Au nanoparticle synthesis and characterization

1. Objective:

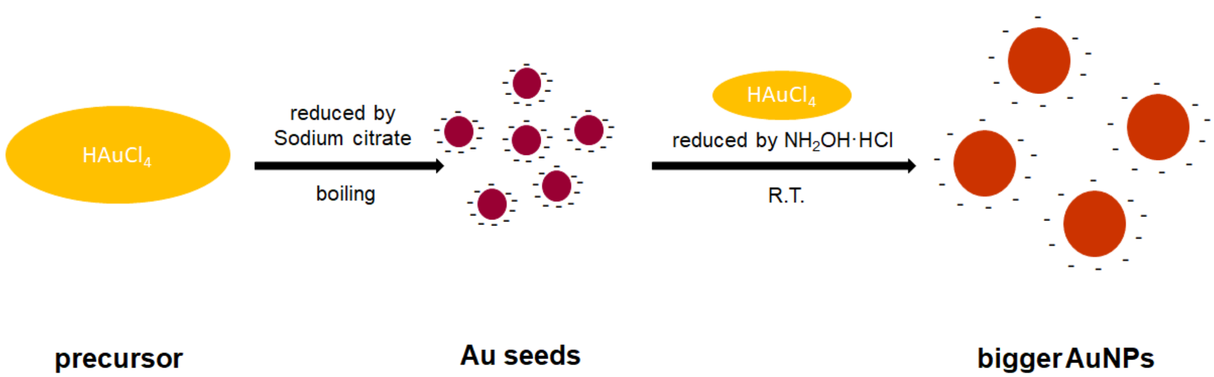
- Synthesize gold (Au) nanoparticle synthesis with control of size
- Use UV-Vis spectroscopy and simulation to study size dependence on optical properties of gold nanoparticles

2. Background:

Nowadays, nanotechnologies have been seen in a wide range of commercial applications such as energy, electronic devices and biomedicine, etc. Au nanoparticles are one of the most commonly used nanomaterials in nanotechnologies due to their unique optical properties. When the light with proper frequency irradiating the Au nanoparticles, the oscillating electric field from the light can move the loosely bound electrons in the nanoparticle back and forth, generating collective oscillations of electrons. This phenomenon is called localized surface plasmon resonance (LSPR). The unique plasmonic feature of Au nanoparticles will cause the light to interact with the nanoparticles by absorption and scattering that differ from their bulk counterparts. The plasmon resonance frequency of the Au nanoparticles is size dependent. With control of the nanoparticle size, many applications such as sensing, drug delivery and bioimaging have been studied.

3. Principle:

3.1 Principle of synthesis



- : citrate

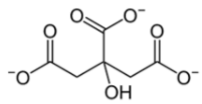


Figure 1. Scheme of AuNPs synthesis

As shown in Figure 1, for the fabrication of Au nanoparticles of varying sizes, a seeded growth method was employed which provides great control over the particle size. The synthesis includes two steps. In the first step, Frens method was used to obtain gold seeds. It is one of the most common and simplest Au nanoparticle syntheses. In this synthesis, Au^{3+} in $HAuCl_4$ is reduced to Au^0 by sodium citrate. Sodium citrate not only acts as the reducing agent, but also is a capping agent to prevent aggregation of Au nanoparticles by the electrostatic repulsion between its negative charges. Then in the second step, at room temperature, these seeds were used in a seed-mediated synthesis to grow the nanoparticles to various sizes. In this synthesis, $NH_2OH{\cdot}HCl$ is used as the reducing agent to $HAuCl_4$ to Au atoms. The Au atoms deposit on the Au seeds to enlarge their sizes. The different sizes are achieved by varying the amount of $HAuCl_4$ and $NH_2OH{\cdot}HCl$. The specified chemical amounts for each one can be found in Table 1.

3.2 Principle of UV-Vis spectroscopy

The size impact on the color of nanoparticles can be directly observed by naked eye during the synthesis. A color change of the solution can be clearly observed when the nanoparticle seeds grow bigger. In addition to eyesight observations about color, the size of nanoparticles can also be characterized using UV-Vis spectroscopy. The interaction of Au nanoparticles with light includes absorption and scattering, and the summation of them is termed extinction. At specific resonance wavelengths, Au nanoparticles are capable of absorbing and scattering light strongly; while at other wavelengths, light is transmitted through the particles. This gives us a maximum peak wavelength (λ_{max}) in the extinction spectrum. UV-Vis spectroscopy allows us to monitor the maximum peak wavelength (λ_{max}) of the nanoparticles, which is sensitive to changes in size and shape of the nanoparticles. A red shift in the peak wavelength of the extinction spectra of the Au nanoparticles should be observed when nanoparticles grow larger in size.

