Name________________________

Chemistry and Art
Nanoparticles in Stained Glass
Pre-Lab Assignment

Pre-Lab Assignment

- This pre-lab assignment is worth 5 points.
- This part of the pre-lab assignment is due *at the beginning* of the lab period, and must be done individually *before you come to lab!*

I. Background Preparation

1. **Read this experiment thoughtfully**
   Mentally note any procedural questions and plan how you and your partner will complete all experiments efficiently during the three-hour lab period.

2. Read background on how stained glass is made:

   Stained glass history: https://www.khanacademy.org/partner-content/getty-museum/getty-decorative-arts/a/stained-glass-history-and-technique

   How stained glass is made: https://www.khanacademy.org/partner-content/getty-museum/getty-decorative-arts/a/how-stained-glass-is-made

3. **Stained glass and nanoparticles** – as demonstrated by kids at the Chicago Museum of Science and Industry and Northwestern University – it's cooler than it sounds!
   http://pbskids.org/dragonflytv/show/stainedglass.html

4. Preview a short video showing how you will make the stained glass panels in this lab.
   https://vimeo.com/channels/nisenet/11048874

II. Safety Hazards/Precautions

1. Complete the following table. Use the MSDS online link on your lab web page. Be sure to follow and specific search instructions from your instructor and be sure the chemical name matches precisely.

Materials	GHS Pictograms (Circle all that apply)	Hazard Statements (Check and list all that apply)
$AgNO_3$ silver nitrate		☐ Corrosive ☐ Toxic ________________ ☐ Flammable ☐ Reactive _______________ ☐ Irritant ☐ Other? ________________
$Na_3C_6H_5O_7 \bullet 2H_2O$ sodium citrate tribasic dihydrate		☐ Corrosive ☐ Toxic ________________ ☐ Flammable ☐ Reactive _______________ ☐ Irritant ☐ Other? ________________
$HAuCl_4 \bullet H_2O$ hydrogen tetrachloroaurate (III) hydrate		☐ Corrosive ☐ Toxic ________________ ☐ Flammable ☐ Reactive _______________ ☐ Irritant ☐ Other? ________________
Waste Disposal	Identify (briefly) how you will dispose of waste materials from this experiment.	

2. **Workplace/Personal Cleanup Notes** (indicate what you will do to clean up yourself and your lab space before you leave the lab):

Questions of the Day

- What is the connection between nanotechnology and stained glass windows?
- How can nanoparticles of gold and silver by synthesized?
- How does light interact with nanoparticles?
- How can I make "stained glass" art using nanoparticles?

Introduction

Nanoscience . . . nanotechnology . . . nanoparticles. Nearly everyone has heard something in the news about the nanoscale world. How it promises the next big scientific revolution. How it will cure disease and solve food and energy problems. The potential dangers associated with it. It can be difficult these days to separate the science from the hype and the truth from the misinformation. Actually, several of the promises of nanotechnology are already beginning to be realized.

In fact, nanomaterials are finding ever-widening use in our everyday lives, ironically as they have for thousands of years. In ancient times, metal nanoparticles were used as pigments; church windows were colored yellow using silver nanoparticles, and red was generated using gold nanoparticles. Today nanoparticles are found in a host of products, including cosmetics, skin creams and sunblock, and stain-resistant fabrics. Carbon nanotubes-small cylinders formed from carbon are being added to bicycle frames, tennis rackets, baseball bats, golf clubs, and bowling ball coatings to make them lighter and stronger, as well as to microelectronics due to their superior conduction properties. Nanoparticles are also finding their way into biomedical applications. Colloidal silver has supposed antibacterial activities, which was recognized even in ancient Greek and Babylonian cultures. In the early 1900s in American hospitals, silver nitrate was used in the eyes of newborn babies to protect against blindness. And NASA used a silver-based water purification system in its space shuttles.

Nanoscience is the study of objects and processes that take place at the nanometer scale. One nanometer is equivalent to 1 *billionth* of a meter. Objects that contain at least one dimension that is below 100 nm are considered nanoscale objects. In this size regime, we are typically dealing with relatively small collections of atoms or molecules. The reason for the interest in the nanoscale stems from the fact that the properties of matter can differ significantly from those observed for bulk materials. For example, as objects become smaller, the resulting increase in surface area leads to increased reactivity. We know this from everyday experience-when building a camp fire, we find it easiest to start the fire using small sticks and not large pieces of wood. Reactions that might proceed slowly with large particles can even become explosive when the starting materials are ground into fine particles.

