The Synthesis and Characterization of Gold and Silver Nanoparticles in Formal and Informal Settings

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Approval Page

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Abstract

Silver nanoparticles were synthesized through the reduction of $AgNO_3$ using $NaBH_4$. The borohydride anions were adsorbed onto silver nanoparticles. The repelling forces of the borohydride anions prevented the aggregation of particles, but the addition of an electrolyte or agitation induced aggregation. A yellow hue was given off by the silver nanoparticle sol that, using a spectrophotometer, had plasmon resonance at 386 nm. The silver nanoparticles were estimated to be 10 to 20 nm in diameter. Gold nanoparticles were synthesized through the reduction of $HAuCl_4$ using $Na_3C_6H_5O_7$. The gold nanoparticle sol gave off a red hue that had plasmon resonance at 515 nm. The gold nanoparticles were estimated to be 10 to 25 nm in diameter.

A gold nanoparticle sol was used in informal education demonstrations for pre-middle school children in an open setting, and for middle school children in an organized setting. The older children were much more receptive to the information. The ineffectiveness of the demonstrations for the younger children was attributed to the lack of hands-on interaction involved with the nanoparticle demonstrations. The nanoparticles were also demonstrated during a college-level materials laboratory. The activity allowed the students to synthesize the nanoparticles and alter the color through aggregation. Students attempted adding PVA to the nanoparticles to create 'stained glass' as a take-away. A list of questions was given to the students to prompt further thinking and evaluate the effectiveness of the activity. The quiz results showed a minimal increase in nanoparticle understanding, but it may have been a factor of an ineffective lab design and not asking the right questions in the quiz. The low cost and learning potential of the reduction of silver nitrate through sodium borohydride could lead to a future addition to current laboratories.

Keywords: materials engineering, nanoparticles, nanoscience, silver, gold, outreach, education, nucleation, reduction, NISEnet, informal, formal

Acknowledgments

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1. Introduction

Nanotechnology is the science of materials 1 to 100 nm in size. When metals reach the nanoscale – in the form of nanoparticles – their properties begin to differ from bulk materials. Even though both bulk materials and nanoparticles are made of the same atoms, it has been seen that even base color will change on the nanoscale. The study of the change in wavelength associated with metal nanoparticles is called nanoplasmonics. The benefits of nanoplasmonics are being explored throughout academia, but they are also effective tools for spreading nanotechnology awareness. The general public must understand the importance of nanoscience so it has a basis to flourish and expand.

1.1 Stakeholders

The stakeholders for this project include the California Polytechnic State University students gaining access to refined nanoparticle capabilities. Also, the most efficient methods for synthesizing silver and gold nanoparticles were defined for the capabilities of the Materials Engineering Department. Methods were determined for characterizing the size of nanoparticles down to 10 nm, and the characterization of nanoparticle size now supplement current nanotechnology projects, such as quantum dots.

Time and resources allocated to Materials Engineering are severely limited. Any exploration for expanding current laboratory curriculum based on student work is beneficial. Also, expanding the Materials Engineering outreach program will ultimately increase the amount of informal education available. The expansion of outreach may help increase the number of students entering Science, Technology, Engineering, and Mathematics (STEM) majors. STEM students are essential for balancing the nation's economy, as they are the future problem solvers. Furthermore, there are is a list of Grand Challenges that must be solved in the next century as determined by the National Academy of Engineering.[1] These challenges – such as making solar energy economical – are vital to the future of humanity. STEM students will be the ones solving these Grand Challenges, and so introducing students to STEM is a high priority.

The outreach programs also have an effect on young children and underrepresented students. Any ethnic group – such as African or Native American – whose representation in higher education is less than their proportion in the general population is considered underrepresented. Outreach efforts target these audiences that would not receive this education elsewhere.

Finally, the Nanoscale Informal Science Education (NISE) Network provided a $3000 mini-grant to be used partially for the purpose of developing nanoscience education in both outreach and a current Materials Engineering lab. NISEnet is a group of scientists and informal educators funded by the National Science Foundation. The goal of the organization is to increase nanoscience awareness in the general population, and NISEnet is led by fourteen museums and universities across the nation.[2]

1.2 Broader Impacts

Sometimes science and society do not communicate well. A politician may block a scientific field for his own reasons, or a scientific topic may become painted as something to fear. A prime example of this can be seen with genetically modified organisms (GMOs). The public did not completely understand GMOs, and their view was swayed by popular opinion. GMOs fell out of popularity and are still met with heavy resistance by some environmentalist groups.[3] The point is that it is equally important to

communicate scientific knowledge to society as it is to develop scientific knowledge. A sweeping, life-altering discovery can be made, but if the public is convinced otherwise, the technology will not be successful. Scientists have to protect the image of nanotechnology so that it has a chance to burgeon. Furthermore, nanotechnology in general benefits from this project. Nanoscience is not understood very well in the public. The K-12 curriculum does not include nanotechnology, and college classes are just starting to incorporate nanoscience information. Unfortunately, over 800 products claim to use nanotechnology, yet common public knowledge is lacking to back up or refute these claims.[4] Essentially, a company can say anything is nanotechnology, whether or not the product actually takes advantage of that nanotechnology. Improving the information being provided for the general populace, especially younger people, will benefit society as a whole.

Nanoscience demonstrations have the potential for sparking interest in young students. In 2007, only 233,000 students graduated with a STEM degree. That means that 15% of all bachelor degrees awarded in 2007 in the U.S. were in STEM. In China 47% of bachelor degrees were awarded in STEM, 38% in Korea, and 28% in Germany.[5] As a result, the Business-Higher Education Forum has set a goal to double STEM graduates by 2015.[5] Every bit of help that goes into this effort will ultimately lead to a better future for the U.S., because without STEM careers the nation will not be able to compete technologically on a global level.

1.3 Design Constraints of Project

1.3.1 Health and Safety

An important impact of nanoparticles, particularly in the area of outreach, is health and safety. The most common chemical that silver nanoparticles are reduced from is silver nitrate, which is corrosive. In one study, which was determining a process for silver nanoparticle synthesis specifically for educational use, sodium borohydride is used as the reducing agent.[6] These same nanoparticles have to be displayed to a wide range of ages. The nanoparticles can even be handled by students if the nanoparticles are converted to a 'glass' form using polyvinyl alcohol.[4] One method of avoiding safety issues is using low concentrations of reagents. In the sodium borohydride reduction, concentrations are as low as 1 mM for both reagents (silver nitrate and sodium borohydride). Even if the stock solution touches skin, damage will be minimal. Another safety procedure is to force anyone handling the chemicals to use gloves. The nanoparticles are theoretically harmless when released into the environment because they will aggregate into much larger pieces. This does not mean the chemicals can be flushed down the drain; regulations relating to the waste must be followed.

Waste was separated into two separate streams: gold and silver nanoparticle waste. The waste concentrated on the presence of toxic sodium borohydride. The gold nanoparticle waste was kept separate to prevent the reacting of any unused sodium borohydride from the silver nanoparticle synthesis, even though the molarity of the sodium borohydride was as low as 2 mM.

1.3.2 Manufacturability

Another major constraint of silver nanoparticle synthesis is manufacturability. As mentioned before, the synthesis process requires very low concentrations. As a result, fine weight and volume measurements are required. Furthermore, the reduction process is extremely sensitive to reagent ratios. In one reduction reaction, if the ratio of sodium borohydride to silver nitrate varies from 2 to 1, then the shelf life of the silver nanoparticles is reduced from weeks to hours.[6] Care must be given to every step of the reduction process to ensure that the silver does not aggregate. For example, 17 mg of silver nitrate is required to create a 1 mM solution in 100 mL of water. If someone walks through the room while this weight measurement is taking place, the vibrations from the walking could sway the measurement. Such a small thing has ruined a batch of silver nanoparticles. In addition, a lab activity requires multiple sets of glassware, stirring rods, and stir plates to be successful. All of these are difficult to acquire in sufficient quantities.

