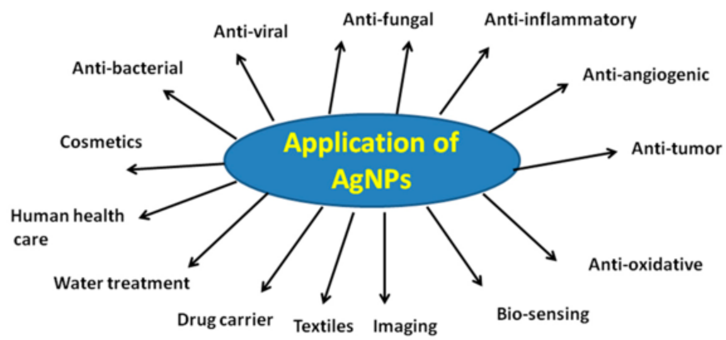
Exploring Silver Nano-particles



Applications of silver nanoparticles. Information from "Silver Nanoparticles: Synthesis, Characterization, Properties, Applications, and Therapeutic Approaches" Xi-Feng Zhang, Zhi-Guo Liu, Wei Shen, Sangiliyandi Gurunathan, Int. J. Mol. Sci. **2016**, 17(9), 1534. doi:10.3390/ijms17091534

As this is the last experiment, you should form groups of 3-4 and present your results at the end of lab in a presentation (see Rubric). Discussion among groups is highly encouraged.

Introduction: This experiment is based on an article and procedure published as "Sweet Nanochemistry: A Fast, Reliable Alternative Synthesis" by Jason Cooke, Dominique Hebert, and Joel A. Kelly published in the Journal of Chemical Education, **2015**, 92, 345−349, dx.doi.org/10.1021/ed5004756. (This introduction was taken and based-on the lab procedure associated with this article.)

Silver nanoparticles had been used for centuries before their true nature had been recognized, most widely as the brilliant yellow color in stained glass and related products. More recently, it has been understood that the color of the nanoparticles resides in a phenomenon known as *surface plasmon resonance*. Although this is a fairly complicated concept, surface plasmon resonance can be qualitatively understood as the absorption of light by oscillating electrons in the conduction band at the surface of the nanoparticle. Essentially, as the electric field of the incident light interacts with the delocalized conduction electrons, light is absorbed and the nanoparticle suspension takes on a characteristic color. The oscillation frequency, and hence observed color, is affected by a variety of factors including the *size* and *shape* of the nanoparticles.

Silver nanoparticles can be formed in aqueous solutions of dissolved salts such as silver nitrate by reaction with reducing agents under carefully controlled conditions, e.g., slow addition of aqueous silver nitrate ($AgNO_3$) to an excess of sodium borohydride ($NaBH_4$) at 0 °C. The excess borohydride ions (BH_4^-) serve to encapsulate the Ag nanoparticles and form spheres of 12 ± 2 nm diameter.

When the reaction is successful, a yellow colloidal suspension results. A colloidal suspension (also called a sol) is composed of very small particles in a liquid medium. It therefore differs from a solution. The absorption maximum of a colloidal suspension tends to shift to longer wavelengths and becomes broader when aggregation occurs to form particles of larger diameter.

The stability of the suspended nanoparticles has been ascribed to the adsorbed layer of borohydride "capping" ions, which lends a negative charge to the surface of the silver nanoparticles. The resulting electrostatic repulsion prevents the nanoparticles from aggregating into spheres of larger sizes. Nevertheless, silver nanoparticles produced in this manner can be short-lived, and often require additional stabilization through use of reagents such as polyvinylpyrrolidone (PVP) if they are to survive for long periods.

In 2003, a "completely green" synthesis of silver nanoparticles was reported as a prestigious communication in the Journal of the American Chemical Society. Green synthesis typically strives for sustainable chemical synthesis through the use of *nontoxic reagents, environmentally benign solvents*, and *renewable materials* wherever possible. Minimization of energy use and waste generation are also important principles. In the context of silver nanoparticles, a green synthesis would be of particular interest if a biomedical application was envisioned, and would seek to replace sodium borohydride with a more benign reducing/capping agent. In the aforementioned article, the authors reported preparing a yellow sol of spherical silver nanoparticles of approximately 3 – 8 nm diameter by gently warming an aqueous solution of $AgNO_3$, β-D-glucose and soluble starch overnight at 40 °C under an atmosphere of argon. The authors proposed that the soluble starch matrix was important in forming size-confined, nanosized pools that could serve as sites for nanoparticle formation. The presence of starch was also proposed to stabilize the nanoparticles and prevent aggregation.