By understanding these properties and learning how to utilize them, scientists and engineers can develop new types of sensors and devices. This technology could have a huge impact on diagnosing diseases, processing and storing information, and other areas. Physical and chemical properties are size-dependent over a certain size range specific to the material and property. When a particle of gold metal is similar in size to wavelengths of visible light (400–750 nm), it interacts with light in interesting ways. The color of a gold nanoparticle solution depends on the size and shape of the nanoparticles. Consider this analogy: tapping a spoon on a glass bottle partly filled with water generates a sound. Vary the volume of water in the bottle and the tone of the sound changes. The tone is dependent on the volume of water. Similarly, <u>the volume and shape of a nanoparticle determines how it interacts with light. Accordingly, this determines the color of a nanoparticle solution</u>. For example, while a large sample of gold, such as in jewelry, appears yellow, a solution of nano-sized particles of gold can appear to be a wide variety of colors, depending on the size of the nanoparticles. In this Experiment, you will examine some of these size-dependent properties of gold and silver nanoparticles, and utilize them to make simulated stained glass.

Preparation of Gold and Silver Nanoparticles

The premise of growing nanoparticles from solution is as follows. Start out with a solution that contains metal *ions* (such as Au^{3+} or Ag^{+}). We start with ions because as you know, solid metals are not soluble in water (but their ions can be). To grow a metallic particle, we have to add electrons to the ions to make them neutral. This process is called *reduction* (we are decreasing the charge from $+ \rightarrow 0$), and the chemical that supplies the electrons is called a *reducing agent*. The reducing agent as a result will become more positively charged since it lost electrons (a process called *oxidation*). But we don't care about what happens to the reducing agent, we're only concerned about the metal. In these reactions, we will use sodium citrate, an organic salt, as the reducing agent for the gold and silver. The sodium citrate reduces the Au^{3+} to nanoparticles of Au metal, and the Ag^{+} to nanoparticles of Ag metal.

The goal of this step is to convert the gold ions (Au^{3+}) into gold atoms (or Ag^{+} into Ag). Eventually, the atoms will stick together in the water forming nanoparticles. But as you can imagine, gold or silver particles should sink to the bottom of the beaker eventually. To keep them afloat, we have to make them more interactive with the water. We do this by coating the surface of the nanoparticles with charged citrate ions from sodium citrate. The particles now "appear" to have a negatively charged surface and will be suspended in the water. A suspension of particles in water that does not settle out over time is called a **colloid**. See Figure 1.

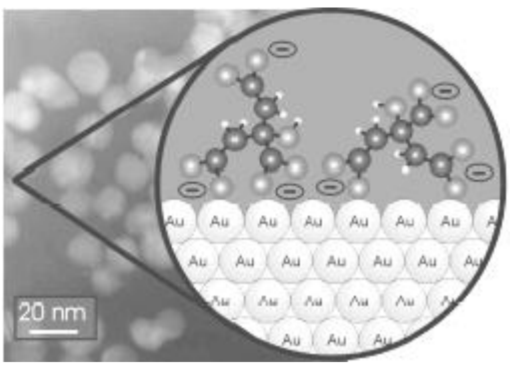


Figure 1

Left: A micrograph (photo from an electron microscope) of 13 nm-diameter Au nano-particles.

Interaction of nanoparticles and light – surface plasmon resonance

The changes in color mentioned above occur because these materials interact with light differently on the nanoscale than on the bulk (macro) scale. The color change arises from a phenomenon called *plasmon resonance*.

In a typical bulk metal, some (the outer shell) 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.

To understand the color of nanoparticle solutions we must mention one of the most important and well-tested theories in science – quantum mechanics. Quantum mechanics is complex, but it governs the behavior of small particles (electrons, atoms, molecules) as well as light particles (photons), among other things. To get a basic understanding you need only learn a couple facts about light, electrons and their interactions.

First, in a metal, the outer shell of electrons are free to move around the entire particle. While still bound to the particle as a whole, no outer shell electron belongs to any one metal atom anymore. This is the "sea" of electrons mentioned above. The surface electrons in a nanoparticle can also behave in a special way. You might want to think, as an analogy, of a planet completely covered with water and no land. A waterworld. Our nanoparticle would have a surface sea of electrons, it would appear to be an "electronworld". In the waterworld, if you dropped a big rock onto the surface, you would make waves. In the "electronworld" the analogy of dropping a rock would be hitting the electron sea with a light particle, a photon. In the same way, surface electron waves would be made. Surface electrons would be "sloshing around" together, making waves, sort of like a bunch of people might make "the wave" in a sports stadium by raising their arms in succession. However, this is where the similarity to water waves ends. Because of the rules of quantum mechanics, in our nanoparticle "electronworld", only waves of certain frequencies (wavelengths) are allowed to exist. The allowed frequencies (waves) depend on the number of electrons and the size of the particle itself, among other things. Thus, every different nanoparticle has its own unique set of allowed surface electron waves that can form. It turns out it is impossible to make surface electron waves that are not allowed by the rules of quantum mechanics. Seems strange but this is the world of quantum mechanics.