The colloid form of the nanoparticles poses difficulties for size and concentration characterization. Since it is a liquid, the colloid is not readily distributed onto surfaces for techniques such as X-ray diffraction (XRD) and atomic force microscopy (AFM).The small amount of nanoparticles present in the colloid solution also makes it difficult to locate anything under AFM, and does not affect XRD peaks enough for the calculation of particle size.

1.3.3 Costs

The final costs must fall within the allocated budget for testing and development. Only a portion of the $3000 mini-grant is going towards testing and development. Fortunately, the synthesis of nanoparticles does not call for large amounts of reagent. The gold salt used in the gold nanoparticle synthesis can be expensive though; the gold salt is roughly fifty times more expensive than the silver salt.

2. Background

Nanoparticles provide a cheap and effective way to teach nanoscience. Through the use of readily available chemicals, nanoparticles can be synthesized in simple reduction reactions. These nanoparticles enhance electric fields and change color entirely because of their nanosize.

2.1 Theory

The change in color that silver exhibits on the nanoscale is attributed to surface plasmon resonance. With a specific energy, an electron will be pushed away from the metal, creating negative and positive regions. The electron will naturally return to its original side, but during the process other electrons have also been moving. This phenomenon is defined as a particle: the surface plasmon. The energy at which the electrons begin to oscillate is specific, and any wavelength of light at that energy will be absorbed. This absorption results in a change in color far different than the original silver color of the base metal. For example, a 30 nm silver nanoparticle will absorb violet-blue light, and will appear yellow-green.[7] A common use of this property is in pregnancy tests. Human chorionic gonadotropin hormone (hCG) is produced in the early stages of pregnancy. The hormone will bind with antibodies

placed on the pregnancy strip, which are attached to gold nanoparticles. The process creates a dense monolayer of gold nanoparticles, which causes the particles to emit red light instead of the normal light-green.[7]

The surface plasmons in nanoparticles are unique in the fact that they are concentrated. When these localized surface plasmons resonate (LSPR), they can enhance a nearby electric fields by a massive 12 orders of magnitude.[7] One application of this electric field enhancement is in light emitting diodes (LEDs). The nanoparticles are placed near the anode and can increase the efficiency of the LED by a factor of thirty in some cases. Other applications of electric field enhancement are in biosensors, surface-enhance Raman spectroscopy, and solar cells.[8]

2.2 Particle Size Characterization

There are numerous methods used to determine the diameter of nanoparticles. Some methods are direct – like microscopy – and others use relationships, such as diffraction. Using a variety of characterization tools will yield stronger results.

2.2.1 Transmission Electron Microscopy

A transmission electron microscope (TEM) can be used in conjunction with a fine carbon-coated copper grid to estimate particle size[6,9] The silver nanoparticles are added to the copper grid using a dropper. A number of particles are randomly and each particle's size is estimated. The size distribution of the particles are then plotted to determine an average particle size of 10-14 nm (Figure 1).[6]

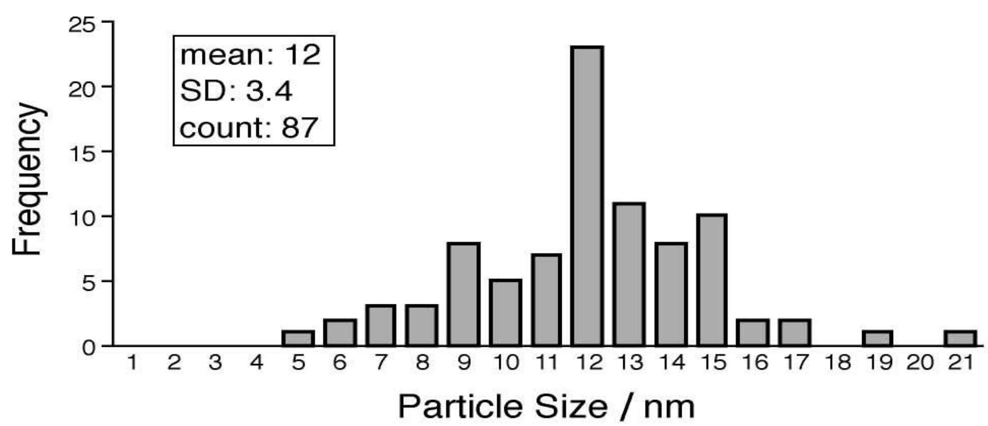


Figure 1: TEM-derived Ag nanoparticle size distribution.[6]

2.2.2 X-Ray Diffraction

Nanoparticle size can be estimated through the use of X-ray diffraction (XRD) using the Debye-Scherrer formula (Equation 1).[9]

$$d = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad [1]$$

d is the mean diameter of the nanoparticles, λ is the wavelength of the X-ray radiation source, β is the angular full width half max (FWHM) of the XRD peak at the diffraction angle θ. The Scherrer equation effectively estimates particle size from 10 – 100 nm. Anything greater than 0.1 μm will yield values that are far too low. The reason for this is that various factors can add width to a diffraction peak. Crystallite size is the biggest contributor, but inhomogeneous strain and instrumental effects can also add width to the diffraction peaks. If strain and instrumental effects are affecting the XRD peaks, then the Scherrer value will be lower than the actual size of the particles being tested.[11] XRD patterns of silver particles will yield four peaks from 20 to 80 2θ/degrees in accordance to its face-centered cubic structure (Figure 2).[9]

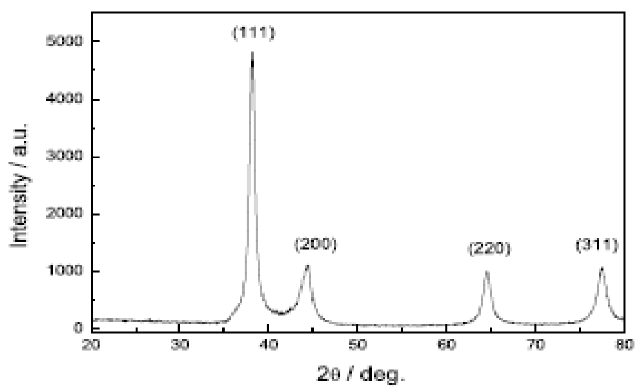


Figure 2: XRD pattern of silver nanoparticles synthesized by inert gas condensation.[9]

2.2.3 Atomic Force Microscopy

The silver sol must first be applied to an even surface to be used in atomic force microscopy (AFM). Usually a uniform silicon wafer is the preferred substrate. One method, coined the drop-on method by Bonsak, holds the silicon wafer at a 45° angle while the silver sol is poured on. The silver sol will run over the wafer relatively evenly, producing a thin film of silver nanoparticles.[10] AFM can then be performed on the silicon surface to find a mean particle size of the nanoparticles (Figure 3).

