emission from gold nanospheres.

3) Record the absorption spectra of gold nanorods as a function of dimensions.

References for You for More Information:

1) "A unified view of propagating and localized surface plasmon resonance biosensors," A. Haes and R.P. Van Duyne, Anal. Bioanal. Chem. **379**, 920-930 (2004).

2) "Au nanoparticles target cancer," Nanotoday, **2**, 18-29 (2007).

3) *Surface-enhanced Raman scattering physics and applications*, K. Kneipp, M. Moskovits, and H. Kneipp (Eds.), Springer Verlag, Berlin (2006).

4) *Plasmonics: Fundamentals and Applications,* Stefan A. Maier, Springer, University of Bath, **183**, 65-80 (2007).

Nanotechnology

Nanotechnology is the engineering of devices that are nanometers in size. To put this in perspective, human cells are micrometers across, over 1000 times larger than the smallest machines being built today, and a nanometer is 10^3 smaller than the diameter of your hair (~70 microns). Some of the best examples of the impact that nanotechnology has already had on daily life are mist sunscreens, which use nanoparticles to better deflect UV rays from the sun, stain resistant pants, which use nano-fibers to help water bead up and run off the fabric, and the incorporation of nanoparticles into automobile paints, golf clubs and tennis racquets. While these examples may sound mundane, they are proof that cutting edge technology can impact our everyday life. Another important focus of nanotechnology is its use in biomedical applications. Research is currently being conducted in using nanomaterials to detect and treat cancer, to help in genetics research, and as sensors of bacteria and toxins that may cause illnesses [1, 2, 3]. The development of these biosensors, as well as many other nanoscience and technology studies, requires

expertise in physics, chemistry, and biology to fully understand the various processes involved such as in the sensing of target molecules.

Nanotechnology and Biosensors

One type of nanosensor utilizes nanowires and gold (Au) nanoparticles in a biosensor complex which has the ability to detect and identify a single virus and thus act as a pathogen detector. This method uses photoinduced electrical currents in the nanowires along with antibody receptors attached to Au nanoparticles (Figure 1). The medical implication of this is to be able to contain and destroy viruses at an early stage. These nanowire sensors have received attention for application outside of the hospital medical range.

Biosensors are becoming a common practice in dental clinics to test for oral cancer. These sensors can test the saliva for cancers associated with increases in levels of RNA compositions. Current research is being conducted to expand cancer sensors to the entire body [7]. Biosensor research is being conducted to uncover a stable accurate way of cellular implantation, so that monitoring becomes an everyday real time system [1] Biosensors are essentially nanotaggers that detect auto produced markers and bind with them. Biosensors bind to proteins, DNA, and RNA by a lock and key mechanism. The nanotaggers then have a unique resonance that exposes the bacteria or virus for human identification [5,7]. Similar sensors are also under development for environmental toxins both in the air and water.

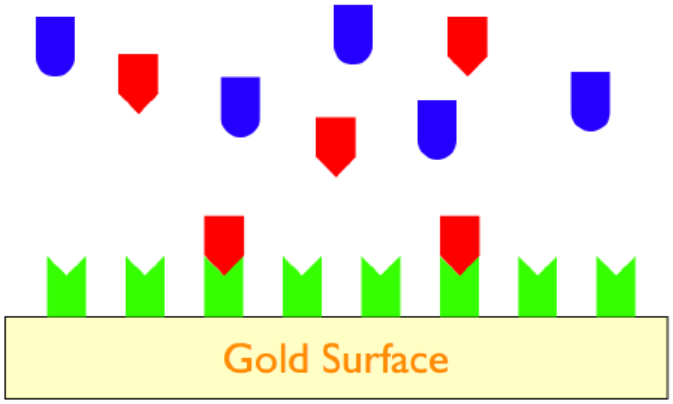

Figure 1: **Biosensor general mechanism** [Nick Geitner, MS Physics 2011, Unpublished Thesis]

The schematic in Fig. 1 assumes you have already spread gold nanoparticles on semiconducting nanowires or nanosheets which are in a circuit that can measure photo-induced current. In other words, as light shines on the sensor a certain amount of charge carriers will be excited within the nanowires from the energy in the impinging photons. However, if we add Au nanoparticles to the sensor, then light of the correct wavelength will produce a surface-induced plasmon in the Au which in turn adds to the electric field on the nanowires and more charges will be excited. Next if the Au has a biochemical molecule attached to it (the green capture molecules), the resonant plasmon wavelength shifts from the bare particles; the final step occurs when the toxin or other molecule of

interest (red particles) are caught by the green molecules in a lock-and-key chemical selection. Figure 1 shows that only red toxin molecules will be caught by the green molecules, while the blue molecules will not chemically bind to the sites. The addition of yet another molecule, the target, to the Au functionalized with the green capture molecules once again shifts the Au plasmon enhancement to a third wavelength and thus the biosensor can be devised with the correct laser wavelength to produce a highly enhanced photocurrent once a toxin is caught. So, the sensor produces a low signal when it is "empty" and a high signal when it has captured a number of toxin molecules.

Looking a little deeper into this Au *plasmon enhanced resonance*, we need to learn more about Au NPs. Gold is an interesting material because it has a property called surface plasmon resonance. Normally, gold is a highly reflective material; however on small scales and under the right conditions, it becomes a very good absorber of light. When the Au NPs absorb light, the electrons near the surface resonate with the light (remember Au is a metal which means it has many free electrons in the conduction band). An exciting light causes the electrons in the Au NPs to "slosh" back and forth in the direction of the light's electric field oscillation (due to the Au's polarization). When electrons accelerate, they create an electric field which is emitted mostly in the direction of the polarization of the exciting field, thus amplifying the input light. If the exciting light is resonant with the Au nanospheres, this amplification can be as much as a factor of 1000 times. The electric field amplification is known as surface plasmon resonance (which we will be trying to measure). It is important to enhance the photoexcited current in a nanowire sensor, because the normal current in the nanowire would otherwise be very small and hard to detect. With a plasmon resonant field, the signal in the biosensor is much more easily detected.

