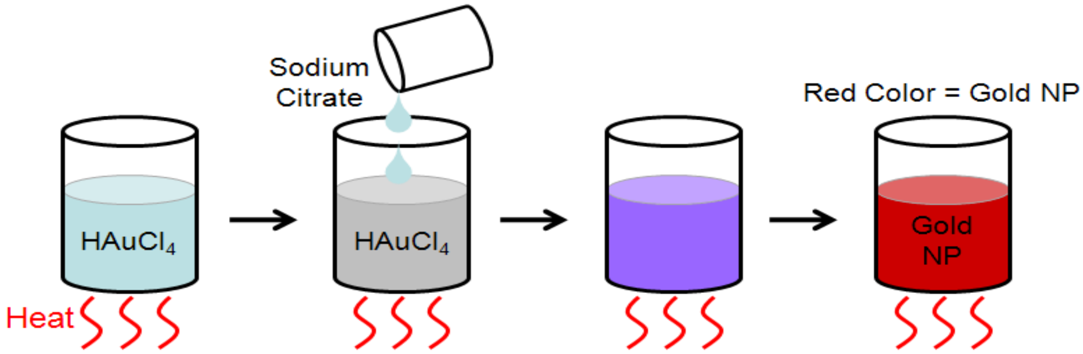
Synthesis of Colloidal Gold Nanoparticles in Solution (35 points)

Objective: The objective of this online lab is to demonstrate and overview the procedures necessary to synthesize colloidal gold nanoparticles from solution-phase precursors as well as use UV-Vis spectrophotometry to measure changes in the color of the resulting colloidal suspension as an electrolyte is added.

The student will watch a series of videos pertaining to each step of synthesizing the gold nanoparticles. These videos will provide detailed insight onto each step of the overall process. After watching the videos the student will be required to answer review questions on ANGEL.

Background: In contrast to homogeneous solutions, a colloid is a mixture that contains two discrete phases of material: the dispersed phase and the continuous phase. Colloids can be just about any combination of the three states of matter. Common colloids include milk, inks, smoke, and toothpaste. For example, milk is a complex mixture of solids and lipids dispersed in a continuous water phase. Due to the very small size of suspended particles (about 1 to 200 nm), they are subjected to Brownian motion and do not settle out over time when properly stabilized. Another interesting property of colloidal mixtures is that they scatter light. Homogeneous solutions do not scatter light. This phenomenon can easily be observed by shining a laser (e.g., laser pointer) through a sample of the gold nanoparticles. If the beam path through the sample is visible, the sample is scattering light. If the beam is not visible, the sample is homogeneous insofar as it does not have small particles. In fact, the light scattering properties of colloidal particles can be put to good use in a technique called dynamic light scattering, which uses scattered light to measure the size distribution of colloidal particles in a sample.

A common way of preparing colloidal metal nanoparticles in solution is to reduce a water-soluble metal salt with a chemical reducing agent. In the case of gold nanoparticles, hydrogen tetrachloroaurate ($HAuCl_4$) and sodium citrate serve as the gold source and reducing agent, respectively. Both materials are soluble in water. When combined and heated, reduction of the gold salt occurs and gold nanoparticles form over a period of minutes. As the reaction progresses, the mixture turns from clear to a deep red color which is indicative of colloidal gold nanoparticles.



The nanoparticle colloid appears red in color due to a unique interaction between light and the electrons of the gold nanoparticles. The interaction is called surface plasmon resonance (SPR) and can be envisioned as the collective oscillation of conduction band electrons in resonance with the electric field of the incident light. The wavelength (color) of the SPR depends on many factors, including: the size and shape of the nanoparticles, the solvent in which they are dispersed, and the presence of surface capping agents which were used in the synthesis reaction. The wavelengths of SPR can be measured with a UV-vis spectrophotometer. Generally, larger particles absorb at slightly longer wavelengths than smaller particles. Also, the more uniform the nanoparticles are (i.e., the narrower the size distribution) the narrower the SPR absorption peak will be. Therefore, UV-vis gives useful information regarding gold nanoparticle samples.