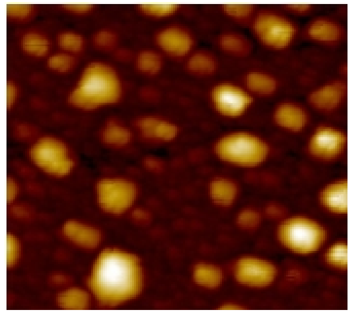


Figure 3: Two dimensional AFM image of a silicon wafer coated in Ag nanoparticles synthesized through the use of sodium borohydride.[10]

2.2.4 Dynamic Light Scattering

Dynamic light scattering is the method of measuring the level of aggregation in silver nanoparticles. Particles in a colloid solution follow Brownian motion as a result of continuing particle collisions and movement. Based on Brownian motion, smaller particles will move quicker. A laser that is shown through the colloid will disperse. The intensity of the dispersed light is dependent on the movement of the colloid particles, and so particle size can be determined using the Stokes-Einstein relationship (Equation 2).

$$D=\frac{k_B T}{6\pi\eta r} \qquad [2]$$

Where D is the diffusion constant, k_B is Boltzmann's constant, T is absolute temperature, η is the viscosity of the solvent, and r is the particle radius.[12]

2.3 Concentration and Optics

Samples of silver colloid can be placed in a spectrophotometer to measure optical densities. Assuming no aggregation, these densities are then used with the Beer-Lambert law to determine the concentration of silver nanoparticles (Equation 3).

$$A=\varepsilon lc \qquad [3]$$

Where A is absorbance, ε is molar absorptivity, l is path length, and c is concentration.[13]
The spectrophotometer can also be used to characterize the spectral response of the silver nanoparticles. The surface plasmon resonance wavelength will be seen as a peak in extinction spectral data (Figure 4).[13]

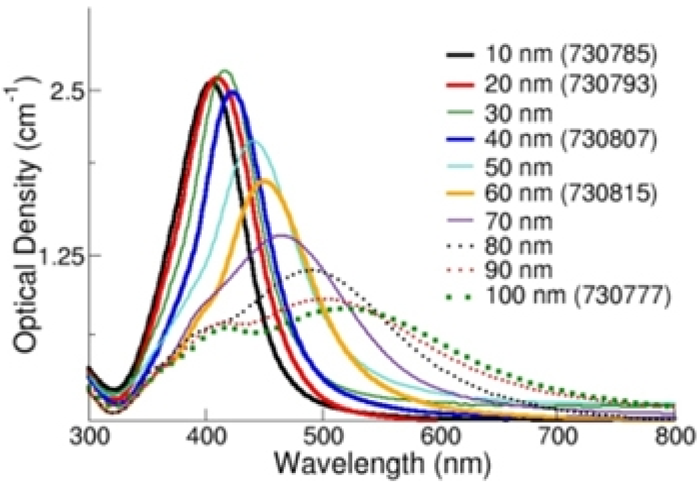
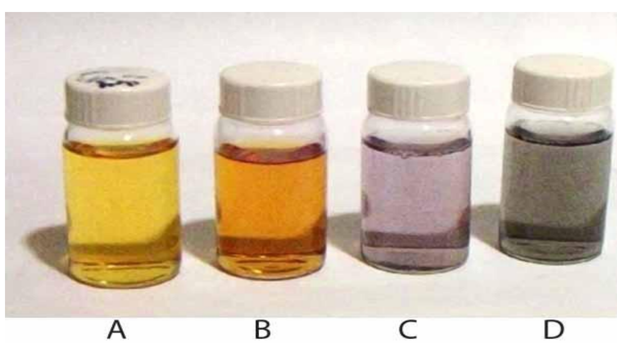


Figure 4: The extinction spectra of silver nanoparticles with diameters ranging from 10-100 nm[13]

2.4 Synthesis of Nanoparticles through Reduction

Silver nanoparticles can be synthesized through reduction using sodium borohydride. The sodium borohydride is put on ice, and silver nitrate is added by drops until the colloid stabilizes. Polyvinylpyrrolidone (PVP) can also be added to help prevent aggregation, but is not necessary for success. When creating silver nanoparticles using sodium borohydride, it was found that the optimal initial concentration of sodium borohydride to silver nitrate was 2 to 1. If the ratio was altered up or down, then the colloid would breakdown in less than an hour. Furthermore, the silver colloid becomes a stable yellow color after a certain amount of stirring, and the colloid could stay this color for weeks to months at a time (Figure 5A). If stirring was continued, the colloid would aggregate and tend towards a grayish color (Figure 5D).[6]



A B C D

Figure 5: Colloidal silver in various stages of aggregation due to stirring, (A) clear yellow sol, (B) dark yellow sol, (C) violet sol , and (D) grayish sol, as aggregation proceeds[6]

Synthesis of silver nanoparticles can also occur through reduction with ethanol. The reaction occurs at about 90 °C with ethanol, linoleic acid, sodium linoleate, and silver nitrate. The ethanol reduces the

silver nitrate into nanoparticles while the linoleic acid produced circular particles. The final product is dispersed in chloroform to create an even silver colloidal solution. The final color of the colloid comes out to be reddish brown.[14]

Yet another silver synthesis method is through the inert gas condensation (IGC) process. During IGC, silver is evaporated under vacuum in the presence of argon gas. Electric current is applied to the silver, and the silver gas exits the vacuum chamber once supersaturation conditions are reached. These silver particles are deposited onto a stainless steel flat surface by flowing liquid nitrogen across it. The IGC process is capable of producing a mean silver nanoparticle size of 16 nm.[9]

Similar to the reduction of silver nitrate in silver, gold nanoparticles can be reduced from hydrogen tetrachloroaurate using sodium citrate. In this reduction, the tetrachloroaurate in heated and stirred. Immediately upon boiling, the trisodium citrate is added, and this creates a deep red colored gold nanoparticle sol.[15]

2.5 Nanoscience Awareness

There are more than 800 products that claim to use nanotechnology. Unfortunately, nanoscience is absent from curricula before college, and even in college the information is very limited. The majority of nanoscience information comes from popular sources, which more often than not is incorrect. National efforts are being made to help provide nanotechnology information through organizations like the Nanoscale Informal Science Education Network and the National Center for Learning and Teaching in Nanoscale Science and Engineering.[4]

In some situations, audiences are not interesting in science. Other audiences who are interested in science feel that science is dry and unrelated to their lives. Therefore it is important to send a message that not only properly educates, but entertains. Each demonstration has to then be tailored to the audience; middle school aged children will be interested by different facets of a demonstration than a college student. Presented information must also be adjusted for the audience, because there is no use saying anything that your audience does not understand.[4]

Silver nanoparticles can be an effective way of portraying nanoscience in an informal or formal academic setting. In one study, a student who enjoyed the experiment stated, “I found it interesting that properties of matter can change on a nanolevel.”[6] There are three main concepts that silver nanoparticles can convey. The first is that nanoparticles of gold and silver act differently than bulk gold and silver, as the student noted above. The second concept is that science is not exclusive, and is connected to things like art. Finally, nanotechnology is not entirely new, and has been used unknowingly since the Middle Ages and even longer in nature.[4]

3. Methods and Materials

3.1 Synthesis of Nanoparticles

Silver Nanoparticles were synthesized through the reduction of silver nitrate using sodium borohydride. 18.9 mg of $NaBH_4$ was added to 250 mL of water to create a 2 mM solution and 17 mg of $AgNO_3$ was added to water to create a 1 mM solution. The sodium borohydride was chilled to roughly 0°C using ice and stirring (Figure 6). 10 mL of the 1 mM $AgNO_3$ was added to 30 mL of the stirred 2 mM $NaBH_4$ solution using a dropper, at about one drop per second until all 10 mL were added. Upon the complete addition of the AgNO3, stirring was stopped. The standard operating procedure for this reaction can be found in Appendix A.

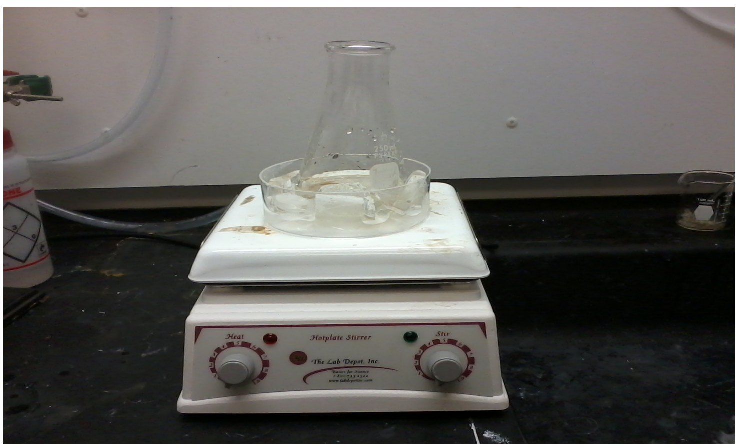


Figure 6: Chilling of $NaBH_4$ during silver nanoparticle synthesis on a stir plate.