Every gold nanoparticle has a particular resonant wavelength based on its size and shape. When light at this resonant wavelength is incident on the nanoparticle, there will be much higher enhancement of the incident field. This can reach 100 or even over 1000 times enhancement. Fig. 2 is an illustration of this situation. The effect is modeled using Maxwell's equations for a polarizable material.

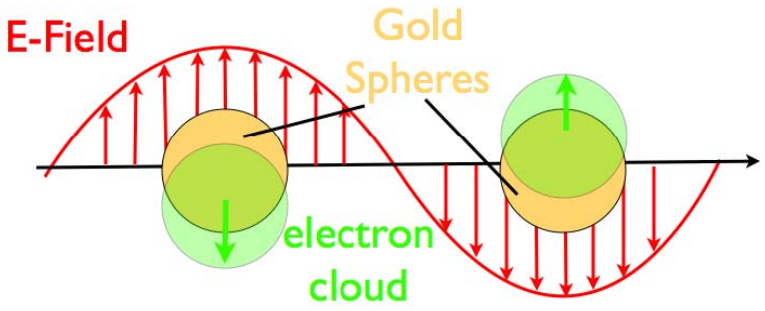

Figure 2: Motion of electron cloud in a gold nanosphere as it feels the force from the incident electric field. [Nick Geitner, MS Physics 2011, Unpublished Thesis]

So, selecting Au nanoparticles of the correct size and shape (morphology) allows you to design a sensor for specific toxins and with particular wavelength responses. Remember, when target molecules are captured, the photoexcited current in the nanowire

will be increased substantially indicating the capture of the toxin or pathogen of interest. This is the basis of an Au NP enhanced nanowire biosensor. In addition, with the correct choice of capture molecule, biosensors can detect many different target molecules from environmental hazards to cancerous cells or other molecules in the blood or body.

Emission and Absorption Spectra, and Light Scattering

Two basic types of spectra exist: emission and absorption. **Emission spectra** are formed when the light emitted from an excited material propagates through a spectrometer. The resulting spectra are a series of lines which relate to the difference in energy between the energy levels of the material. For instance, the Balmer series in Hydrogen was formed by the emitted light from electrons as they made the transition from upper energy levels dropping to the n=2 level of the atom. **Absorption spectra** are formed when white light is sent through a material and the transmitted light is measured by the spectrometer. The spectra in this case will consist of a broad spectrum from the white light source with dips in the spectrum where the light was absorbed by the electrons of the material in their ground, or lower energy, states as they jump to upper levels removing energy from the input light. A third mechanism can occur when light encounters particles (the old why is the sky blue at midday and red at night). This mechanism is **scattering**. In this laboratory experiment, we will measure the absorption spectrum of gold nanoparticles and then observe the **either the scattered or emitted spectra**. Which is it? See the next few sections!

Mie Theory: For spherical particles [following the work of Maier from Ref. 4 at top of lab]

Mie Theory is able to predict absorption and scattering characteristics of very small particles suspended in solution. We will use this theory to calculate the size of our gold nanoparticles based on their spectra. For particles with $R \ll \lambda$, Mie theory is used to calculate the extinction cross section of the material, C_{ext}, which is related to the light lost after the initial light beam is introduced to the material. In other words, this is an "effective area" of the material, which causes absorption and scattering.

So let's begin. Mie theory is central to this lab, and a bit more detail on where it comes from may be helpful. We begin with the familiar equation relating the electric field, $\vec{E}$, to the electric potential, Φ, and Laplace's equation for a charge free region.

$$\vec{E} = -\vec{\nabla}\Phi \tag{1}$$

$$\nabla^2\Phi = 0 \tag{2}$$

In this case with spherical symmetry, the solutions to Laplace's equations can be written as a superposition of Legendre polynomials.

$$\Phi(r,\theta) = \sum_l (A_l r^l + B_l r^{-(l+1)}) P_l(\cos\theta) \tag{3}$$

Here the variable r represents the distance out from the origin (center of sphere). We will split the problem into two regions, the volume inside the sphere Φ_{in}, and the volume outside the sphere, Φ_{out} (Figure 3).

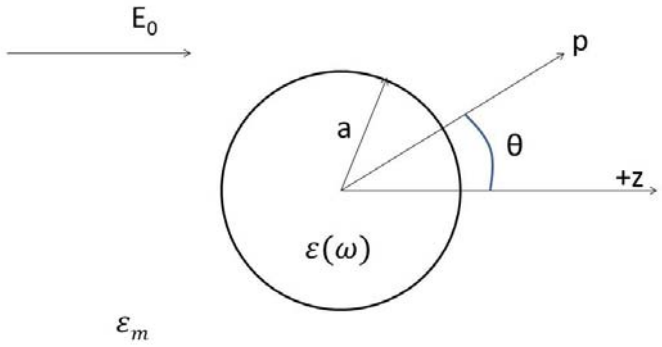

Figure 3: A diagram of the spherical system being analyzed with Mie theory with applied field, Eo, propagating along z, radius of sphere is now designated by a, and the two dielectric constants refer to that inside the nanosphere and that of the medium in which the sphere resides respectively.