Starch is the second most abundant biomolecule on earth and is predominantly composed of the branched amylopectin and linear chain amylose polymers of glucose (Figure 1). Amylose adopts left-handed helical structures in the solid state (Figure 2), but whether dissolved starch retains this structure or adopts a more random coiled arrangement has been a subject of some debate. The largest central cavity available in the amylose helices has a diameter of about 0.4 nm, which is large enough to accommodate small molecules such as iodine and n-butanol. However, this is at least an order of magnitude less than the diameter of the smallest silver nanoparticles that are expected, and so it is clearly not possible for the nanoparticles to form and remain within the tight helices. Rather, it is likely that the flexible arrangement of the amylose chains in solution and abundance of hydroxyl groups create protected areas that encapsulate the nanoparticles as are produced, thereby providing protection against further aggregation and particle growth.

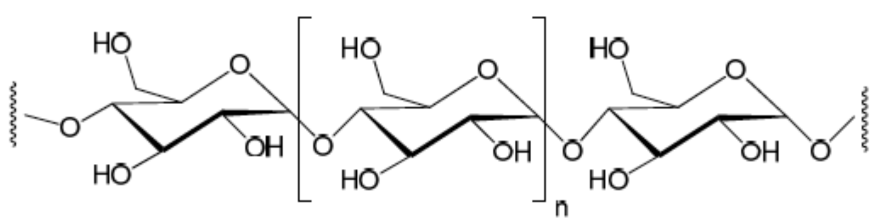


Figure 1. The structure of amylose comprised of repeating glucose units.

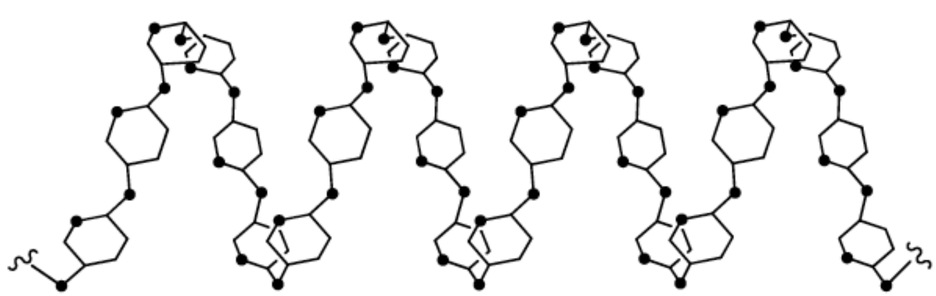
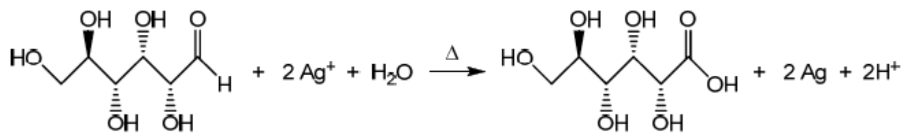


Figure 2. A depiction of the helical structure of amylose adopted in the solid state. For clarity, only ring atoms are shown. Oxygen atoms are represented by •.

Glucose is an example of a reducing sugar, which contains an aldehyde function in its linear form that can be oxidized to a carboxylic acid under the correct conditions. In neutral water, the process can be depicted as:



As starch is fundamentally a polymer comprised of glucose units, it is logical to include the monomeric reducing sugar to act as the reducing agent for the synthesis of the nanoparticles. In the absence of added glucose, we would have to rely upon the hydrolysis of starch to produce the glucose necessary to reduce Ag+; this is typically a slow process and would require either longer reaction times than are feasible for the undergraduate laboratory or higher temperatures that would only be attainable within a sealed bomb. As the above chemical equation suggests, the oxidation of glucose produces two equivalents of acid. The production of silver nanoparticles has been found to be pH dependent, with the best results occurring in neutral or mildly basic water. Therefore, it is important to include a buffer (sodium citrate in the present case) to neutralize the acid that is produced. The sodium citrate that is added can also act as a capping agent to stabilize the surface of the silver nanoparticles as they form. Although the citrate anion is also a mild reducing agent, it is neither as fast to act nor as reliable as glucose in the present synthesis under consideration.