3.3 Optical property effects of size

The most important characteristic of Au nanoparticles is their intrinsic optical properties, that is , their localized surface plasmon resonances. The feature is based on the collective oscillation of free electrons within the Au nanoparticles upon interaction with an external electromagnetic source. The extinction peak position (λ_{max}) in the UV-Vis spectrum depends on the particle size and shape, and their environment. In terms of particle size, the extinction peak shifts to longer and redder wavelengths as particle size increases. According to complementary color theory, when light of a certain wavelength is absorbed or scattered in the UV-Vis spectrum and generates extinction peak, its color is complementary to the color of the light that is transmitted through the particles and observed by eyesight. As shown in Figure 2, for example, an extinction of light in the blue-green portion of the spectrum will result in a rich red color in solution, and an extinction of light in the red portion will result in a pale blue or purple color in solution.

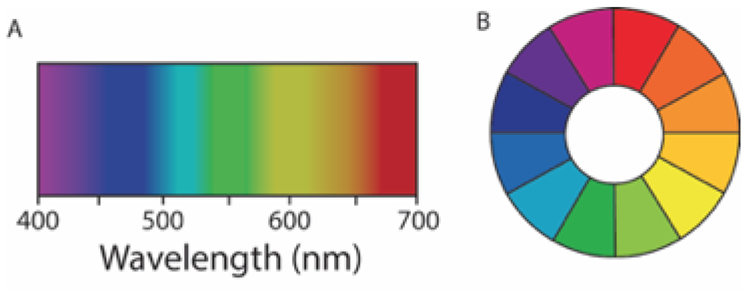


Figure 2. The visible spectrum and color wheel.

4. Experimental procedure:

Preparation of stock solutions

- 0.025 M gold (III) chloride trihydrate ($HAuCl_4$): Dissolve 1 gram of $HAuCl_4$ in 100 mL of DI water.
- 0.0388 M sodium citrate: dissolve 1.14 grams of sodium citrate in 100 mL of DI water
- 0.010 M hydroxylamine hydrochloride ($NH_2OH\cdot HCl$): dissolve 35 mg of $NH_2OH\cdot HCl$ in 50 mL of DI water

Au nanoparticles synthesis

Part 1: Au nanoparticle seeds

Gold nanoparticles were synthesized using the Frens' method. In this synthesis, $HAuCl_4$ is reduced by sodium citrate, which also acts as the capping agent. The synthesis of ~40 nm Au nanoparticle seeds is done as follows:

1. Add 99 mL of DI water to a 150 mL beaker with a stir bar.

2. Add 1.0 mL of $HAuCl_4$ stock solution (0.025 M) to the DI water. The heat and spin dials on the hot plate are turned to 6 and 8 respectively. A watch glass is placed on top of the beaker to limit heat and vapor loss.

3. Once the stirring solution begins to boil, 1.0 mL of sodium citrate stock solution (0.0388 M) is added to the beaker.

The solution is heated for 20mins to complete the reaction. There will be obvious color changes during the reaction. After 20 minutes, the solution can be removed from the hot plate and allowed to cool to room temperature. This solution will then be used as the seed solution to grow the particles to larger sizes.

A video is provided for the demonstration of the experimental procedure. The amount of chemicals used and the experiment setup in the video may vary from this experiment. https://www.youtube.com/watch?v=3lbOiJgdwFA. Watch the video and record your observations of color change in Table 2.

Part 2: Seed-mediated growth of Au nanoparticles

Once at room temperature the seeds can be used to grow the nanoparticles to various sizes. In this synthesis, $NH_2OH{\cdot}HCl$ is used as the reducing agent. The different sizes are achieved by varying the amount of $HAuCl_4$ and $NH_2OH{\cdot}HCl$. The specified chemical amounts for each can be found in Table 1. The seed-mediated growth synthesis is done at room temperature.

1. 5.3 mL DI water is added to a glass vial and placed on top of a stir plate.

2. Add 0.4 mL of Au nanoparticle seeds from the prior "seed" synthesis.

3. Add sodium citrate (refer to Table 1) stock solution to the beaker.

4. After 4 minutes, add the $HAuCl_4$ stock solution (refer to Table 1) drop by drop to the stirring solution.

5. After 8 minutes, add $NH_2OH{\cdot}HCl$ solution (0.010 M) (refer to Table 1) drop by drop, waiting 10 seconds between each drop.

A color change in the solution will be apparent within the first few minutes. The solution should continue to stir for 1 hour, so that the particle size can stabilize. To obtain better control of the size of particles, we will supply the gold seeds so that every group will use the seeds synthesized in the same batch.

Students are required to perform 4 syntheses at the same time. The amounts of reagents are listed in Table 1.