Applying boundary conditions that the field is not infinite at the origin, and reduces to the applied field at infinity, we are left with

$$\Phi_{in} = -\frac{3\epsilon_m}{\epsilon + 2\epsilon_m} E_0 r \cos\theta \tag{4}$$

And

$$\Phi_{out} = -E_0 r \cos\theta + \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} E_0 a^3 \frac{\cos\theta}{r^2} \tag{5}$$

Now we can define a polarization for the nanosphere

$$\vec{p} = \epsilon_0 \epsilon_m \alpha \vec{E}_0 \tag{6}$$

Where α is the polarizability

$$\alpha = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \tag{7}$$

We are now prepared to write the electric field inside and outside the sphere

$$\vec{E}_{in} = \frac{2\epsilon_m}{\epsilon + 2\epsilon_m} \vec{E}_0 \tag{8}$$

And

$$\vec{E}_{out} = \vec{E}_0 \frac{3\hat{n}(\hat{n} \cdot \vec{p}) - \vec{p}}{4\pi\epsilon_0 \epsilon_m r^3} \tag{9}$$

Since ε is wavelength dependent, there exists a resonance condition for both the

polarizability and the interior electric field. This condition is commonly known as the Frölich condition.

$$Re[\epsilon(\omega)] = -2\epsilon_m \tag{10}$$

By allowing the applied electric field to change with time via

$$\vec{E}(r,t) = E_0 e^{-i\omega t}\hat{z} \tag{11}$$

It is clear that the particle will interact with the electric field absorbing or scattering the light. We can write absorption and scattering cross sections, describing how the strongly the particle will absorb or scatter. The sum of absorption and scattering is known as extinction, given by the following equation.

$$C_{ext} = \frac{24\pi^2 a^3 \epsilon_m^{\frac{3}{2}}}{\lambda} \frac{\epsilon_i}{(\epsilon_r + 2\epsilon_m)^2 + \epsilon_i^2} \tag{12}$$

Note that the extinction coefficient is wavelength dependent and possesses a resonance satisfying the Frölich condition. Also, keep in mind that the variable a, is the radius of the nanosphere, R, for ease of comparison with other equations in the lab experiment. The necessary values for the dielectric constants, both real and imaginary, are found in Fig. 4.

Dielectric Constant for Au

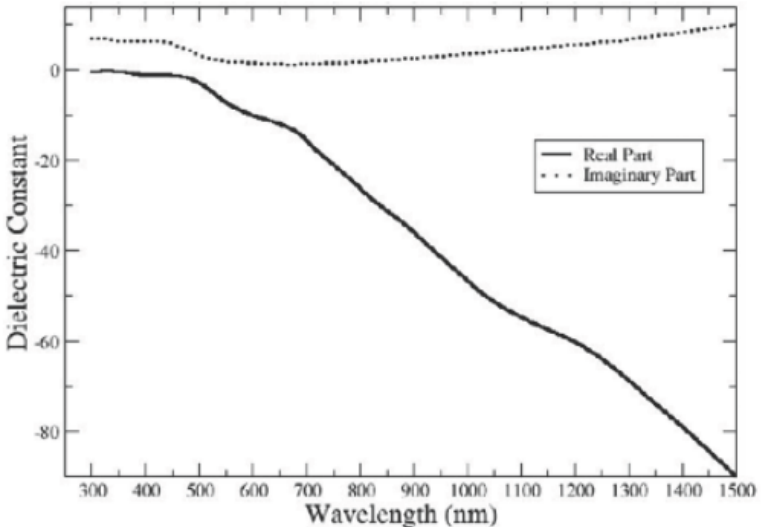

Figure 4: The wavelength dependence of the real and imaginary parts of the dielectric constant of gold [5]

In Eq. 12, C_{ext} is defined as the extinction cross section of the material. This is an "effective area" of the material, which causes absorption and scattering. More specifically, it is the area that, when multiplied by the intensity of incident electromagnetic waves, gives the power of light available to be absorbed and scattered.

The intensity of incident light is a power per area, and has units $\frac{W}{m^2}$ while C_{ext} has units m^2. In Eq. 1, λ is the peak wavelength of the spectrum, ε_m is the dielectric constant of the medium in which the particles are residing - in this case, water (80.36 at room temperature). Also, ε_r is the real and ε_i the imaginary part of the dielectric constant of our material, Au, which is wavelength dependent. The maximum extinction occurs at a wavelength where the real and imaginary portions of the dielectric constant of the gold nanosphere are most highly polarized, or when $\left|\varepsilon + 2\varepsilon_m\right|$ is a minimum.

When we consider nanoparticles which are not spherically symmetric, then the polarizability takes a new form. The expression for the polarizability for a generic, non-symmetric Au nanoparticle is found below with A and B being functions of the morphology of the less symmetric nanoparticle. Note that the polarizability is still dependent on the dielectric constant of Au (both real and imaginary).

$$\alpha \approx \frac{V}{\left(L + \frac{\varepsilon_m}{\varepsilon - \varepsilon_m}\right) + A\varepsilon_m x^2 + B\varepsilon_m^2 x^4 - i\frac{4\pi^2\varepsilon_m^{3/2}}{3}\frac{V}{\lambda_0^3}} \qquad (13)$$

Thus, the Mie theory above while strictly for Au nanospheres, can be modified to include particles of different morphologies.

While analytical solutions to Mie theory become more and more complex, then physicists look to other methods of predicting the behavior of light's interaction with variously-shaped, asymmetrical nanoparticles. In this case, computational physics allows us to find solutions to Maxwell's equations for the electromagnetic field in and surrounding different morphologies of nanoparticles.

How is this enhanced electric field reflected in the solutions for different Au nanoparticles?

The solutions to Eq. 8, 12 & 13 all show that the electric field is enhanced due to the wavelength dependency of the dielectric constant for simple nanoparticles morphologies. However, using a computational method known as a Finite Difference Time Domain (FDTD) calculation, it is possible to determine the magnitude and position of the enhanced electric field around any arbitrary Au nanoparticle's shape. FDTD refers to changing the differential equations back into their Δ-forms like you first saw in pre-calculus. Then with some input conditions, the equations are solved in small time steps for each position in the calculational grid. The new solutions for these tiny time steps are then used as the next input into the Δ-equations, and so forth until the output reaches a steady state. This is then reported as the solution to the differential equations.