Polyvinyl alcohol (PVA) was dissolved into the silver sol. The sol was first heated and stirred on a hotplate, and PVA was added slowly until a 4% solution was made. With the 40 mL silver solution, 1.5 g of PVA was added. The solution was stirred until most of the PVA was dissolved, and the solution was decanted into another container leaving trapped air and undissolved PVA behind.

Gold nanoparticles were synthesized by reducing hydrogen tetrachloroaurate using sodium citrate. 1.0 g of $HAuCl_4 \cdot 3H_2O$ was added to 250 mL of water to create a 1 mM solution. A 1% solution of $Na_3C_6H_5O_7 \cdot 2H_2O$ was created by adding 0.5 g to 50 mL of water. The tetrachloroaurate was heated and stirred until the water in solution started to boil. The trisodium citrate is then immediately added. Heat and stirring are stopped once a red hue is created.

3.2 Characterization

Sols of varying colors were placed into a holder and processed through an Ocean Optics USB4000 Fiber Optics Spectrometer. The spectrometer can only detect light in the ultraviolet and visible light range (UV/Vis). A light source transmitted white light through each sol, and the remaining light was sent through fiber optic cables to the spectrometer. Information was finally sent to a computer and processed using the Spectrasuite software package (Figure 7).

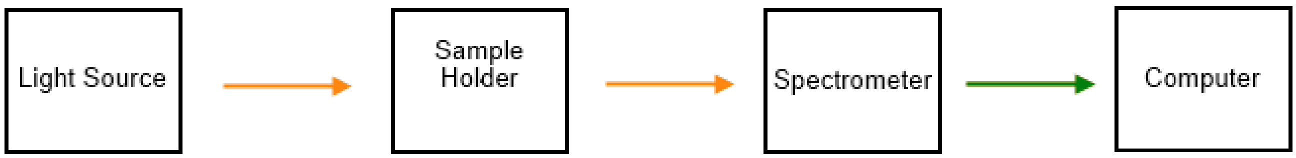


Figure 7: Schematic representation of spectrometer set-up. Orange arrows indicate fiber optic cable connections, and the green arrow indicates a USB connection between the spectrometer and computer.

The fiber optic cables consisted of 0.75 m UV/Vis multi-mode optical fibers. Each fiber has a fused silica core with a diameter of 200 μm and a fluorine/silica cladding with a diameter of 250 μm. A protective tubing surrounded the optical fiber to prevent scratching or breaking. An SMA-SMA bulkhead adapter, which could be inserted into to the spectrometer to deliver the light, was attached to each end of the optical fibers with epoxy.

Absorbance data was collected over an integrated time of 30 ms, taken 30 times, and averaged. Spectrometry was performed for as-processed and purposely aggregated colloids for both silver and gold. The first color tested was that found immediately upon completion of synthesis – yellow for silver and red for gold. Further spectrometry was done for the same solutions, but with the addition of 0.5 g NaCl to prompt the aggregation of nanoparticles. The aggregated silver sol tested was a gray-violet, while the aggregated gold sol was a deep purple.

3.3 Nanoparticle Educational Activities

NISE nanogold demonstrations were given to boys and girls of varying ages. The demonstration included two bottles of nanoparticles – with particles 80 and 20 nanometers in diameter – and stained glass pieces. A bright white light was shown through the 80 nm nanoparticle solution against a white piece of paper to show a change in color in transmittance (Figure 8). The goal of the demonstration was to show the differences in properties because of the size of the gold.

A lab was adapted from the silver synthesis process – described earlier - for second year college students in the Materials Engineering Department at California Polytechnic State University of San Luis Obispo. Students slowly the $AgNO_3$ to 30 mL of chilled and stirred $NaBH_4$. Upon the complete addition of silver nitrate, students separated 5 mL of the silver sol and added a drop of 0.3% PVP to the remaining solution. The students added roughly 0.5 g of NaCl to the 5 mL silver sol without PVP to observe changes in color. The remaining solution containing PVP was added to clear vials that were processed through spectroscopy (Figure 7). Students observed the wavelengths absorbed by the silver nanoparticles. The silver sol was then placed on a hot plate, stirred, and heated up to around 90°C. PVA was added to the hot silver sol until a 4% solution was created. The solution was decanted into molds, leaving behind undissolved PVA and trapped air. The students were tested before and after the activity to evaluate the lab efficacy. Other students who did not participate in the lab activity were given the

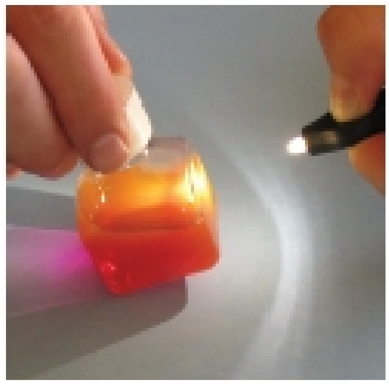


Figure 8: White light being shown through a gold nanoparticle colloid. A shorter wavelength of violet is produced on the white paper.[16]

NISE nanogold demonstration, and tested the same as the previous students. The standard operating procedure for the silver synthesis can be found in Appendix A and the quizzes given to students can be found in Appendix B.

4. Results and Discussion

4.1 Synthesis and Characterization of Nanoparticles

The two nanoparticles synthesized most for educational purposes are gold and silver. These two metals are chosen because their surface plasmon resonance absorbance falls within the visible spectrum, so changes are visible to the naked eye. The main reason that silver was chosen over gold for synthesis in the sophomore materials laboratory was because of the high cost of gold. Currently, gold costs 58 times more than silver, so gold is not a practical reagent for a continuing laboratory activity.

Three silver nanoparticle synthesis methods were considered for their practicality (Table I). Inert gas condensation was immediately ignored because of the large amounts of equipment required to perform the process.[15] The next process ruled out was the ethanol reduction of silver nitrate because of its high cost, required equipment, and extended times. Specifically, the ethanol reduction costs over eight times more than the sodium borohydride reduction, and takes over ten times as long.[6,14] Therefore the

reduction of silver nitrate by sodium borohydride was chosen, even though the process requires hazardous chemicals.

Table I: Comparison of Three Distinct Silver Nanoparticle Synthesis Methods[6,14,15]

	Cost	Special Equipment	Hazardous Materials	Time
Inert Gas Condensation	-	Yes	None	-
Ethanol Reduction	High	Yes	Low	360 minutes
Sodium Borohydride Reduction	Low	No	High	30 minutes

4.1.1 Synthesis of Nanoparticles

As previously mentioned, both gold and silver nanoparticles were synthesized. Only one batch of gold nanoparticles were created to compare with the silver nanoparticle process. The gold nanoparticle sol was aggregated with NaCl, and data was collected. Eight batches of silver nanoparticles were synthesized throughout the project (Table II). The first attempt was unsuccessful due to the sensitivity of the concentrations of the reagents and a lack of required equipment. Later, in the second attempt, it was realized that the reagents had to be carefully weighed to achieve a stable colloid. Finally, in the third attempt, the reagents were carefully measured and a yellow sol was produced (Figure 9). Furthermore, PVP was added immediately after completion of the reduction reaction. It was discovered that adding PVP had a drastic effect on the stability of the silver sol.

Table II: Silver Nanoparticle Synthesis Batch Information and Reasons for Success

	Color	Absorbed Wavelength	Reason for Result
Batch 1	Dark Gray	Undetectable	Imprecise Measurements
Batch 2	Dark Gray	Undetectable	Imprecise Measurements
Batch 3	Yellow	-	Addition of PVP
Batch 4	Orange	396 nm	Over Stirring
Batch 5	Yellow	385 nm	-
Batch 6-8	Yellow	~383 nm	-

Figure 9: Successfully produced yellow-colored silver sol. Success was largely attributed to the addition of PVP.