Taking the above into account, it is therefore of interest to investigate whether silver nanoparticles can form in the absence of starch, and to study their relative stability compared to silver nanoparticles produced with starch present. This can be conveniently achieved by adding a solution containing an electrolyte such as NaCl, whose presence tends to disrupt the protective capping layer and cause aggregation into particles of larger size.

The silver nanoparticles you will prepare in today's lab can be characterized by measuring the UV-vis absorption spectrum. The average diameter of the silver nanoparticles can be estimated by the wavelength of the maximum absorption as shown in the left side figure below. The effect of the addition of salt to the colloidal suspension of silver nanoparticles can also be assessed by UV-vis spectroscopy as shown in the right-side figure below.

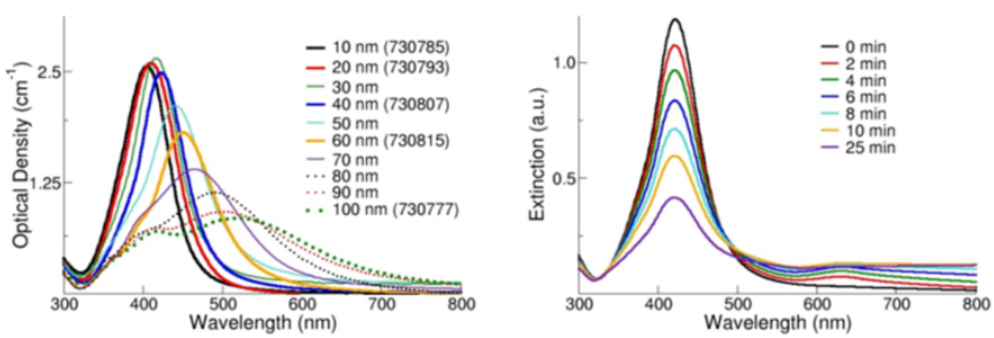


Figure 3. (Left) Extinction (scattering + absorption) spectra of silver nanoparticles with diameters ranging from 10-100 nm at mass concentrations of 0.02 mg/mL. (Right) Extinction spectra of silver nanoparticles after the addition of a destabilizing salt solution.

From: http://www.sigmaaldrich.com/technical-documents/articles/materials-science/nanomaterials/silver-nanoparticles.html (accessed 11/9/2019)]

Pre-lab assignment (20 pts)

In your lab notebook:

1. Write a brief (2-3 sentence) introduction to the lab.
2. Create a safety information table including the chemicals used in the lab, the hazards associated with them, and any safety handling precautions.
3. Briefly describe the relationship between average particle size and wavelength of absorption.
4. Briefly describe the effect of adding salt on the absorption spectrum of the silver nanoparticle suspension.

Materials:

Chemicals:	**Supplies & Equipment:**
D-(+)-glucose, ACS reagent	IR thermometer (used for the laser pointer)
Silver nitrate, ACS reagent	UV-Vis Spectrometer
Starch, soluble, ACS reagent	UV-Vis cuvettes and cuvette holders
Trisodium citrate dihydrate, ACS reagent	Weighing paper
1M Sodium Chloride	
FD&C Yellow Dye #5	

Waste Disposal and Clean-Up:
All aqueous waste from the experiment must be placed in the designated silver recovery container and must not be rinsed down the sink.

Experimental Procedure

The following procedure was modified from material accompanying the Journal of Chemical Education article "Sweet Nanochemistry: A Fast, Reliable Alternative Synthesis" (**2015**, 92, 345−349).