In Fig. 5-7, the enhanced electric field around a Au nanosphere, a Au nanotriangle, and a blunted Au nanotriangle are shown from FDTD calculations performed by Erich See using a software program called Optiwave.

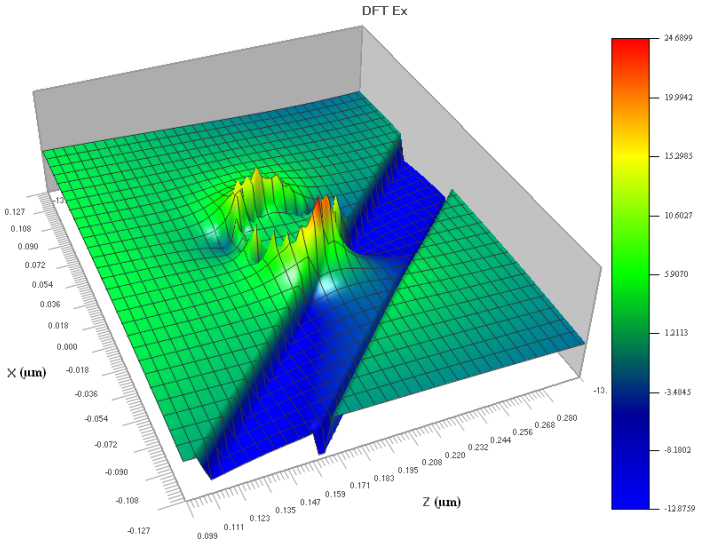

Figure 5: Electric field of 50 nm Au nanosphere sitting on a 50 nm thick CdS nanosheet. The incoming light (554 nm) propagates along z, and is polarized along x. The resulting Au resonant enhancement is shown in the vertical direction with topographical color scheme of dark blue being the least intense light to red the most intense. [Erich See, MS Physics 2010, Unpublished Thesis]

The peak intensity of the nanosphere is seen just at the edge of the nanosheet; it is 18 times brighter than the incident light, but it quickly falls off once it enters the CdS. The enhanced field dies off quickly at the top of the nanosheet as well for the symmetric Au nanosphere.

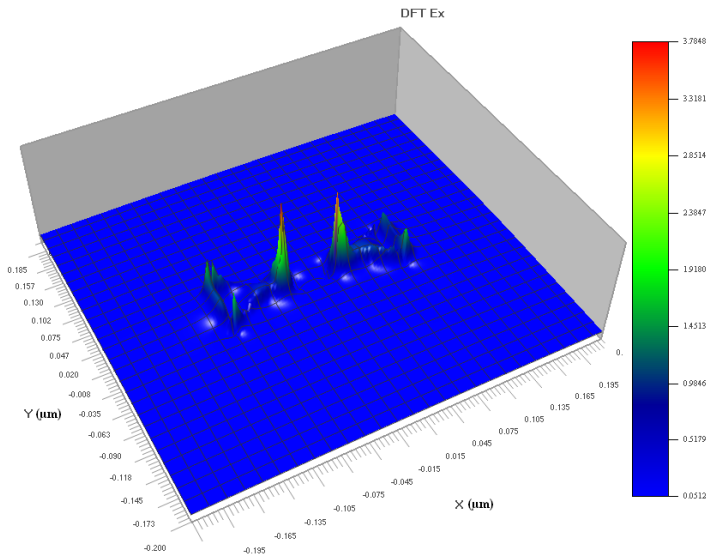

Figure 6: FDTD calculation of the electric field enhancement of 2 Au triangles placed tip to tip (50 nm separation) illuminated with 678 nm light. The intensity is again shown topographically. Here the electric field is that one would find 5 nm into the CdS nanosheet. [Erich See, MS Physics 2010, Unpublished Thesis]

In the case of the triangle dimer, the size of the graph was increased and so it is harder to see the enhanced coloring around each triangle compared to the sphere. The nanotriangles are each 75nm in height and 50nm across their bases. Yet, it is clear that the enhanced electric field is located wherever the tips of the triangles are, with the highest electric field (28 times the input) found at the sharpest tips where the triangles face one another. The enhancement also continues through the full thickness of the nanosheet and it spreads out to cover a large area as it propagates inward.

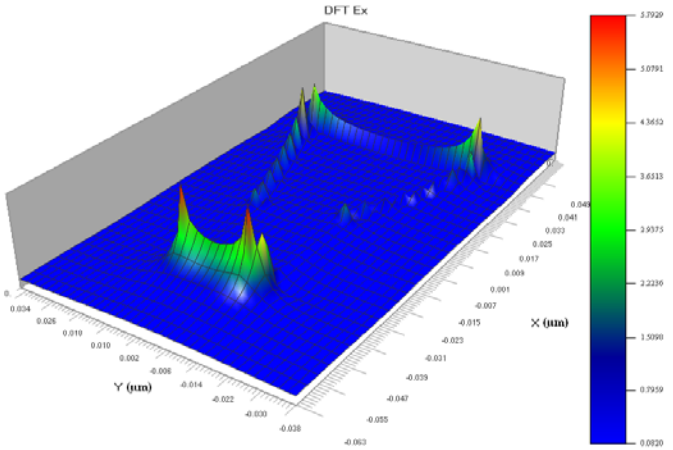

Figure 7: Enhancement of the electric field for a triangle with a blocked tip (20nm across) with all other dimensions the same as above, but at a wavelength of 606 nm. [Erich See, MS Physics 2010, Unpublished Thesis]

Here we see the effect of blunting off the point of a traingular shaped Au nanoparticle. While the electric field is still enhanced at each corner, the magnitude of the enhancement has dropped to 2.5 at the brightest spots.