When white light (all colors of the rainbow, between 400-700nm wavelength) shines on the surface of a metal, some of the light waves will be in ***resonance*** with the particular allowed frequencies for a given nanoparticle. Resonance means the frequency of the light wave/particle (photon) matches that of the allowed surface electron wave of the nanoparticle. When this occurs, this particular light wave can cause the surface electrons of the nanoparticle to begin oscillating at that same (resonant) frequency. This phenomenon, where light of a particular frequency causes the surface electrons to oscillate at that same frequency is called *surface plasmon resonance*. The surface electron wave that is generated is called a *plasmon*. For example, suppose the rules of quantum mechanics dictate that a nanoparticle of some particular composition and size has an allowed surface electron wave (a plasmon) with a frequency of 4.4×10^{14} Hz (cycles/sec). Then, of all the wavelengths of light shined on the nanoparticle, only the one light wave with a corresponding frequency equal to 4.4×10^{14} Hz will be absorbed by the nanoparticle – that wave is *in resonance* with the plasmon. A light wave with a frequency of 4.4×10^{14} Hz has a wavelength equal to 680 nm. This is a photon of red light. Thus, our nanoparticle will absorb red light out of the visible spectrum. In the same way, different sizes or compositions of nanoparticles will absorb different colors of light. Nanoparticles of some metals, such as gold and silver, resonate at frequencies within the visible spectrum of light.

Perceived color of nanoparticles

It would be tempting to think our nanoparticle in the previous example would thus look red, because it was the red light that excited the plasmon. But this is not true. In fact, the nanoparticle would look blue. To understand why, we need to discuss what is known as perceived color when light is absorbed from the spectrum.

When nanoparticles absorb light, the observer sees the light that is transmitted through the formulation, causing the observer to perceive light that is the opposite color than the absorbed color. By "opposite color" we mean with reference to the artists *color wheel*, shown in Figure 2 on the next page.

For example, small gold nanoparticles absorb blue and green light. When white light interacts with these particles, blue and green light is absorbed and red light is transmitted through the material. To the eye of the observer the nanoparticle formulation appears red. Notice red and orange are opposite to blue and green on the color wheel.

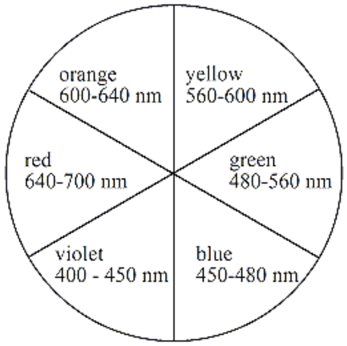


Figure 2. The perceived color one sees is determined by the color opposite to the absorbed color on the color wheel.

What has the nanoscale have to do with this?

One of the main reasons nanoparticles act differently from bulk is due to their increased surface area. The same volume of silver has a much greater surface area when the particles are decreased in size. (See Figure 3 below.)

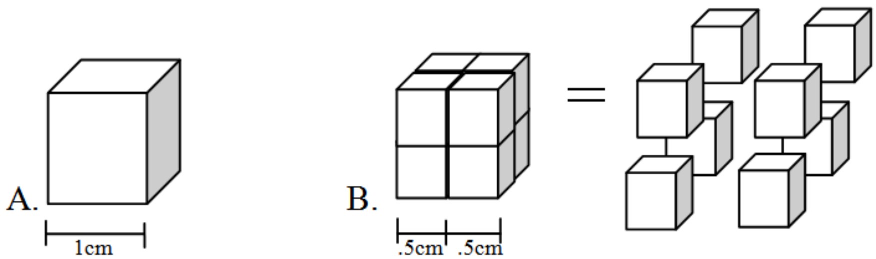


Figure 3. Sample A and Sample B contain the same amount of silver. The surface area of Sample A is 6 cm^2. Although the volume is the same, the total surface area of the 8 particles that make up Sample B is 12 cm^2.

In nanoparticles of metals, there are fewer atoms, and thus fewer electrons, compared to a macroscale sample. Because of this, the electrons are better able to coordinate and move together (as an analogy, 10 students in a classroom can move in a coordinated fashion more easily than 10,000 students in a stadium), and their behavior is governed by quantum mechanics. So, comparing a macroscale vs. a nanoparticle scale sample of silver of the same mass, there is much more surface area compared to volume in the nanoparticles whereas in the macroparticle, most of the particle is in the “bulk”, interior. The properties of the nanoparticles are governed much more by surface properties (such as surface plasmon resonance) than they are in macroscale samples. The colors and properties we see of macroscale metals are primarily a result of non-surface interactions. The opposite is true of nanoparticles.

History of stained glass

Interestingly, nanoparticles of gold and silver were utilized as far back as the middle ages in stained glass windows. Medieval artisans unknowingly became nanotechnologists during the glass-making process. Artisans mixed different compounds (like gold chloride and other metal oxides and chlorides) into the 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.