The gold nanoparticles remain suspended in solution because of their small size and due to the citrate ions which coat their surfaces. Citrate ions are negatively charged. When two nanoparticles come close to each other, the negative charges repel each other and push the particles apart. This electrostatic repulsion between neighboring nanoparticles prevents them from aggregating together. However, the addition of ions (e.g., salts) to the nanoparticle suspension can screen the citrate surface charges. Screening has the effect of neutralizing repulsive forces between particles. So, in the presence of screening ions, nanoparticles can approach each other, stick together, and form larger aggregates. This type of behavior results in color changes because aggregates have different optical properties than the originally well-dispersed individual nanoparticles.

In order to actually measure the size of the synthesized gold nanoparticles, the Veeco di Innova could be used in intermittent contact (tapping) mode. With the use of this tool and the UV-vis spectrophotometer a variety of properties about the colloidal particles can be obtained.

Experiment: During this exercise, colloidal gold nanoparticles will be synthesized and characterized using the UV-vis spectrophotometer.

Step 1: Making the Colloidal Solution

The most common method for the preparation of colloidal gold involves the reduction of gold(III) ions by citrate ions in dilute (.1mM) aqueous solution. The gold(III) ions are usually added to water in the form of hydrogen tetrachloroaurate ($HAuCl_4$). Citrate ions ($C_6H_5O_7^{-3}$), which are most likely oxidized to acetone dicarboxylate ions ($C_5H_4O_4^{-2}$), act as a two-electron reducing agent. The half reactions for the synthesis of colloidal gold are given in Equations 1 and 2.

$$\textbf{1. } Au^{+3}(aq) + 3e^{-} \rightarrow Au(s)$$

$$\textbf{2. } C_6H_5O_7^{-3}(aq) + H_2O(l) \rightarrow C_5H_4O_4^{-2}(aq) + CO_2(g) + H_3O^{+}(aq) + 2e^{-}$$

Watch the formation of colloidal gold nanoparticles video at the link below:

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=77d319f8-8c57-488a-97cb-5

Step 2: Finding Spectroscopic Information

Colloidal gold consists of gold nanoparticles that range in size from approximately 5-50 nm. An absorbance peak at 520 nm indicates the formation of gold nanoparticles with a diameter of 20-40 nm. The optical properties of gold nanoparticles are not only unique; they are useful in providing the basis for commercial products such as medical diagnostic kits for HIV detection, biosensors for DNA analysis, lasers, and optical filters.

Watch how to find spectroscopic information about colloidal nanoparticles at the link below:

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=f68da97d-d21f-4e50-9820-a

Step 3: Adding NaCl

Adding NaCl, a strong electrolyte, shields the negative charges of the colloidal gold nanoparticles and causes them to clump together to form larger aggregates.

Watch the formation of gold nanoparticles conglomerating due to adding a strong electrolyte at the link below:

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=be1204f8-0f68-4409-9bc0-6

Step 4: Finding Spectroscopic Information

In general, the wavelength of maximum absorbance shifts to a higher wavelength (>520 nm) when the mean particle size suspended in the colloid increases to above 40 nm. The color change from red to purple as a result of adding sodium chloride illustrates this effect.

Watch how to find spectroscopic information about conglomerated nanoparticles at the link below:

http://www.engr.psu.edu/mediaportal/flvplayer.aspx?FileID=09f75c29-9350-4fa2-86f6-b

Questions to be answered on ANGEL (NO HARD COPY REQUIRED)

1. The wavelength (color) of the SPR depends on many factors. Check all that apply. (6)

2. Colloidal gold nanoparticles are approximately what size? (2)

3. What is the charge of the gold nanoparticles? (2)

4. What is the color of the colloidal solution? (2)

5. The average diameter of the gold nanoparticles depends on which of the following? You may check more than one. (4)

6. What wavelength absorbance correlates to gold nanoparticles having an average diameter of 20-40nm? (2)

7. In contrast to homogeneous solutions, a colloid is a mixture that contains two discrete phases of material. What are the two phases? (2)

8. What was the default wavelength parameters used for the spectrophotometer? (2)

9. What was the wavelength of the peak of the spectrophotometer graph for the colloidal particles? (2)

10. What is the color of the conglomerated solution? (2)

11. What does the wider peak on the spectrophotometers graph correspond to? (2)

12. What was the wavelength of the peak of the spectrophotometer graph for the conglomerated particles? (2pts)

13. What happens to the colloid when the NaCl was added to the solution? (3)

14) Could sugar (sucrose) be used as a screening agent instead of sodium chloride? (3)