So, what lessons have the FDTD figures provided to us? The rounder the nanoparticle, the _____ and the lower the penetration values; while the sharper the tip, the _____. What else do you note about the resonant wavlengths of light in terms of the nanoparticle's morphology?

Your Experiment:

You will find the optical setup on an "optical breadboard" where optical components can be tied down using ¼-20 screws and Al ties. A whitelight source passes through some lenses, a neutral density filter (which decreases the intensity of the incoming light), and then the cuvette with the Au nanospheres in it. The breadboard is setup so that you can measure the light exiting the cuvette along the incoming path, which will tell us the particles' extinction, and so that you can measure the light coming out the cuvette at 90 degrees from the incoming light.

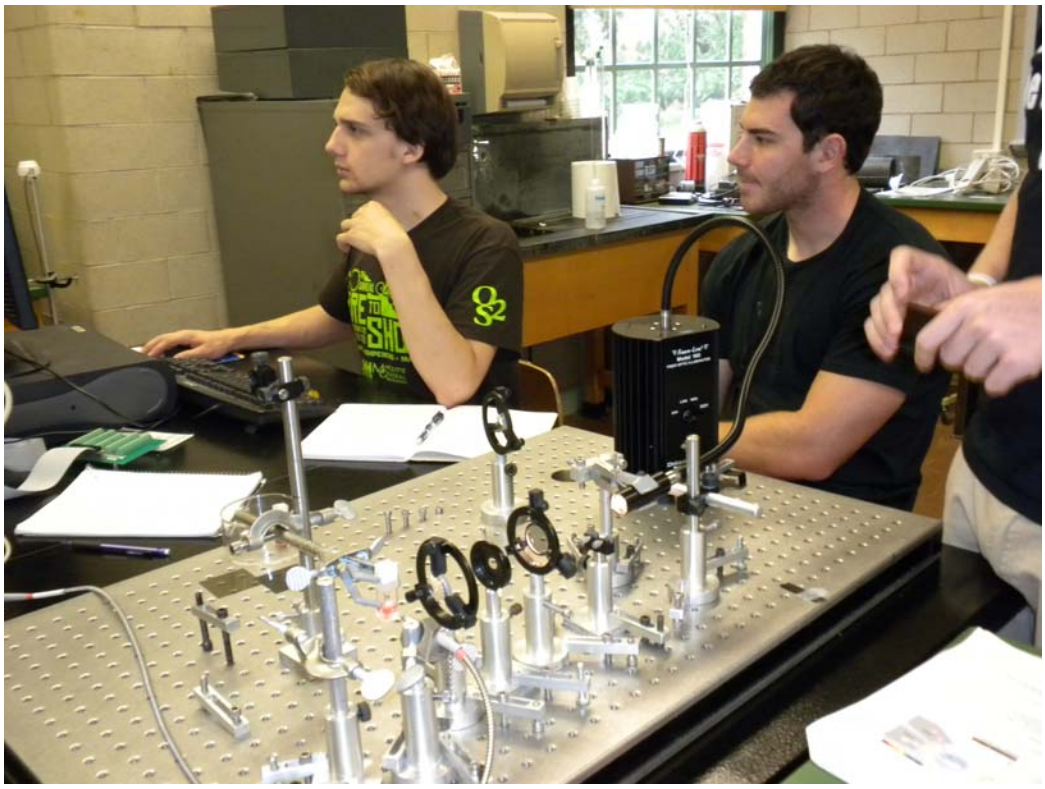

Figure 8: Optical setup for studying Au nanoparticles: white light source at left propagates to cuvette with red liquid (Au nanospheres) in it and the fiber (now set up to the side) collects the spectrum.

From the information in the FDTD modeled figures above, you can choose a spectrometer that should be able to measure the absorption of the white light across its spectrum. If you choose the wrong spectrometer, just change it out. Remember, with complete unknowns, go with a broader wavelength spectrometer to start out with and then focus in to specific ranges of interest.

These next two types of measurements are the first steps one would take for designing a biosensor using Au NPs. We will be considering the bare Au NPs herein. First, an absorption spectrum must be recorded, then the scattering/emission spectra is needed. In Part B, absorption spectra of Au nanorods will be recorded as a function of nanorod dimension to test them for use in a biosensor.

(A) You have 2 cuvettes with Au nanospheres in them. Each cuvette has bare gold nanoparticles of different diameter and you will want to follow the directions below to determine the radius of the nanospheres in the sample. A data sheet on all your nanoparticles will be provided to assist you. A spectral shift between samples is related to the nanospheres' size.

(B) The other 3 cuvettes have Au nanorods of different sizes in them. The student in Fig. 8 is placing a new sample into the setup. A nanorod is just what it sounds like, a cylindrically shaped particle with a slightly rounded tip. You will take the absorption spectra for these 3 samples and see if they have the same general characteristics that you predict (before measuring).

Figure 9: Students adjust a cuvette holding a new sample of Au nanoparticles.

For Your Experiment and Report:

Your experiment:

(1) Each of you should make a prediction on a) the direction of the wavelength shift for the variously sized Au nanospheres - think about finite square wells and how the energy levels change with size of the well, as the same thinking applies here.

(2) Consider (and describe) what lessons the FDTD figures provide to us? (in terms of size, morphology, and peak wavelengths, etc)

(3) Draw the initial experimental diagram for recording both types of spectra. This may need to be adjusted later.

(4) With your group, decide on the steps you should use to find each type of spectra given the spectrometers which are available – you need to think of wavelength/energy

range, resolution and calibration here. Did you consider other light sources? How many measurements (and of what) are necessary to provide the information required to determine the extinction spectra and the scattered/emitted spectra?