<u>Time line</u>
3000 BCE – Discovery of glass in Egypt and Sumeria
30 BCE-640 CE – Lycurgus cup (glass cup from Roman Empire; changes color when held up to light due to colloidial gold and silver particles in glass)
500 CE -1450 CE – Stained glass windows (Middle Ages or Medieval Period)
1885 CE. – Tiffany & Co. stained glass (Industrial Age)
1974 CE – Norio Taniguchi coins the term "nanotechnology"

The Medieval period in Europe lasted from approx 500 A.D.-1450 A.D. This was when knights and noblemen ruled towns, castles and countryside. Churches played a big role in daily life as Christianity spread organized religion through Europe.

Color in stained glass has historically been related to emotions. The meditative feeling a person gets upon entering a church partially results from the interior lighting. Rich reds and glorious yellows are two colors that were traditionally used in stained glass because of the emotions they invoke. Also, books were rare during this time, and many people were illiterate. In addition to being pieces of art, stained glass windows assumed an educational role by telling stories through pictures. Stained glass windows in cathedrals during the medieval period acted as a visual Bible for the poor.

Often medieval stained glass artisans worked on-site, making and cutting glass sheets and assembling the windows panels in the locations where they were to be installed. Many large French cathedrals (especially in Chartres) often went through two or three generations of stained glass makers before completion.

Making colored glass

The glass itself was made from melted sand (SiO_2). Pure sand required very high temperatures, near 2,500 ºF. However, artisans discovered that adding additional ingredients caused sand to melt at a much lower temperature. A mixture of sand, soda ash, lime, potash and lead oxide caused the sand to melt at temperatures around 1,500 ºF. Once molten, coloring agents, or *colorants*, were added.

The colors in the stained glass can be attributed to different chemical compounds that were added to the molten glass during processing. In some cases, the colorants were part of the basic glass making process (i.e. impurities found in the sand used to make the glass, or from smoke generated in the firing process).

Artisans noted that different compounds gave rise to different colors. For instance, ruby glass was created by adding gold chloride, while uranium glass, which glows in the dark, was created by adding uranium oxide. On the next page is a table that lists the different chemical pigments that artisans used to color glass. The sources for chemical colorants (typically metal oxides, sulfides and chlorides) were minerals.

Chemical compound added	Resulting color
iron oxides	greens, browns
manganese oxides	deep amber, amethyst
cobalt oxide	deep blue, violet
silver nitrate	yellow
gold chloride	ruby red
selenium oxides	reds
carbon oxides	amber/brown
mix of manganese, cobalt and iron	black
antimony oxides	white
sulfur compounds	yellow, amber, brown
copper compounds	light blue, red, green
tin compounds	white
lead compounds	yellow
nickel oxide	violet
chromic oxide	emerald green
uranium oxide	fluorescent yellow, green
sulfur	yellow, amber
cadmium sulfide	yellow
selenium oxide	red

Pigment chart adapted from: *http://chemistry.about.com/cs/inorganic/a/aa032503a.htm* and *http://geology.com/articles/color-in-glass.shtml* (accessed September 11, 2013) Additional information from Armitage, E. Liddall, *Stained Glass History, Technology and Practice*, Leonard Hill Books Limited (London), 1959.

The artisans didn't know it back then, but the color they observed after adding gold chloride and silver nitrate came from nanoparticles of gold and silver created during the glass process. The different ways that nanoparticles interact with light produced the red and yellow colors the artisans observed. (*The other colors observed were generally not due to nanoscale phenomena*.)

Stained glass window assembly

In the Medieval Period, artisans designed a pattern for a window panel and determined the size for its particular location. Once the pattern was determined, pieces of colored glass were cut roughly from large sheets to the approximate sizes and shapes using a heated rod or poker. To obtain the exact size and shape, artisans then used use a diamond grinder to grind down the glass to its desired shape. After all the pieces were cut to size, they were pinned onto a soft surface. The pieces of glass were then assembled into a window using lead strips (called *lead came*) to hold the glass in place. The joints between the glass and the lead strips were soldered together, to fill in the gaps between the glass and the premade lead came. Lastly, the window was glazed to strengthen all of the glass/lead joints.

In the mid to late 1800s, a new method evolved for assembling stained glass windows called the "Tiffany LaFarge Method." This method arose because artists wanted to create designs using glass pieces too intricate and delicate for the lead came method. In the Tiffany LaFarge method, copper foiling is used in place of the lead came. The copper foil could be fitted around the smaller, more delicate pieces, allowing artists to create more intricate designs.