Other attributing factors included discontinuing agitation upon the complete addition of silver nitrate, continuous addition of silver nitrate, and a sufficient distilled water source. The next batch created was used in spectroscopy, and it was discovered that the nanoparticles exhibited a distinct absorbance peak. The last few batches of silver nanoparticles were synthesized for the sophomore laboratory and further data collection.

4.1.2 Characterization by Spectroscopy

The as-produced sols, the yellow-colored silver colloid and red-colored gold colloid, produced absorbance peaks characteristic of the light being produced (Figure 10). Specifically, the silver sol produced an absorbance peak at 386 nm and the gold sol had a peak at 515 nm. A 386 nm wavelength of visible light creates a deep violet. The color violet is complementary with yellow, which coincides with the color reflected. Similarly, a wavelength of light at 515 nm produces a green hue, which is complementary with red. Comparing the plasmon resonance wavelengths to literature, the nanoparticles can be estimated to be 10 to 20 nm and 10 to 25 nm for the silver and gold sols, respectively.[6,15]

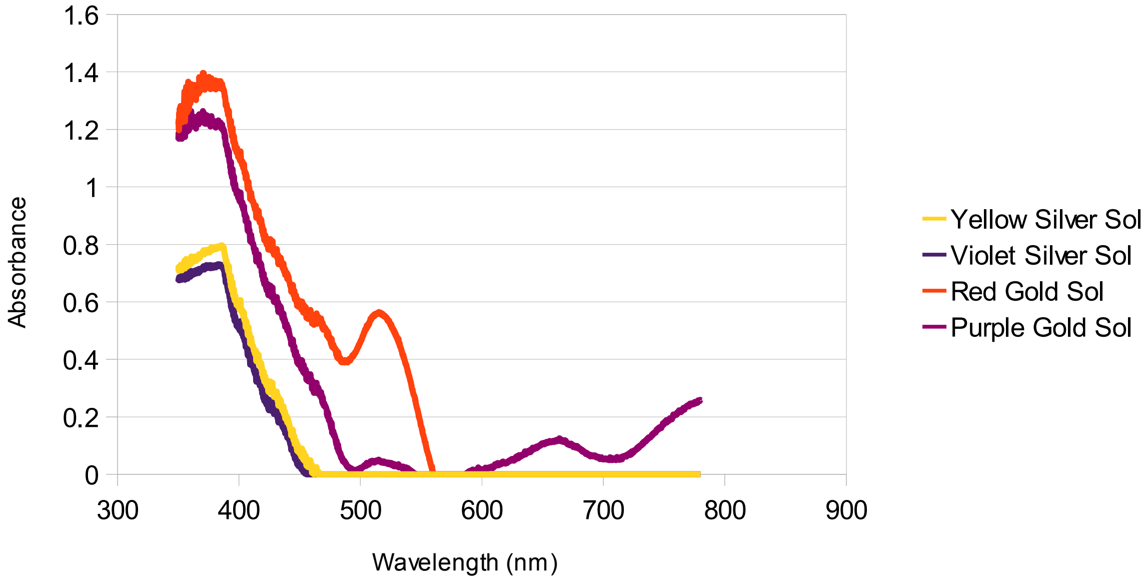


Figure 10: Absorbance peaks describing the wavelengths of light absorbed by the surface plasmon resonance of the silver and gold sols. Plasmon resonance peaks were found at 386 nm for the silver sol and 515 nm for the gold.

After NaCl was added to the silver and gold sols, it was found that the color changed drastically. In both cases, the wavelength of light reflected was a shorter wavelength around purple. The silver sol had an absorbed wavelength of 373 nm and the gold sol had a wavelength of 515 nm (Figure 10). Both of these values are close to the absorbance values found with the initial nanoparticle solutions. The new absorbance peaks were found to be broadened when compared to the as-produced sols.
With both of the gold sol samples tested, there were large absorbance peaks at 385 nm. These peaks were attributed to the color of the original bulk material, which reflects a color around yellow. The reason another peak is not seen for the silver sols is because the bulk material's absorption wavelength falls in an ultraviolet range not detectable by the spectrometer.

Before a reducing agent is added to the silver solution, there are only silver ions. The reducing agent, sodium borohydride, will force silver atoms to form in solution. The concentration of silver atoms will rise rapidly until supersaturation is achieved, at which aggregation will occur. The size of the initial particles will depend on the number of nucleation sites: the more sites the smaller the particles.[17] The amount of nucleation sites is dependent on the amount of reducing agent. As the reducing agent is increased, there will be more nuclei and thus smaller nanoparticles. With too much reducing agent, the nucleation sites will form at different times and destabilize much quicker.[17] This destabilization is part of the reason why the reduction of silver nitrate through sodium borohydride is sensitive to the ratio of borohydride to nitrate (for example if the ratio of sodium borohydride to silver nitrate changes from 2 to 1 to 2.1 to 1, then the colloid will quickly aggregate). Further, the presence of an electrolyte, such as chloride, will compress the adsorbed borohydride anion layer on the silver nanoparticles. The compression destabilizes the nanoparticles, forcing aggregation into larger particles.[17]

4.2 Educational Activities

4.2.1 Informal Settings

The nanogold demonstration was given to two groups of children: a group around 3-8 years of age and middle school aged students. The first demonstration, with the younger children, was given in a children's museum (Figure 11). The children had plenty of activities and games to choose from that were more interesting – such as making candy molecules. The main goal of scientific outreach activities for young children is to excite and build an interest in science, and this nanoparticle demonstration was found to be ineffective in this end. The nanogold demonstration would need to be more hands-on to be effective, and the concepts required too much explanation for the age range receiving the information at the children's museum.

Figure 11: The gold nanoparticle demonstration being given to a young girl at the children's museum.

The second group of boys and girls that received the nanoparticle demonstration signed up for the activity, so the group was predisposed to listening to the information. The students were already curious about the science being presented, and so the end effect was much greater than that observed in the museum setting (Figure 12). Further, the students rotated through every activity instead of choosing the ones that looked the most interesting. With that said, the students readily comprehended the information presented. The boys and girls were not able to explain how the nanogold had a different color than its bulk material, but the students did understand the connection between the colloid's size and change in properties. Most of the boys and girls asked questions about the concepts, and some tried to relate the phenomena to familiar concepts. For example, one boy asked if the color produced by the nanoparticles was used in lighting, specifically in light emitting diodes.

Figure 12: A group of boys and girls observe the scattering of white light shown through the gold nanoparticle sol.

4.2.2 Formal Settings

4.2.2.1 Laboratory

All students were successful in synthesizing the silver nanoparticles, but the the laboratory still lacked organization. During the lab only two students learned that plasmon resonance is why nanoparticles have a different color than its bulk material. The reason these students understood the mechanism behind nanoparticle's color was because they asked the lab instructor about it. Even though the information was directly on the laboratory description, the only students who understood plasmon resonance were the ones who had it explained. One possible way to solve this problem could be to have a pre-laboratory description of what is to come. Either have the students read the document before they come to class, or have a short lecture describing essential background information. Furthermore, nanotechnology information is taught in the winter quarter for second year materials engineers. If the laboratory were to be given as the information was being taught in lecture, the students would then both understand what is happening and reinforce the concepts. The biggest suggestion from the students was to explain things more thoroughly, as many of them did not understand why laboratory steps were being done despite having a handout. Another issue involving organization was with the PVP. The silver colloid only needs 0.01% PVP in solution to prevent aggregation, and contaminated glassware was preventing the demonstration of aggregating particles after the addition of an electrolyte. All glassware – in the future – will have to be cleaned with a solvent in between uses, or more glassware used to prevent contamination.