(5) Record any additional measurements or adjustments you made after completing your first readings for the different spectra.

(6) Record the transmitted spectrum of two Au nanospheres (NSs) first. Take note of how the spectra change with general size of the NSs (from the TEM micrographs you are provided).

(7) Predict what happens when nanoparticles (NPs) are functionalized rather than bare, and then using your knowledge of the shape of the nanorods compared to nanospheres predict the general shape of the spectra you expect to record for NRs, and finally c) how the spectra will change for different sized nanorods.

(8) Then record the scattered/emitted spectrum for the Au nanospheres. Finally move on to the transmitted spectra of the Au nanorods.

Calculations and Analysis from the Recorded Data:

1) We can use the words "extinction spectrum" and "absorption spectrum" interchangeably. In fact, the spectra you calculate from the transmission spectra are actually extinction spectra (as they include both absorbed light and light which is scattered away from the throughput beam), however from a practical standpoint we can call the spectra, absorption spectra, as you have already found out how little light is actually scattered from the NPs.

2) Use Excel to import the standard spectra and the transmitted spectra and then calculate the extinction spectra. Graph the spectra.

3) Using the extinction spectrum for a particular Au NS and the Mie theory [hint: graphs & discussion above], see if you can determine the size of the Au NSs. To what degree of confidence have you determined this? Why?

4) Describe any experimental adjustments you had to make as you conducted your experiment and the reasons behind them.

5) Graph the spectra of 3 sizes of Au nanorods. Did the spectra look like your predictions? What differs between them?

Theoretical Treatment of Light Interacting with Media

1) See the Attached Description of how Maxwell's equations can provide insight into the propagation and interaction of light a) in free space, b) in a dielectric medium, and c) in a conducting medium like the Au nanoparticles. Follow the directions to develop the theory in each case. This provides another way to understand how the electric field of a

Au particle can enhance the incoming light and thus make a biosensor work better, i.e. be more sensitive. (Part 1 required, Parts 2&3 for Extra Credit)

2) For the purposes of this experiment, $C_{ext} = -\frac{Abs}{L*I*n}$ where Abs is the intensity of light absorbed at the wavelength in question, L is the absorption path length, I is the incident light intensity at the peak wavelength, and n is the number of gold nanospheres per unit volume present in your solution.

Use this expression for C_{ext} and any other values from your experiment that you need. Substitute these into Eqn. 1 along with values for ε for the peak absorption λ. Calculate R of your different nanosphere samples and comparison with the actual values. To what degree of confidence have you determined these values? Why?

Conclusions

1) Discuss your 5 spectra with regard to plasmon resonance energies and nanoparticles morphology.

2) ***Recap on NanoBioSensors:*** If you were going to continue from here and make more measurements to design a biosensor, you would have to measure the absorption and scattering/emission spectra of the Au nanoparticles both with and without the capture molecules attached. The two spectra you would take would be first with the Au nanospheres functionalized with a capture molecule called streptavidin, and then with functionalized Au nanoparticles with biotin added. Biotin is easily captured by streptavidin. This is analgous to the behaviour of the biosensor. However, these molecules make good test compounds as they are not biohazards (!). The last move would be to design the nanodevice specifically for the actual chemicals, toxins, etc you want your biosensor to be measuring.

So, how might you use the information from your experiments to design the most efficient biosensor? What if you only had particular wavelengths of diode lasers available, how could you use what you have learned to take advantage of this "limitation?"

3) What other conclusions can you draw from these measurements?

Acknowledgements

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Filling Cuvettes with Nanoparticles

You Have:

- Cuvettes with plastic lids
- Glass pipets with bulbs to attach to upper end
- Small containers of several different Au nanoparticle shapes and sizes
- Gloves
- A machined plastic holder which can hold up to 6 cuvettes at a time
- Markers to label the lids of the cuvettes to keep track of which contains which sample

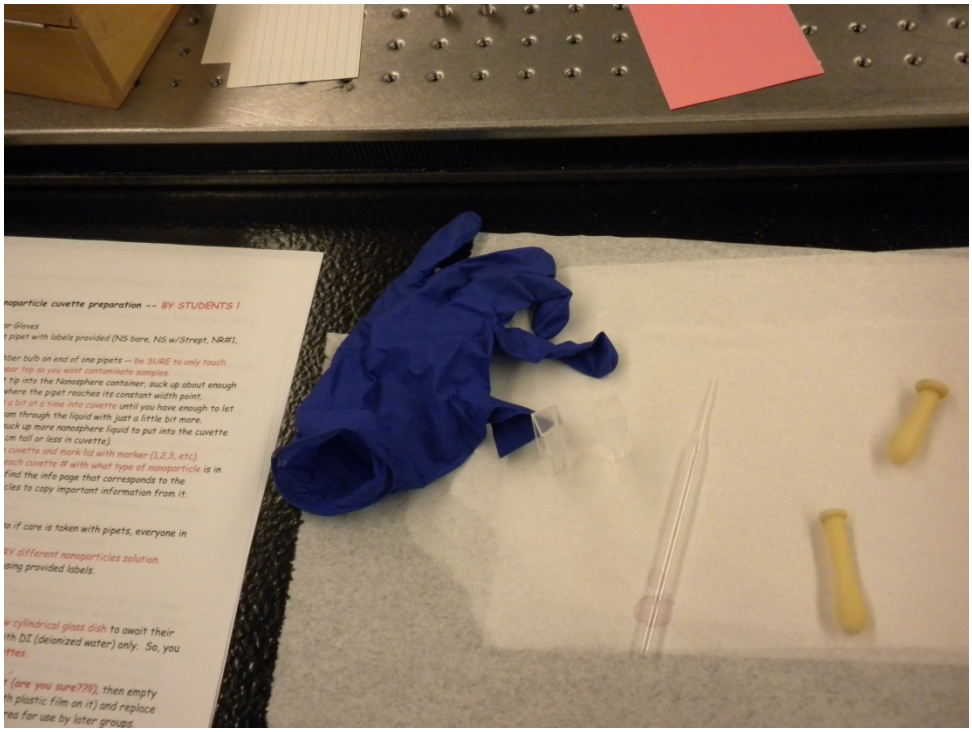

Figure 1: Picture of sample preparation materials

For safety, put on the latex gloves provided (*let someone else do this job if you have a latex allergy***).**