This experiment

In this experiment, you will

1. Prepare a plastic panel with a design of your choosing to simulate a stained-glass panel
2. Prepare separate solutions of gold and silver nanoparticles
3. Synthesize a "glass" made up of a polymer that will absorb the colored nanoparticles.
4. Apply the colored "glass" polymer to your plastic panel design and let dry overnight. The result will be a rigid simulated stained glass panel

Safety Precautions

- ***Gloves should be worn during this lab at all times.***
- *$AgNO_3$, is corrosive and causes burns if it comes in contact with the skin and eyes.*
- *Sodium citrate may act as an irritant to the skin, eyes, and respiratory tract.*

Waste Management

- <u>All</u> waste solutions and solids containing silver or gold must be collected in the appropriate waste container in the lab.
- Silver and gold waste must NOT be flushed down the drain.
- Waste polyvinyl alcohol (PVA) solutions should be diluted and flushed down the drain. You instructor may require you to observe other disposal regulations.
- Waste solid PVA (without nanoparticles) may be disposed of in the trash.

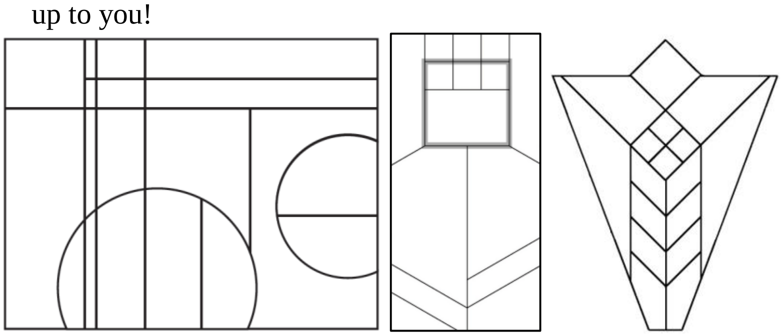
Procedure

Part I - Preparing the Template

1. Obtain the following materials:

    - Plastic sheet or plexiglass panel
    - Cardboard or foamboard backing
    - Simulated liquid leading solution (squeeze bottle)
    - Permanent black marker
    - Design pattern (make your own, see below)

2. Select a pattern for a stained glass panel. The pattern can be anything you choose: a preexisting stained glass pattern, a logo, a free hand drawing, etc. A tracing template can be created in a graphics program, such as MS Word or other drawing programs, or a template downloaded from the Internet. One interesting and easy option is to print and enlarge an existing logo or image and trace it. Your instructor may have templates. Some "Prairie Style" stained glass panels, originated by architect Frank Lloyd Wright are shown below. You can search the internet for more inspiration: http://www.prairiedesigns.com/browse.pl, or whatever style or image you choose, its up to you!



3. Place a piece of plexiglass/plastic on a piece of cardboard or foamboard.
4. Trace a pattern on the plexiglass/plastic panel with a permanent black marker. Slowly trace over the marker lines with the simulated liquid leading. Draw lines that are approximately 1/8", with no gaps. If the lines do not meet, the solutions will not be contained. The liquid leading requires at least 30 minutes to dry.
5. Clean up: Wipe up any excess liquid leading. Make sure caps on liquid leading bottles are tightly secured. Set panel aside to dry **overnight**.

Part II – Preparing Gold Nanoparticle Stained Glass

1. Obtain the following materials

- Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \bullet H_2O$), 1 mM solution
- Sodium citrate solution , 38.8 mM solution (NOTE: for Gold Nanoparticle Synthesis Only – don't mix up with 1% sodium citrate used for silver nanoparticle synthesis)
- Beaker (50 mL)
- 50 mL Graduated cylinder
- Stir/hot plate
- Stir bar
- Solid polyvinyl alcohol (PVA)
- Scale
- Weigh boat
- Spatula

2. Measure out 30 mL hydrogen tetrachloroaurate (III) hydrate solution into a 50 mL graduated cylinder.

3. Pour the measured hydrogen tetrachloroaurate (III) hydrate solution into a 50 mL beaker.

4. Add a magnetic stir bar and heat the solution to gentle boil on a stir/hot plate while stirring.

5. After the solution begins to boil, add 3 mL of the sodium citrate tribasic dehydrate solution.

6. Continue to boil and stir the solution until it is deep red in color (about 10 min).

7. When the solution is a deep red color, turn off the hot plate and stirrer and let the solution cool.

8. Slowly, add enough polyvinyl alcohol (PVA) solid to the warm solution to make a 4% (mass/volume) solution (about **1 g for a 32 mL mixture**).

9. Heat the solution gently to dissolve the PVA. Note: some of the PVA many not dissolve, but the solution should be heated, while stirring, until a majority of the solid dissolves.

