

# SYNTHESIS AND ANALYSIS OF SILVER/GOLD NANOPARTICLES

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## Background

All physical and chemical properties are size dependent, and the properties of materials on the nanosize scale have important consequences in wide ranging fields. Exploiting nanoscale behavior will eventually lead scientists to develop devices that can selectively attack diseased cells, increase computer speed or improve chemical and biological sensors. The composition, size, shape and environment of nanosized particles strongly influence their ultimate utility. Chemical dyes were the first use of metal nanoparticles, dating back hundreds of years. Glass blowers used gold and silver colloids as the coloring agents in stained glass windows. Gold nanoparticles (having a size of 10 -15 nm) produce a red or purple hue while silver nanoparticles (with a size of 20 -30 nm) produce a yellow or brown hue. Another very important field leading the development of nanotechnology is catalysis where nanosized materials composed either of transition metals like platinum or metal oxides often facilitate chemical processes by increasing the rate of the reaction. By making catalyst particles very small, large surface areas are achieved with a small volume of material. In the field of medicine, biological and chemical sensors are made of nanoscale particles that are very sensitive to their local environment, making them ideal for detection of trace amounts of many substances, including bacteria, DNA and environmental toxins. The electronics industry is focused on using nanoparticles in data storage devices, which are dependent on the number of memory elements that can be packed into a given area. By making features that are very small, more information can be encoded into a given area increasing computer speed.

Nanotechnology is the general name of the sciences that are interested in the study of materials on the nanometer-sized scale for the purpose of developing practical applications. The prefix “nano” means one billionth of something, for example: 1 nanometer is  $1 \times 10^{-9}$  meter. A typical atom has a diameter of about one third of a nanometer while a human hair has the diameter of approximately 200,000 nanometers. Research in the nanotechnology field is just beginning, yet interesting science is already being done which will have significant impacts on our daily lives in the years to come.<sup>3,4</sup>

The nanoscale system we will be studying in lab is a silver colloid. A very similar procedure can be used for gold nanoparticles, but only silver will be described here. The colloid is made of nanoscale silver particles suspended in an aqueous solution. The particles are negatively charged and in the solution and they remain suspended due to the repulsion of the negative charges between the particles. If we add an electrolyte to our colloid solution, we can aggregate the colloidal particles into clusters and even form a monolayer of silver particles. This monolayer will sink to the bottom of the vial. As this occurs, the optical properties of the colloid are changing. We will use visible absorption

spectroscopy to measure the changes in the colloid by measuring the absorbed wavelengths (color change of the colloid) as the silver precipitates out of the solution.

### **Absorption Spectroscopy**

Absorption spectroscopy is an analytical technique used to determine the identities and quantities of substances. The technique is based upon the interaction of electromagnetic radiation with matter. Electrons in atoms or molecules can be raised, or “excited”, from one energy state to another by the absorption of electromagnetic radiation. The transition of an electron from one energy state to another is permitted only if the energy of the radiation is equal to the energy difference between the two states.

Electronic energy states vary from one atom or molecule to another; therefore, the radiation absorbed by one substance will usually differ from that absorbed by another substance. For example, a solution of silver nanoparticles strongly absorbs radiation near the wavelengths 400 nm and 300 nm due to the s-p (conduction band) and d-s (interband) transitions of electrons respectively. [Units of wavelength are typically used to identify radiation in the visible region of the electromagnetic spectrum. Wavelength is inversely proportional to energy.] Since the wavelengths of radiation absorbed by a chemical species are dependent upon the energy states within that species, an absorption spectrum can often be used to identify a substance.

An absorption spectrum is a plot of absorbance of electromagnetic radiation passing through a sample vs. wavelength (or energy). The range of electromagnetic radiation chosen to analyze a sample depends upon the energy required to cause transitions within the absorbing species. Colored solutions contain species that absorb in the visible region of the electromagnetic spectrum (350 nm – 750 nm); colorless solutions contain species that absorb outside the visible region.

### **Color**

Electromagnetic radiation looks white when all wavelengths of radiation from 350 nm to 750 nm are present. White light is composed of various hues of red, orange, yellow, green, blue, indigo, and violet light. When a species absorbs selected portions of the visible light spectrum, color results. For example, the solution of gold nanoparticles mentioned above is a red solution that strongly absorbs light at 520 nm (green light) and 450 nm (blue light). The red color of the solution is the result obtained when the green and blue components of white light are removed. The color of the solution, therefore, represents a composite of all colors transmitted (i.e., not absorbed) by the particles. It is often possible to determine the color (or wavelength) of light absorbed by a species based on the color of the solution and vice versa. In simple cases, where a solution absorbs light in only one region of the visible spectrum, the color of the solution is complementary to the color of light absorbed by the solution. Colors, complementary colors, and corresponding wavelengths are summarized in Table 1<sup>1</sup>.