Steps of Sample Preparation:

1. Put on latex gloves – gloves are used to provide an extra layer of protection in case of spills. Scientists do not yet know the health risks involved with nanoparticles, but we will use the accepted risk equation:

RISK = TOXICITY x EXPOSURE TIME

Luckily, Au is the gold standard of health safety trials and you may have eaten gold in super expensive foods or drinks, and thus should have little toxicity. However, the Au in this experiment is very tiny (nanometers). So since we do not know what the ultimate toxicity may be, we reduce the risk with reduced exposure time. This means that if any nanoparticle liquid falls on your gloved hand, remove the glove immediately turning the outside inward and allow your instructor to dispose of it.

2. Each nanosample will be drawn from its glass container with its OWN pipet. Pipet bulbs can be interchanged, as very little liquid is needed for the samples.

3. Draw liquid into the pipet – just up to where the pipet begins to widen. Then release the nanoparticles (in water) into a cuvette. You only need sufficient liquid to fill the cuvette in the bottom sample area (where it changes width, or approximately 0.5 cm high). Re-fill the pipet with more liquid if necessary.

4. Remove the bulb and place the used pipet down on the absorbing paper next to the original sample bottle and then put a lid on the cuvette. Mark the cuvette lid with a code (numbers

1,2,… or A,B,…) that you keep track of for when you take the spectrum of each.

5. Wipe any liquid from the outside of the cuvette and then place into the machined sample holder until you need that sample to take data from it.

6. Keep track of which code goes with which sample spec sheet from the manufacturer for use in your data analysis later.

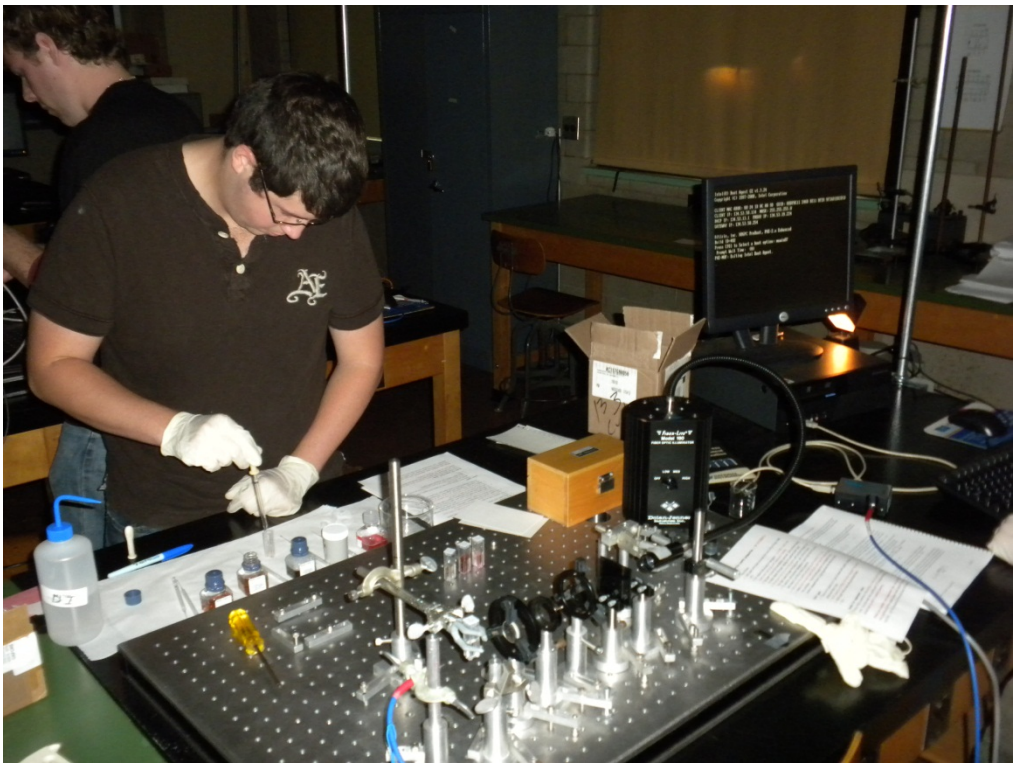

Figure 2: Student filling a cuvette in the lab.

7. Remember to make a cuvette sample with deionized water in it for your comparison standard in the experiment.

8. Finally, remove gloves and continue with the experiment.

Traveling Wave Solutions to Maxwell's Equations

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1. Recall Maxwell's equations in differential form:

$$\nabla \cdot \vec{E} = \frac{\rho}{\epsilon_0} \tag{1}$$

$$\nabla \cdot \vec{B} = 0 \tag{2}$$

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{3}$$

$$\nabla \times \vec{B} = \mu_0 \vec{J} + \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t} \tag{4}$$

Where

$$\epsilon_0 = 8.854 \times 10^{-12} \frac{F}{m} \tag{5}$$

$$\mu_0 = 1.257 \times 10^{-6} \frac{mkg}{s^2 A^2} \tag{6}$$

Using these equations, we will use separation of variables to find a differential equation in $\vec{E}$ in free space and show that one solution is a wave. First we take the cross product of both sides of equation (3).