10. While waiting for the PVA to dissolve, you may begin Part III below.

Part III – Preparing Silver Nanoparticle Stained Glass

1. Obtain the following materials

- 1 mM silver nitrate ($AgNO_3$) solution
- 1% sodium citrate solution (NOTE: for Silver Nanoparticle Synthesis Only)
- Beaker (250 mL)
- 10 mL Graduated cylinder
- 25 mL test tube
- Spatula
- Test tube rack
- Test tube holder
- Stir/hot plate
- Solid polyvinyl alcohol (PVA)
- Scale
- Weigh boat

2. Heat 200 mL of water to a boil in a beaker.

3. In a graduated cylinder, measure 20 mL of 1 mM silver nitrate solution then add the solution to a small test tube.

4. Place this test tube in the boiling water; let heat for 10 minutes.

5. Add 3.5 mL of 1% sodium citrate to the hot silver nitrate solution.

6. Continue to heat until the silver nitrate solution changes to a yellowish color (~15 minutes).

7. Remove the test tube and set in a test tube rack to cool.

8. Pour the silver solution from the test tube into the beaker.

9. Place the beaker on the hot plate and heat the solution gently.

10. Slowly, add enough polyvinyl alcohol (PVA) solid to the warm solution to make a 4% (mass/volume) solution (about 1 g for a 32 mL solution).

11. Heat the solution gently to dissolve the PVA. Note: some of the PVA many not dissolve, but the solution should be heated, while stirring, until a majority of the solid dissolves.

Part IV: Do We Really Have Nanoparticles?

We might wonder if we really did manufacture gold nanoparticles as shown above, or if we really just dissolved the gold ions (Au^{3+}) into the water. We would expect that if we had simply dissolved gold ions, that we would form a **<u>true solution</u>**, which is a **homogeneous mixture**. If on the other hand we have formed true nanoparticles of gold, we should expect to see a **heterogeneous mixture** of gold nanoparticles suspended in water, called a **<u>colloid</u>**. A true solution is homogeneous down to the size of the particles. In other words, we would have water molecules and gold ions, plus the citrate ions, all in one phase. We would not be able to see, even with a powerful microscope, phases or regions of collections of one type of pure substance distributed unevenly. The solute gold ions and citrate ions would be evenly dispersed throughout the water molecules, forming a solution. On the other hand, a heterogeneous mixture called a colloid actually *does have* microscopic regions of separated phases of pure substances. We would expect to see regions of gold particles (which are collections of atoms) in distinct particles or phases separate from the water. We may not see it at the macroscopic level, but if we could look deep enough, we would see the separate phases.

Both solutions and colloids are mixtures, whose properties depend on the proportions of the constituents.

Fortunately, there is a way to differentiate the presence of a true solution or simply a heterogeneous mixture (including colloids). That way is through the interaction of light with matter! The following are known:

- True solutions do not scatter light that is shone through them. In other words, if you take a beam of light from a flashlight or laser, you will NOT be able to see the beam of light as it passes through the solution.
- Colloids *scatter* light shone through them. If you take a beam of light and shine it through a colloid, you *will see* the beam as it passes through the mixture (not solution). For example, on a foggy or dusty night, you can see a flashlight beam because water droplets or dust particles are suspended in air forming a colloid, which scatters light. This is called the ***Tyndall Effect***. Milk is another example of a colloid that scatters light…try it!

Procedure:

1. Obtain a handheld laser from your instructor. Shine the laser through the original Au^{3+} or Ag^{+} solutions ($HAuCl_4$ or $AgNO_3$). Can you see the beam as it travels through the solution?
2. Shine the laser through the mixture of gold and silver nanoparticles. Can you see the beam as it travels through the mixture?
3. Record your observations and conclusions on the Report Sheet.

Part V- Making the Stained Glass Panel

Video: You can review the video of how to make the stained glass panel by going to the website below:

https://vimeo.com/channels/nisenet/11048874

1. When dry, retrieve your stained glass template. To limit moving the stained glass panel, place the panel with design where it will sit overnight to dry.

2. Using a separate pipette for each color nanoparticle solution, fill each section of the design with the desired color as close to the top of the simulated liquid leading as possible.

3. Let stand to dry overnight.

4. For better results, once allowed to dry overnight add an additional layer of nanoparticle solution. Again, let dry overnight.

5. Thoroughly clean the equipment with soapy water and a brush. Be sure not to lose the stir bars.

References

- http://www.nisenet.org/catalog/programs/nanoparticle_stained_glass_classroom_program "Nanoparticle Stained Glass (classroom Program)." *NISE Network*. Web. 01 Aug. 2011. <http://www.nisenet.org/catalog/programs/nanoparticle_stained_glass_classroom_program>.

- NSCC Nano 101 - Gold Nanoparticle Sensor Lab

- http://nanocomposix.com/pages/plasmonics Web. 07 June, 2016.

- Chemistry and Nanotechnology: What are Nanoparticles and How Can I Make Some? *Jim Schneider,* "Portland Community College Chemistry 221 Lab Manual", 2016.

NSF – DUE Award #1204279

Name________________________

Chemistry and Art
Nanoparticles in Stained Glass

Report Sheet

Observations

1. Draw a diagram of what your stained glass panel looked like.

2. Describe the color of the gold nanoparticle mixture.

3. Describe the color of the silver nanoparticle mixture.

Part IV: Do We Really Have Nanoparticles?