### **Spectroscopy and Color of Colloidal Particles**

In the case of nanoscale metal particles, the absorption wavelength associated with the s-p transitions depends on the *shape* and *size* of the particle. This is a unique property of nanoparticles that is due to the fact that the s-p (conduction) electrons are largely free to move about throughout the nanoparticle, and their energies are therefore sensitive to the shape and size of the box that contains them. For colloidal silver particles, the shape and size dependence of the absorption wavelength is such that the color of the particles depends on their preparation, with larger particles and more asymmetric particles absorbing at longer wavelengths than smaller, more spherical, particles. The longer wavelengths correspond to lower frequencies, which means that the electrons in a bigger box oscillate with a lower frequency than those in a smaller box.

<b>Wavelength (nm)</b>	<b>Absorbed Color</b>	<b>Complementary Color</b>
650-780	red	blue-green
595-650	orange	greenish blue
560-595	yellow-green	purple
500-560	green	red-purple
490-500	bluish green	red
480-490	greenish blue	orange
435-480	blue	yellow
380-435	violet	yellow-green

**Table 1.** Absorbance and Complementary Color<sup>2</sup>

When nanoparticles aggregate, the wavelengths of light absorbed change. This occurs when we add an electrolyte to the colloid silver solution, as it leads to the formation of clusters of particles, or even a monolayer of particles on a surface. This sticking together of the particles changes their color in a similar way to the change of color associated with changing size or shape of the particles. Indeed, when two particles stick together, the absorption produced is very similar to that of a single rod-like particle having a length equal to the sum of the diameters of the two particles.

In addition to the wavelengths of energy absorbed and emitted by the nanoparticles, the light scattered by the colloid can also be studied. By shining white light (containing all wavelengths of energy) on the sample and detecting the light scattered from the sample at a 90° angle, the efficiency of absorption can be determined. This scattered light comes from an incomplete absorption at the s-p transition energy and therefore has a different color than the transmitted light observed as the color of the solution.

## Part 1 Synthesis of the silver colloid

### Procedure<sup>3,4</sup>

Pour 50 mL of 0.001 M stock solution of silver nitrate into a clean 250 mL beaker. Add a stirring rod. Heat the solution to a boil while stirring. Add DI water as necessary to maintain the 50 mL volume.

Measure out 5 mL of 0.0388 M sodium citrate solution. Pour the sodium citrate solution into the beaker. Note the changes in the colloid appearance after the addition of sodium citrate solution. Boil for 10 minutes. (Again, add DI water as necessary to maintain the 55 mL volume.) Remove from heat and continue stirring for 15 minutes.

How does the silver salt interact with the sodium citrate dihydrate?

Draw a diagram on the molecular level of what is happening as the colloid forms in solution.

## Part 2 Analysis of the silver colloid<sup>3,4</sup>

Collect five clean dry glass vials. Add 5 mL of the silver solution to each of the five vials. Add 10 drops of 1M NaCl, 1 M HCl, 1 M NaOH, and 1 M glucose to each vial respectively with stirring. Clearly label the vials. Compare the appearance of the silver colloid in each of the vials. Record any changes in the colloid between the vials.

Measure the pH of all five vials. How does the addition of an ionic substance change the pH of the colloid solution?

How does the appearance of the colloid change as you add different types of solutions (acids, bases, salts, sugar)?

Of the solutions that induced a change in the appearance of the colloid solution, what do they have in common?

Dilute 2 mL of the original silver colloid solution with 10 mL of DI water. Using the HP spectrophotometer record a UV-Vis spectrum from (300 to 800 nm) of the colloid solution (remember to first take a blank spectrum with DI water.) Then add 0.100 mL (~4 drops) of electrolyte solution, you can choose either the acid, base or salt. Be sure to mix the solution in the cuvette after the addition of the electrolyte. Record a spectrum after the addition of the electrolyte at a time interval of 5 minutes. Compare the maximum wavelength of both spectra, and propose a theory for what is happening to the colloid in the solution. Remember to record the absorbance value for each  $I_{\max}$  as well as any other changes you observe in both the solution and spectra.

## Scattering Analysis

Take a sample of the original silver colloid and shine a white light flashlight onto the sample by placing the flashlight on the bottom of the vial with the light shining up to the ceiling through the colloid solution. Using a white piece of paper at a 90° angle from the sample, determine the color of the light scattered by the sample. How does the

wavelength of this light correspond to the light being absorbed by or transmitted through the sample?

### **Interpretation of results**

The change of color of the silver colloid upon aggregation is one of the unique properties of nanoscale materials. Please answer the following questions based on your observations and on the information provided above.

1. Based on your experiments above, can you explain the color change of the initially prepared colloid in terms of your measured absorption spectrum?
2. Is the change in your absorption spectrum with electrolyte addition consistent with expectations based on the shape and size dependence of the s-p absorption features?
3. Can you imagine what our world would be like if the observed variation of color with size, shape and aggregation were true of macroscopic objects? In particular, if this concept applied to silver coins, how would the color of silver coins change when they are stacked on top of one another compared to individual coins? Hint: assume that the color chart given above applies.