$$\nabla \times (\nabla \times \vec{E}) = \nabla \times \left(-\frac{\partial \vec{B}}{\partial t} \right) \tag{7}$$

Note that in the right hand side, the cross product of the partial derivative is the same as the partial derivative of the cross product, or

$$\nabla \times (\nabla \times \vec{E}) = -\frac{\partial}{\partial t}(\nabla \times \vec{B}) \tag{8}$$

We will now employ the following vector identity

$$\nabla \times \nabla \times \vec{G} = \nabla(\nabla \cdot \vec{G}) - \nabla^2 \vec{G} \tag{9}$$

to get

$$\nabla(\nabla \cdot \vec{E}) - \nabla^2 \vec{E} = -\frac{\partial}{\partial t}(\nabla \times \vec{B}) \tag{10}$$

Substituting in equations (1) and (4) we get

$$\nabla \left(\frac{\rho}{\epsilon_0}\right) - \nabla^2 \vec{E} = -\frac{\partial}{\partial t}\left(\mu_0 \vec{J} + \mu_0 \epsilon_0 \frac{\partial \vec{E}}{\partial t}\right) \tag{11}$$

However, since we are in free space, charge density, ρ, and current density, $\vec{J}$, are both 0, and we have

$$\nabla^2 \vec{E} = \mu_0 \epsilon_0 \frac{\partial^2 \vec{E}}{\partial t^2} \tag{12}$$

$$\left(\nabla^2 - \mu_0 \epsilon_0 \frac{\partial^2}{\partial t^2}\right) \vec{E} = 0 \tag{13}$$

You may now recognize this as a wave equation, but let's plug in a periodic solution to make sure it works. (11) is general, and would work in 3D, but let's restrict ourselves to 1D for this exercise. Let

$$\vec{E}(x,t) = sin(\omega t - kx) \tag{14}$$

Confirm that (12) is a solution to (11) and find the constraint on $\frac{\omega}{k}$, then substitute in the given values for ϵ_0 and μ_0. What are the units? Hopefully, it will be familiar!

2. Now we will consider a nonconducting, nonmagnetic dielectric medium. It is useful at this point to define the polarization,

$$\vec{P} = (\epsilon - \epsilon_0)\vec{E} \tag{15}$$

where ϵ is the permittivity of the dielectric medium. The electric displacement field, $\vec{D}$ is given by

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P} = \epsilon \vec{E} \tag{16}$$
$$\tag{17}$$

Let us also define a magnetizing field as follows

$$\vec{H} = \frac{1}{\mu_0}\vec{B} - \vec{M} \tag{18}$$

Where $\vec{M}$ is the magnetization of the material, in this case, since the material is nonmagnetic,

$$\vec{M} = 0 \tag{19}$$
$$\vec{H} = \frac{\vec{B}}{\mu_0} \tag{20}$$

We now have Maxwell's equations of the form

$$\nabla \cdot \vec{D} = 0 \tag{21}$$
$$\nabla \cdot \vec{B} = 0 \tag{22}$$
$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{23}$$
$$\nabla \times \vec{H} = \frac{\partial \vec{D}}{\partial t} \tag{24}$$

Following the same procedure as in (1), find a general solution to the resulting differential equation and show that it is a wave. What is the speed of the wave, v?. What is $\frac{c}{v}$ (the index of refraction) where

$$c = \frac{1}{\sqrt{\mu_0 \epsilon_0}} \tag{25}$$

3. Now consider a nonmagentic, conducting medium, like our gold nanoparticles. In this case, we have Maxwell's equations of the form

$$\nabla \cdot \vec{D} = \rho_f \tag{26}$$

$$\nabla \cdot \vec{B} = 0 \tag{27}$$

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \tag{28}$$

$$\nabla \times \vec{H} = \vec{J}_f + \frac{\partial \vec{D}}{\partial t} \tag{29}$$

Where ρ_f is the free charge and $\vec{J}_f$ is the free current density. Use the same process to develop a differential equation (it should look something like (11)). Without solving the differential equation, how can you tell that it is still a wave? What extra terms are now present that were not in problem 1? What do they represent?

Other Information for the Au Nanoparticle Photoabsorption Lab:

1) Gold nanospheres and nanorods can be purchased online from: www.Nanopartz.com or similar companies.

(a) Nanopartz allows you to purchase a "sample assortment" which provides you the capability to choose 5 different nanoparticle shapes and sizes. You can also tailor your selection to the spectrometer you have available for your lab.

(b) Nanopartz (and I would ask for this from other companies) provides a Certificate of Analysis for each gold nanoparticle sample you purchase. It contains (among other details) information on absorption peak wavelengths, sizes and dispersion of size, concentration of particles, and supernatant in which they are contained. It also has a spectrum and TEM images of particles from the same synthesis batch.

(c) I black out size and absorption peaks, as well as the spectrum and the size scale bar on the TEM, as students are to be measuring/calculating these characteristics as part of the experiment.

2) Hints to Remember about the Spectra:

(a) The # of peaks in a spectrum reflect the # of different axes of the nanoparticle geometry, e.g. nanospheres have a single peak, nanorods have 2 peaks one for the long axis and one for the cross-section.

(b) The position of the peaks shifts with particle size. The smaller the particle, the larger the energy of the spectral peak, and thus the shorter the wavelength.

(c) Because of the complex geometrical factors in the extinction coefficient, nanospheres of diameter X will not have spectral peaks at the same position as nanorods of diameter X and length Y. However, the relative positional shifts with size still follow the comment in (b).

3) Analysis of Spectra:

A simple spreadsheet can be used to import the data from your spectrometer as long as it is in TXT form. With one column for wavelength and another for intensity, you can use the spreadsheet to calculate the ratio of the transmitted spectra to the input spectra and then subtract that ratio from 1 for each wavelength.