Finally, the students should have something to take home after the laboratory. The PVA 'stained glass' was not consistent enough to be used as a take-away. PVA is not soluble in room temperature water, so the water has to be heated up. At the same time, if the temperature is increased too much, then the silver colloid will rapidly aggregate (Figure 13). The temperature at which this occurs is currently not

defined. If the PVA process remains a part of the laboratory, then this process will have to be refined. An alternative solution involves giving the students a vial of their silver sol to take home, although this may pose safety risks involved with the sodium borohydride.

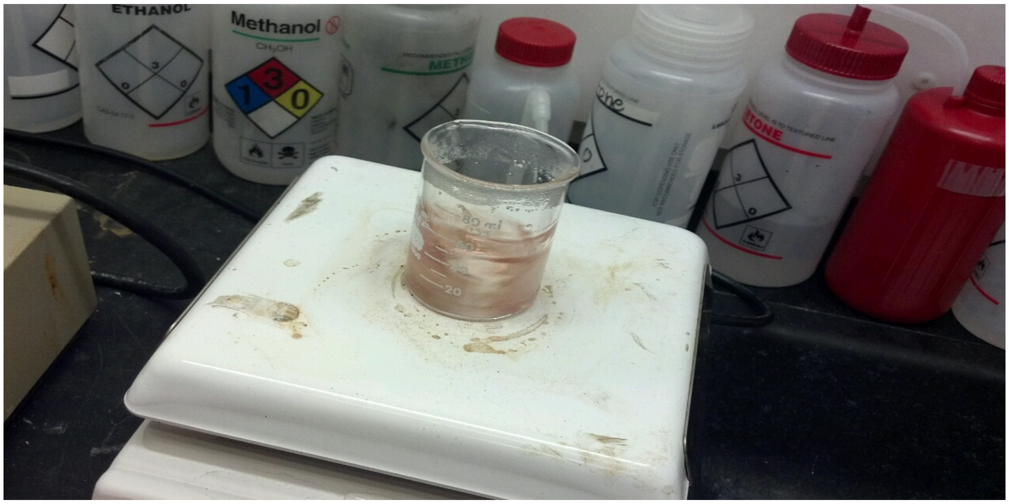


Figure 13: The polyvinyl alcohol (PVA) 'glass' process in action. In this case the temperature became too high and the silver sol aggregated to a grayish purple color.

The one effect that most of the students found interesting was the demonstration of the Tyndall Effect. The Tyndall Effect occurs when a light – in this case a laser – is shown through a colloid suspension containing particles under 100 nm. The laser will scatter and create interesting patterns (Figure 14). The point of the demonstration is to prove that the solutions are not just colored water, and that it is actually the size of the nanoparticles creating the color being reflected.

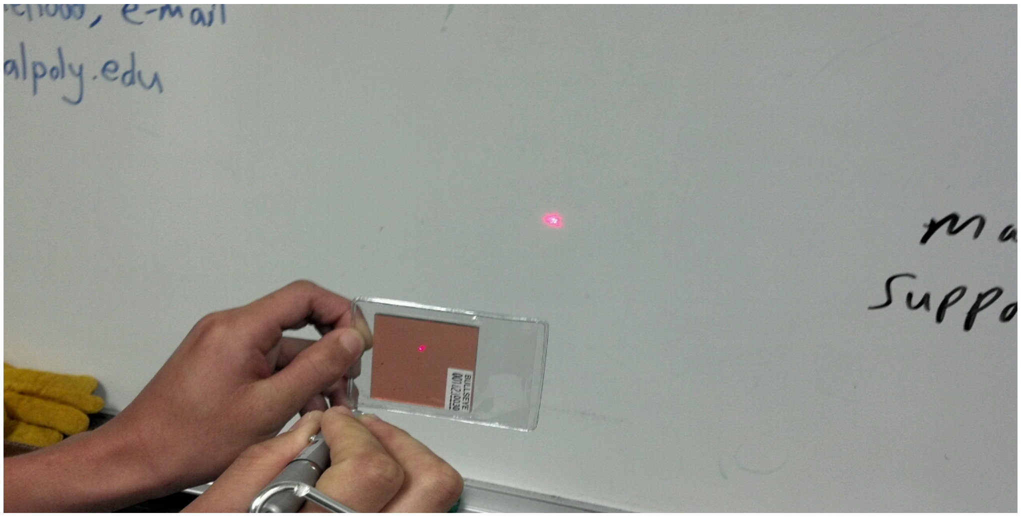


Figure 14: A student shines a laser through a stained glass sample that was created using nanoparticles. The laser scatters and an enlarged circle is seen on the board behind the stained glass.

4.2.2.2 Evaluation

The effectiveness of the nanoparticle laboratory given to sophomore materials engineering students was measured through tests given before and after the activity. The tests were also given to another group of similar students who were only given the nanogold NISEnet demonstration. The test answers were broken up into general concepts that, based on the goals of the laboratory, should have been gleaned by the students (Table III). The concepts considered important were the mechanism of general color, plasmon resonance, and plasmon resonance's effect on color. There was no net increase in the understanding of basic color. In the activity, color was defined as that being reflected while other colors are absorbed. Further, no student could explain why nanoparticles change the color of a material before the laboratory, but afterward two students provided an adequate explanation. Finally, a distracting question was added to the questions stating that the material's electron band gap was the source of color. Only a few students answered the question with this answer. It should be noted that the question asked to select all that applied, so some students selected all or none of the answers described in Table III. The group of students who only had the gold nanoparticle demonstration as a preface for their quizzes did not answer any of the questions correctly. The lack of correct answers was attributed to demonstration description given to them. The description stressed transmittance when it described how nanoparticles affect color. Transmittance is an important part of understanding how color is affected by nanoparticles, but it is not the only part. The result was that every student saw the word transmittance and gave it as their answer, even though the answer did not make sense for transmittance. All of these quiz questions can be found in Appendix B.

Table III: Quiz Results Before and After the Nanoparticle Laboratory

	General Color	Nanoparticle Color	E-Gap Color
Pre-Lab	6 of 29	0 of 29	4 of 29
Post-Lab, with Activity	6 of 13	2 of 13	4 of 29
Post-Lab, without Activity	0 of 9	0 of 9	0 of 9

At first glance, the laboratory quiz results make it seem that the activity was ineffective as a teaching tool. Note though that results in any study is dependent on the tool used to find data, and the tests given to the students revealed information other than was intended. For example, one question asked what the color of a colloidal suspension was mainly dependent on. Even though the question said to answer all that applied, the wording made it seem that there was one answer. For example, at one point during the lab, it was mentioned that too high of a temperature could cause the silver sol to aggregate during the PVA process. This statement added further ambiguity to the question on the quiz, as ambient temperature was one of the possible answers.

5. Conclusions

This study synthesized gold and silver nanoparticles and evaluated their efficacy as a teaching tool. Absorbance spectrometry data was taken for the nanoparticles. Nanoparticle demonstrations were given to various ages of children and a laboratory was adapted for second year materials engineering students. The effectiveness of the lab was evaluated using quizzes and observations.

1. The reduction of silver nitrate by sodium borohydride was decided to be more practical for an activity than ethanol reduction, inert gas condensation, and gold nanoparticles based on cost, required equipment, potential hazard, and required time.
2. Silver and gold nanoparticles were synthesized and characterized by spectroscopy. The silver sol exhibited a yellow hue and an absorbance peak at 386 nm. The gold sol exhibited a red hue and an absorbance peak at 515 nm. Based on these absorbance peaks, the nanoparticles were estimated to be 10 to 20 nm and 10 to 25 nm in diameter for the silver and gold sols, respectively.
3. The gold nanoparticle demonstration is not an effective teaching tool for children aged 3-10, but it is effective for middle school aged children. The younger children need more hands-on activities to remain vested in the demonstration compared to the older boys and girls.
4. The nanoparticle laboratory requires further organization to be successful. Specifically, the PVA 'stained glass' needs to be refined, PVP contamination needs to be avoided, and background information needs to be provided beforehand. Further, concentrations of reagents need to be carefully measured for success.