4. Observations when shining laser light through original $AgNO_3$ and $HAuCl_4$ solutions.

5. Observations when shining laser light through gold nanoparticle mixture.

6. Observations when shining laser light through silver nanoparticle mixtures.

7. What conclusion do you make about the presence of nanoparticles in your prepared mixture?

Analysis

1. What is the connection between nanotechnology and stained glass windows?

2. What evidence is there that a chemical reaction occurred in the synthesis of gold and silver nanoparticles?

3. At the macroscale, gold is yellowish and silver is…silver colored. Why does the color of these materials change at the nanoscale (i.e. why are the colors of the gold and silver different at the nanoscale than at the macroscale.).

4. A silver coin with a diameter of 4.00 cm (such as the U.S. silver dollar) contains 26.96 grams of silver and has a surface area of 27.7 cm^2.
   A. If the same 26.96 grams of coin silver were divided into spherical nanoparticles 1.00 nanometer in diameter, what would be their combined surface area? Note: Density of silver: 10.49 g/cm^3, Molar mass silver: 107.9 g/mol. The surface area of a sphere is $A_{sphere} = 4\pi r^2$. Volume of a sphere is $V_{sphere} = 4/3\pi r^3$.

   B. How many times more surface area is there for the nanoparticles compared to the silver coin of same mass?

Instructor's Guide

Timing:

As noted in the procedure, this lab will require a number of days to complete. These are:

- Day 1: Use liquid leading to produce a window template. This must dry overnight (cannot be used the same day.
- Day 2+: Produce nanoparticles and the PVA solutions. Apply the PVA/nanoparticle mixtures to the window template. The PVA must dry at least 1 day, depending on thickness. If the liquid is applied more thickly, then it will take more than one day to dry. Alternatively, thin layers can be applied on a daily basis to build up to a thicker "window pane".

Issues:

This lab works best (most recommended) if solutions are all made of ultra-pure reverse-osmosis water (>18 MΩ). Never use tap water. Less pure water (i.e. DI) can also work.

The easiest part of this lab is actually the production of the gold and silver nanoparticles. If the directions are followed, red (gold) and yellow (silver) nanoparticles generally form without fail. The two most difficult aspects of the experiment are 1) Using liquid leading to make the window template, and 2) producing the polyvinyl alcohol solution with the nanoparticles to produce reasonable solutions. In reality, most all of these work well if you have the time.

PVA is difficult to get into solution. Students should follow the recommended mass of PVA powder and add it slowly to the nanoparticles mixtures. It will take quite a while for it to dissolve at high temperature. They must be patient and persistent. Students can use a stir plate and stir bar to help.

(NOTE: if you wanted to play around, you could take some of the 4% PVA/nanoparticle solution and crosslink it with borax solution to make nanoparticle colored slime! That is very fun. If you wait long enough the slime will eventually dry out, although if it too much borax solution is added it may be too heavily crosslinked and it won't flow nicely into the window design.)

Materials:

Liquid leading can be difficult to find locally in hobby stores. The best bet is to buy from Amazon.com: https://www.amazon.com/s/ref=nb_sb_noss_2?url=search-alias%3Daps&field-keywords=liquid+leading
Plaid Gallery is the most common and cheapest brand.

Window template: Plexiglas can be used since it is very sturdy, but it is somewhat expensive. Any other plastic sheets can be used, even overhead (acetate) transparencies, as the liquid leading will help maintain structural rigidity. However, the thicker the pieces of plastic you can find the better.

It is helpful to have the students draw the designs and make the stained glass with the plastic sheet on a white surface. One option is to cut up white posterboard (cardboard or corrugated plastic) to the size of the plastic sheets.

Report Sheet Answer Key

1. What is the connection between nanotechnology and stained glass windows?

   Red and yellow stained glass was made historically (and unwittingly) by artisans creating gold and silver nanoparticles and either dissolving them into or applying them onto glass panels.

2. What evidence is there that a chemical reaction occurred in the synthesis of gold and silver nanoparticles?

   Examples of evidence include color changes, gas evolution (depending on method) and particularly the fact of how a beam of (laser) light interacted with the mixtures before and after reaction. Before the reaction the silver and gold solutions were…solutions, no scattering of light. After the reaction the Tyndall effect was noticeable, as the beam was scattered by the larger size particles (nanoparticles)

3. At the macroscale, gold is yellowish and silver is…silver colored. Why does the color of these materials change at the nanoscale (i.e. why are the colors of the gold and silver different at the nanoscale than at the macroscale.).