### References:

<sup>1</sup> Hunsberger, Lynn Experiment 13 UV-Vis Absorption Spectroscopy General Chemistry Laboratory Manual 1999.

<sup>2</sup> Owen, Tony Fundamentals of Modern UV-Visible Spectroscopy, Hewlett-Packard, 1996;p.21

<sup>3</sup> J Chem. Ed. **76**, 7, **1999** 949-955

<sup>4</sup> Nanotechnology/Nanoscience Module Center for Nanotechnology Northwestern University 2002

# **NANOSPHERE OPTICS LAB: Application to Silver Nanoparticles**

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## **INTRODUCTION**

This addendum to ‘Synthesis and Analysis of Silver Nanoparticles,’ will use computational electrodynamics calculations, also available at nanohub.org, to predict the ultraviolet-visible spectrum (UV-Vis) of silver nanoparticles.

The tool you will be using is entitled “Nanosphere Optics Lab”, and it can be found on the list of ‘My tools’ on the ‘My nanohub’ webpage. The ‘Nanosphere Optics Lab’ is based on Mie theory, which was developed in 1908 by Gustav Mie. Mie theory describes the light-particle interaction for particles on the length scale of wavelength. For more information and references the ‘About this tool’ link can be clicked after opening the ‘Nanosphere Optics Lab.’

### **A. Mie Theory**

Understanding how light interacts with small particles is necessary for a description of a wide range of physical phenomenon. When light is incident on a particle the charges in the material are set in motion. This coupling of the light wave to the charged particles gives rise to absorption, via energy transfer to the surrounding medium, and scattering, via re-radiation of the light wave.

For objects whose dimensions are much larger than the wavelength of visible light ( $> 1 \mu\text{m}$ ) geometric optics will suffice. Geometric optics allows us to understand why shadows are formed, how lenses work, and many other intuitive phenomena. However, when the particle size is on the order of the wavelength of light or smaller a more complicated approach is necessary. For a solution to this problem we turn to electromagnetic theory in the form of the classical Maxwell's equations. In general, the exact solution of the Maxwell equations for an arbitrary particle is complex. However, we can gain insight into the light-particle interaction by examining the absorption and scattering due to spherical particles. The formal solution to this problem was first given by Gustav Mie in 1908 and is now known as Mie theory.

You will use these computational tools to aid the interpretation of your experimentally observed UV-Vis spectra.

## HOW TO USE ‘NANOSPHERE OPTICS LAB’

Once the ‘Nanosphere Optics Lab’ is open, the user can select the ‘Particle Composition’ from the pull-down menu. In this case, the ‘Particle Composition’ is silver, Ag. Next, the ‘Surrounding Medium Refractive Index’ should be set to display ‘1.33’ since that is the refractive index of water. The user should then enter a guess for the size of nanoparticle they believe they synthesized. The ‘Beginning Wavelength’ and ‘Ending Wavelength’ correspond to the wavelengths for the x-axis on the UV-Vis spectrum. Clicking on the ‘Simulate’ button will then start the calculation.

Immediately after the calculation begins the output file should appear as it is being written to the right of the input fields. After the calculation has completed, the predicted ‘Extinction Cross Section’ spectrum for the nanosphere size input is displayed. The ‘Extinction Cross Section’ spectrum takes into account scattered light in addition to absorbed light and thus is directly comparable with your measured UV-Vis spectrum. To obtain the lambda max simply place the pointer over the peak of interest. A box will appear containing the efficiency (y-axis value) and the wavelength. If you want to zoom in on a peak, click beside the peak and drag. While dragging, a box will appear showing you what section of the spectrum you will be zooming into. To go back to the full spectrum click on the button with a black square on it located to the right of the spectrum below the ‘Result’ pull-down menu.

You can continue to run numerous calculations by re-entering/ modifying any input data and re-clicking the ‘Simulate’ button. To view previously calculated spectrum use the ‘Simulation’ bar below the spectrum. In order to view all the spectra on the same graph, press the ‘All’ button located to the left of the ‘Simulation’ bar.

## DISCUSSION QUESTIONS

- 1.) How does the extinction maximum vary with (a) particle size and (b) refractive index of the surrounding medium?
- 2.) What value of the particle size gives the best agreement with your experimental spectrum of the silver colloid?
- 3.) Can you match both the width and  $\lambda_{max}$  of the experimental and theoretical spectrum? If not, propose a possible explanation.
- 4.) When you make the comparison between your UV-Vis spectrum and the theoretical calculation, you use the “Extinction Spectrum” which is the sum of scattering and absorption. Why is this more appropriate than simply the calculated absorption?