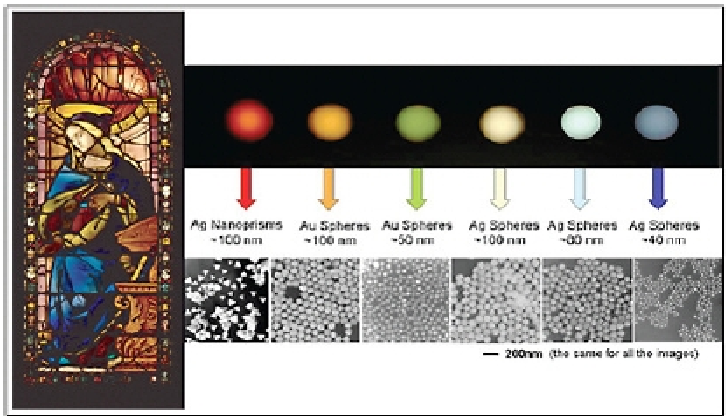
6. References

1. "Grand Challenges." *Grand Challenges for Engineering*. National Academy of Engineering. Web. 07 May 2012. <http://www.engineeringchallenges.org/cms/challenges.aspx>.
2. "Welcome to the NISE Network." *NISE Network*. Web. 9 Mar. 2012. <http://www.nisenet.org/about>.
3. Whitman, Deborah B. "Genetically Modified Foods: Harmful or Helpful?" *Genetically Modified Foods: Harmful or Helpful?* Web. 9 Mar. 2012. <http://www.csa.com/discoveryguides/gmfood/overview.php>.
4. "Nanoparticle Stained Glass." *NISE Network*. NSF. Web. 09 Mar. 2012. <http://www.nisenet.org/catalog/programs/nanoparticle-stained-glass-classroom-program>.
5. "Increasing the Number of STEM Graduates: Insights from the U.S. STEM Education & Modeling Project." *Business-Higher Education Forum*. Web. 7 May 2012. <4. http://www.bhef.com/solutions/documents/BHEF_STEM_Report.pdf>.
6. Solomon, Sally D., Mozghan Bahadory, Aravindan V. Jeyarajasingam, Susan A. Rutkowsky, and Charles Boritz. "Synthesis and Study of Silver Nanoparticles." *Journal of Chemical Education* 84.2 (2007): 322-25. *ACS Publications*. Web. 9 Mar. 2012. <http://pubs.acs.org/doi/pdf/10.1021/ed084p322>.
7. Stockman, Mark I. "Nanoplasmonics: The Physics Behind the Applications." *Georgia State University: Department of Physics and Astronomy*. Web. 9 Mar. 2012. <http://www.phy-astr.gsu.edu/stockman/data/Stockman_Phys_Today_2011_Physics_behind_Applications.pdf>.
8. Gu, Xuefeng, Teng Qiu, Wenjun Zhang, and Paul K. Chu. "Light-emitting Diodes Enhanced by Localized Surface Plasmon Resonance." *Nanoscale Research Letters*. Web. 09 Mar. 2012. <http://www.nanoscalereslett.com/content/6/1/199>.
9. Raffi, M., T. M. Bhatti, J. I. Akhter, A. Hameed, and M. M. Hasan. "Antibacterial Characterization of Silver Nanoparticles against E: Coli ATCC-15224." *Journal of Materials Science* 24.2 (2008): 192-96. Print.
10. Bonsak, Jack. *Chemical Synthesis of Silver Nanoparticles for Light Trapping Applications in Silicon Solar Cells*. Thesis. University of Oslo, 2010. Web. 9 Mar. 2012.
11. Suryanarayana, C., and M. Grant. Norton. "Determination of Crystallite Size and Lattice Strain." *X-Ray Diffraction: A Practical Approach*. New York: Plenum, 1998. 207-21. Print.
12. Power, A., Betts, A, Cassidy, J.:Silver Nanoparticle Polymer Composite Based Humidity Sensor. Analyst, 2010, 135, pp.1645 - 1652
13. Oldenburg, Steven J. "Silver Nanoparticles: Properties and Applications." *Sigma-Aldrich*. Web. 9 Mar. 2012. <13. http://www.sigmaaldrich.com/materials-science/nanomaterials/silver-nanoparticles.html>.
14. Das, R., S. S. Nath, D. Chakdar, G. Gope, and R. Bhattacharjee. "Preparation of Silver Nanoparticles and Their Characterization." Web. 09 Mar. 2012. <http://www.azonano.com/article.aspx?ArticleID=2318>.
15. McFarland, Adam D., Christy L. Haynes, Chad A. Mirkin, Richard P. Van Duyne, and Hilary A. Godwin. "Color My Nanoworld." *Journal of Chemical Education* 81.4 (2004): 544A-44B. *ACS Publications*. Web. 9 Mar. 2012.
16. Transmittance of White Light through a Gold Sol. Digital image. *Nanoscale Informal Science Education Network*. National Science Foundation. Web. 3 June 2012.
17. Chaudhuri, Basab, and Syamal Raychaudhuri. "Manufacturing High-Quality Gold Sol." *IVD Technology*. Web. 2 June 2012. <http://www.ivdtechnology.com/article/manufacturing-high-quality-gold-sol>.

Appendix A

Silver Nanoparticle Synthesis:
Modern techniques to make medieval stained glass

Can you fabricate silver (Ag) nanoparticles to create different colors, as in medieval stained glass? In this lab activity, you will utilize your chemistry skills to create a colloidal suspension of nanoparticles and investigate the relationship between nanoparticle size and color.



This lab will focus on the synthesis of silver nanoparticles through a reduction. Silver nitrate will be added to sodium borohydride to create nanosized spheres of silver. These silver spheres attract borohydride anions which cover the surface of the spheres. The anions repel each other, preventing any further grouping together (aggregation). The effectiveness of the borohydride anions heavily depends on the ratio of borohydride concentration to silver concentration. Further, agitation will induce aggregation, and all silver nanoparticle colloids will aggregate given enough time.

A. Creating the stock solutions:

1. Compute how many grams of $AgNO_3$ in 100 mL distilled water are needed to create a stock solution of **1mM $AgNO_3$**.

2. Compute how many grams of $NaBH_4$ in 250 mL distilled water are needed to create a stock solution of **2mM $NaBH_4$**.

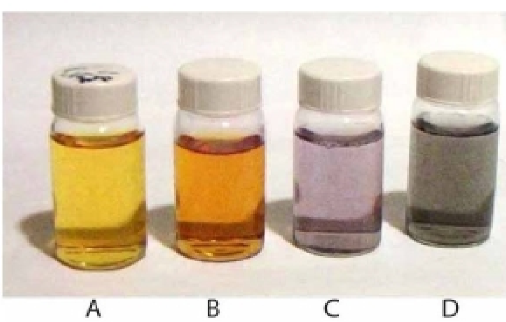


Figure 1. Colloidal silver in various stages of aggregation, (A) clear yellow sol, (B) dark yellow sol, (C) violet sol, and (D) grayish sol, as aggregation proceeds.

These stock solutions must have tight controls on the molarities in order for the process to occur as intended. Deviations result in aggregation of the nanoparticles with time, and a change in color (Figure 1).

An additional way to avoid aggregation is through the addition of polyvinylpyrrolidone (PVP). A couple drops will be added to the colloidal suspension of silver nanoparticles to help stabilize them.

3. Create a 0.3% *polyvinylpyrrolidone* (**PVP**) solution by dissolving 0.1g of PVP in 33 mL distilled water.

4. Weigh out polyvinyl alcohol (**PVA**) to obtain a 4% solution (for 32 mL it is about 1.3 g of PVA). PVP and PVA do not need to be as exact as the other chemicals).