   The color of these materials change at the nanoscale because many properties, color included, are dependent upon the size of the particles. At the macroscale, most of the atoms are in the bulk of the material, not at the surface (i.e. the surface/volume ratio is very small) and the majority of physical properties are a result of the bulk properties (any surface interactions are generally overshadowed by bulk properties. At the nanoscale, for the same mass of material, the surface/volume ratio is increased significantly, to the point where the physical properties are dictated by the surface interactions. For example, the colors of gold and silver at the nanoscale no are predominantly from the surface plasmon resonance. The bulk interactions with light are minimal in comparison.

4. A silver coin with a diameter of 4.00 cm (such as the U.S. silver dollar) contains 26.96 grams of silver and has a surface area of 27.7 cm^2. If the same 26.96 grams of coin silver were divided into particles 1.00 nanometer in diameter, what would be their combined surface area?

   A.

   Volume of a silver coin:

   Radius = 2.00 cm
   Density of silver: 10.49 g/cm^3
   Molar mass silver: 107.9 g/mol

   Volume = 26.96 g·(1 cm^3/10.49 g) = 2.57 cm^3
   This is the total volume of all the nanoparticles as well

   Volume of 1 nanoparticle:

   $$V_{sphere} = 4/3\ \pi r^3 = 4/3\ \pi(0.50\text{ nm})^3 = 0.524\text{ nm}^3\ (1\text{ cm}/10^7\text{ nm})^3 = 5.24 \times 10^{-22}\text{ cm}^3/\text{nanoparticle}$$

   Continued…

Total number of nanoparticles:
$V_{total}/V_{nanoparticle} = 2.57\ cm^3/5.24 \times 10^{-22}\ cm^3 = 4.91 \times 10^{21}$ **nanoparticles**

Surface area of each nanoparticle:
$A_{sphere} = 4\pi r^2 = 4\pi(0.050\ nm)^2 = 0.0314\ nm^2 = 3.14 \times 10^{-16}\ cm^2$**/nanoparticle**

Total surface area:

4.91×10^{21} **nanoparticles** $\times\ 3.14 \times 10^{-16}\ cm^2$**/nanoparticle** $= 1.54 \times 10^{6}\ cm^2$ **!!**

B.
How many times more surface area: $1.54 \times 10^{6}\ cm^2/27.7\ cm^2$

= 55,700 times more surface area than the coin!!

Lab Prep Sheet per class of 24 students (12 pairs)

Splitting Water

CHEMICALS & SOLUTIONS					
Chemical	**Concentration**	**Total Quantity**	**Distribution Notes**	**Amount used per student PAIR**	
❑ Simulated liquid "leading"	See note below		12 bottles	1 bottle	
polyvinyl alcohol **granules**	dry powder/granu les	50 g	divide into 6 jars	2-3 g	
Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot H_2O$) solution	1 mM	400 mL	divide into 6 bottles	30 mL	
Sodium citrate tribasic dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) solution	38.8 mM	40 mL	divide into 6 dropper bottles, each containing at least 6 mL LABEL: **"SODIUM CITRATE for GOLD NANOPARTICLE SYNTHESIS ONLY!"**	3 mL	
$AgNO_3$ solution	1 mM	250 mL	divide into 6 bottles	20 mL	
Sodium citrate tribasic dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) solution	1 % Dissolve 1.0 g $Na_3C_6H_5O_7 \cdot 2H_2O$ (sodium citrate) in 100 mL ultra pure R.O. water.	50 mL	6 dropper bottles Label as: "**Sodium citrate for SILVER synthesis only**"	3.5 mL	

Lab Tech Notes:
Liquid leading can be difficult to find locally in hobby stores. The best bet is to buy from Amazon.com: https://www.amazon.com/s/ref=nb_sb_noss_2?url=search-alias%3Daps&field-keywords=liquid+leading
Plaid Gallery is the most common and cheapest brand.

Water: Always use the HIGHEST PURITY water your school has available, never tap water. If necessary, purchase reverse osmosis water to make **all solutions**.

Lab Prep Sheet

EQUIPMENT, GLASSWARE & MODELS		
Quantity	**Equipment / Model**	**Distribution Notes**
❑ 12	stir bars	
❑ 12	stir plates	
❑ 24	weigh boats	
❑ 12	spatula	
❑ 12	50-mL beakers	
❑ 12	250-mL beakers	
❑ 12	25-mL test tubes + test tube holders	
❑ 12	test tube rack	
12	balance	
12	stir rods	
12	plastic squares cut from sheets, or sheets of Plexiglas about 4 or 5 in. on a side. The more rigid the plastic the better. Must be transparent and colorless	
12	foam core or white poster board squares – same size as plastic squares above	
12	black permanent markers	
12	handheld lasers (pen lasers, etc.) Can't be LEDs	
Lab Tech Notes:		

❑ WASTE CONTAINER(S)
Waste collection jar for colloidal Ag, Au and $AgNO_3$, $HAuCl_4$
Waste trisodium citrate can be flushed down the drain, or collected in a waste jar.
Waste polyvinyl alcohol can be either added to a waste jar or flushed down the drain with plenty of water