Table 1. Amount of chemicals used for seed-mediated growth. Each row in the table will produce Au nanoparticles of varying sizes.

	Sodium Citrate (μL)	$HAuCl_4$ (μL)	$NH_2OH \cdot HCl$ (μL)
1	10	8	11
2	20	23	34
3	50	50	75
4	100	90	140

Aside from experimental results, students can go to http://nordlander.rice.edu/miewidget to plot extinction spectrum simulated by Mie theory. Use gold as the core material and type in 40, 60, 80, 120, 140 as diameter. The medium is water with a refractive index of 1.33. Record the peak wavelength in Table 3.

Optical study

Upon completion of the seed-mediated growth synthesis, the gold nanoparticles are then characterized using UV-Vis spectroscopy. At specific resonance wavelengths, Au nanoparticles are capable of absorbing and scattering light strongly; while at other wavelengths, light is transmitted through the particles.

Students will perform UV-Vis measurement and record the wavelength of the peak in Table 4.

5. Data and simulation

In the virtual lab, most experiment results will be provided as below, whereas observation record, data analysis and simulation will still be carried out by students.

During the synthesis of Au nanoparticle seed, the solution will end up in a wine red color as shown in Figure 3A. In the part of seed-mediated growth of Au nanoparticles, as-made Au nanoparticles are used as seeds, and the solutions resulting from the amounts indicated in each row of the Table 1 is shown in Figure 3B. The corresponding extinction spectra is provided in Figure 3C.

For the information of λ_{max} values in the extinction spectra, λ_{max} of Au nanoparticle seeds (black solid line) is 530.6 ± 1.1 nm, that of growth 1 (red line) is 548.3 ± 4.1 nm, that of growth 2 (blue line) is 561.2 ± 6.1 nm, that of growth 3 (green line) is 576.9 ± 7.6 nm, and that of growth 4 (purple line) is 588.5 ± 10.0 nm. The standard deviations of λmax are calculated on the basis of 15 samples.

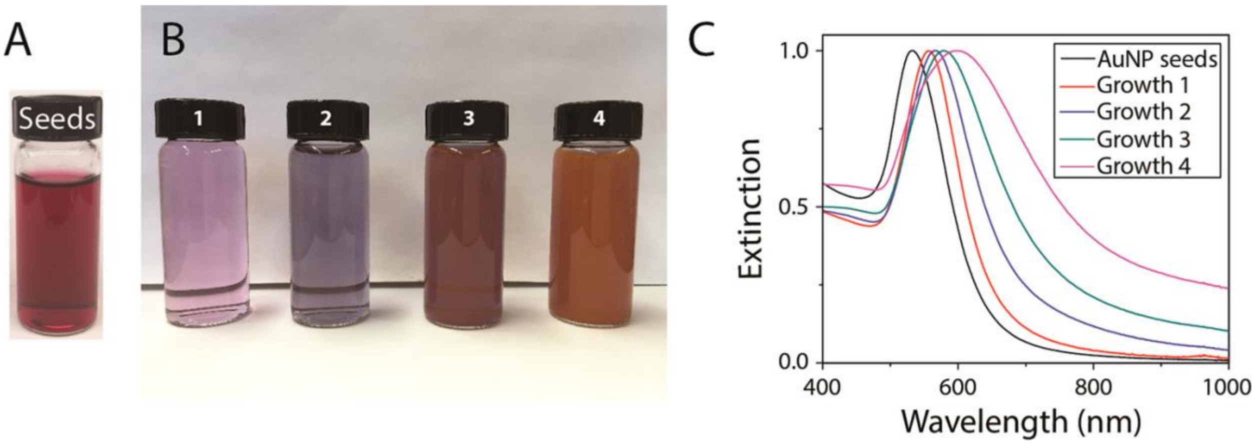


Figure 3. Results of seed-mediated growth of varying sizes of spherical gold nanoparticles.

Table 2. Color observations of the solution from the provided Au nanoparticle synthesis video.

Time (min)	Color

Table 3. Simulation of extinction spectrum

Diameter of Au nanoparticle (nm)	Peak wavelength (nm)

Table 4. Optical study by UV-Vis spectroscopy

Amount of precursor (ml)	**Peak wavelength (nm)**

Compare the measured extinction spectrum with the simulated extinction spectrum, and estimate the diameter of the synthesized Au nanoparticles.

6. Additional questions

1. How does the amount of precursors affect the final product size?
2. If you add less seed in part 2 syntheses, would you expect the diameter of the product to increase or decrease? Explain.
3. Combined with spectroscopy results and complementary color theory, explain the observed color of Au nanoparticle seed solution and that of seed-mediated growth of Au nanoparticle solution in Figure 3. Please provide comprehensive explanation.

References

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