The PVA will be used as a substitute to glass as a way to hold the Ag nanoparticles in a transparent solid.

B. Creating the colloidal suspension of nanoparticles:

1. Add 30 mL of the 2 mM $NaBH_4$ to a 250 mL Erlenmeyer flask. Place a stir bar into the flask and set into a dish filled with ice. Place this on a stir plate and stir for about 20 minutes.

2. Add 2 mL of 1 mM $AgNO_3$ dropwise to the $NaBH_4$ to begin formation of the silver nanoparticles. Add this continuously at about 1 drop per second until all of the $AgNO_3$ is gone and immediately stop stirring.

3. The liquid should appear light yellow, indicating the presence of nanoparticles. Transfer a small amount to a test tube. (Some nanoparticles are to be used for characterization, and some are needed to make stained glass.)

The Chemical Reaction:

$AgNO_3 + NaBH_4 \rightarrow Ag + ½ H_2 + ½ B_2H_6 + NaNO_3$

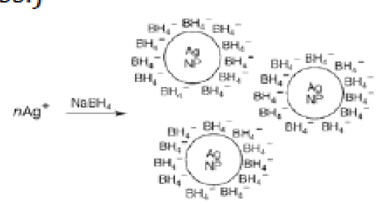


Figure 5. Repulsive forces separate Ag nanoparticles (NP) with adsorbed borohydride.

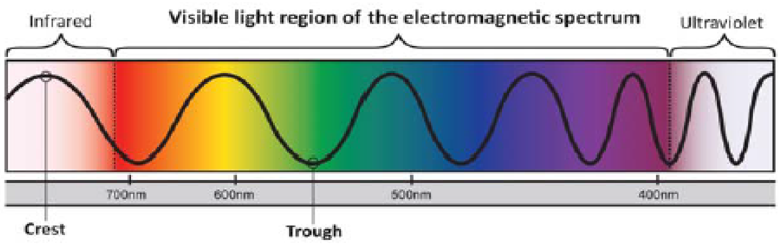
From the reaction, the silver nanoparticles are kept in suspension by the repulsive electrostatic forces between particles due to the adsorbed borohydride.

4. Add 1 to 2 drops of 0.3% PVP to the remaining solution in the Erlenmeyer flask.

C. Characterizing the nanoparticles (in different ways):

1. LASER: To verify the presence of nanoparticles, shine a laser through the solution. If the laser scatters in the solution, then – based on the **Tyndall Effect** – there are definitely nanoparticles.

2. Spectroscopy: Transfer a small amount of the silver sol to a vial and place it in the spectrometry apparatus. Make sure the program is using the absorbance setting and adjust the integrated time at the top left until a clear peak is visible. What wavelength of light is being absorbed? What wavelength is being reflected?



Why do the silver nanoparticles appear yellow?

In a typical bulk metal, some electrons are free to move around and are not tied to a single nucleus. From an electronic viewpoint, the metal looks like a sea of electrons. When light shines on the surface of a metal, some of the light waves move along the surface of the metal and give rise to a **plasmon** – a group of electrons moving back and forth in sync across the surface of the metal. The plasmon is said to be in resonance with light when the frequency of the plasmon's oscillation (the rate at which the electrons are moving back and forth) is the same as the frequency of the light that produced it. These electrons absorb energy from light, and a new color is reflected.

In nanoparticles of metals, there are fewer atoms, and thus fewer electrons. Because of this, the electrons are better able to coordinate and move together - just like 10 students in a classroom can move in a coordinated fashion more easily than 10,000 students in a stadium. Nanoparticles of some metals, such as gold and silver, resonate at frequencies within the visible spectrum of light. The gold nanoparticles in stained glass resonate at the frequency of green light waves, so they emit reddish purple light. The silver nanoparticles resonate at the frequency of bluish-violet light, so they emit yellow light.

3. NanoDays Kit: Nano Gold and transmitted light with LED: Place the container of nanoparticles on white paper, and tilt the bottle. Shine the light through the bottle. What color do you see on the paper?

When you look at the container of gold nanoparticles under regular ambient light, you see the longer, red wavelengths of light that are scattered (absorbed and reflected) by the tiny particles of nano gold. But when you look at the light that shines through the container and onto the paper, you see the shorter, purple wavelengths of light that are transmitted by the suspension of nano gold.

D. Creating modern medieval stained glass:

1. Mix together 1.5 M NaCl. This concentration does not need to be exact. Add a couple drops to the test tube that does not contain PVP. Note any changes. Slowly add PVA solid to the remaining solution in the Erlenmeyer flask to create a 4% solution. The solution should be hot and stirred: turn up the temperature knob to 7 and make the stirring as fast as possible without causing problems.

Note: some of the PVA may not dissolve. The high temperature can 'bond' the PVA to the bottom of the beaker, which is difficult to clean. Be careful.

2. Decant solution into mold while keeping air bubbles and undissolved PVA in the Erlenmeyer flask. Allow to evaporate either overnight or in a low temperature oven for thirty minutes (the lowest possible temperature, 50°C).

So what does this lab have to do with stained glass? In medieval times, artisans mixed different compounds (like gold chloride and other metal oxides and chlorides) into molten glass. When they added the gold chloride, it turned the molten glass a rich ruby color. The artisans didn't know it back then, but the color came from nanoparticles of gold, and the different way that nanoparticles interact with light produced a rich ruby color.

Modern artist creating nanoparticles in art:
Kate Nichols (artist in residence at Berkeley Labs)
http://voodhu.wordpress.com/2012/01/03/13/

Appendix B

Pre-Lab Quiz

1. A nano-sized particle contains roughly:
    a) 0.1 atoms
    b) 1-10 atoms
    c) 100-10,000 atoms
    d) 10^6 atoms
    e) 6 x 10^{23} atoms

2. The color of a colloidal suspension of nanoparticles can change colors with the addition of certain substances. T / F

3. The color of a colloidal suspension of silver (Ag) or gold (Au) nanoparticles is mainly dependent on the: [Choose all that apply]
    a) ambient temperature
    b) electronic band gap
    c) number of nanoparticles
    d) size of nanoparticles
    e) none of the above

4. The red color of nano gold is due to: [Choose all that apply]
    a) plasmon resonance
    b) the band gap energy
    c) wavelengths corresponding to red (~700 nm) being absorbed
    d) wavelengths corresponding to red (~700 nm) being transmitted
    e) wavelengths corresponding to blue (~450 nm) being reflected

5. Surface repulsive forces keep nanoparticles separated in solution. T / F

6. Nanoparticles have no practical applications and are currently not found in use. T / F

Post-Activity Quiz

1. Aggregation of nanoparticles in solution causes color changes. T / F

2. The color progression of nano gold seen in the figure to the right (Left to Right) is due to:

    a) changes in the band gap
    b) increase in nanoparticle size
    c) decrease in nanoparticle size
    d) increase in the concentration of nanoparticles
    e) decrease in the concentration of nanoparticles
    f) none of the above

3. The color of a colloidal suspension of silver (Ag) or gold (Au) nanoparticles is mainly dependent on the: [Choose all that apply]
    a) ambient temperature
    b) electronic band gap
    c) number of nanoparticles
    d) size of nanoparticles
    e) none of the above

4. The yellow color of nano silver is due to: [Choose all that apply]
    a) plasmon resonance
    b) the band gap energy
    c) wavelengths corresponding to red (~700 nm) being absorbed
    d) wavelengths corresponding to red (~700 nm) being transmitted
    e) wavelengths corresponding to blue (~450 nm) being reflected
    f) other: please explain

5. Aggregation of nanoparticles can be brought about by the addition of electrolytes such as NaCl. T / F

6. Give an example of an application for nanosilver or nanogold.

7. What new thing(s) did you learn from the activity?

8. What aspects did you like about the activity, and what suggestions do you have to improve it?