I - Synthesis of silver nanoparticles

1. Weigh about 0.03 g of soluble starch onto a weighing paper and transfer to a clean 25 mL Erlenmeyer flask. **It is important to begin with a clean flask in order to avoid contaminating the reactions, wash the flask thoroughly if necessary.**
2. Add about 8.0 mL of 3.75×10^{-4} M aqueous silver nitrate solution to the Erlenmeyer flask.
3. Gently heat the flask until the starch is dissolved.
4. Using a clean, plastic syringe add about 1.5 mL of a 1.25×10^{-2} M aqueous sodium citrate solution to the Erlenmeyer flask.
5. Using a clean, plastic syringe (do not cross contaminate the syringe), add about 0.50 mL of a 0.10 M aqueous D-glucose solution to the Erlenmeyer flask.
6. Heat the solution in the flask to a gentle boil. Continue heating until a deep yellow solution forms (i.e. at this point, stop heating). Allow the flask to cool to room temperature.

Note: if no color change is observed, it is probably caused by the presence of acid or another contamination that was present in your flask from the beginning. If this occurs, rinse your flask thoroughly and try again.

II- Characterization of silver nanoparticles

1. **Measure out 5 mL of your solution into a graduated cylinder. Add 5 mL of distilled water to the graduated cylinder and mix thoroughly. Use this 1:1 dilution for the next step. Save your remaining solution for part III.**
2. UV-Vis spectrum: record the UV-vis spectrum in a plastic cuvette following the directions given below.

Procedure for obtaining a UV-Vis spectrum

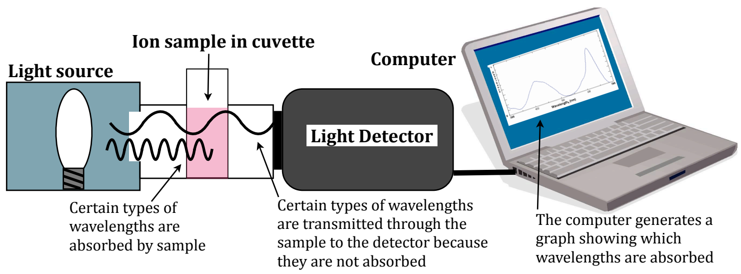


Figure 4. UV-Visible Spectrometer: components include a light source, a sample, and a detector.

A UV-vis spectrometer has a UV-vis light source, a sample compartment (which holds the sample), and a detector in a linear arrangement. UV-vis measurements are made by placing solutions into cuvettes, which are in turn placed into the sample compartment of the instrument. When a UV-vis spectrum is acquired, light passes through the sample, and the instrument records how much light was absorbed by the sample.

The instructions below will allow you to obtain a spectrum which will automatically be uploaded into your ICN account.

1. Obtain 2 similar, clean, dry cuvettes and a cuvette holder. Handle cuvettes with gloves so they stay clean.
2. Fill one of the cuvettes half full with distilled water. Label the cuvette, “blank.”
3. Fill another cuvette half full with the silver nanoparticle solution.
4. Place the cuvettes into the holder, cap them, and take the cuvettes along with your lab notebook to a UV-vis spectrometer.
5. Record the instrument name and number in your lab notebook. Ask your laboratory instructor to point out the parts of the spectrometer to you.
6. Using the spectrometer:
   a) First, you will need to blank the instrument. Pick up the cuvette containing distilled water. Use a Kim wipe to clean the cuvette of smudges and then place it in the spectrometer sample holder.
   b) Enter your ICN account name in the account box (the same one that you use to access your Progress Page). If the box is not shown, press the ~ key.
   ***use keyboard only, never use mouse or touchpad.**
   c) Press the *ENTER* key and wait for a scan message.
   d) Insert sample and press the *SPACE BAR* to scan sample.
   e) Press the *SPACE BAR* again to accept the scan. Repeat steps ‘d’ and ‘e’ for other samples.
   f) When you are done with the scans, record the computer-generated file name of each spectrum in your notebook and indicate the sample that corresponds to the file name.
   g) Press the ~ key to save your files on the server

h) Wait for the final prompt and hit *ENTER*, this will set the program up for the next user.

When using the spectrometer, the UV-vis program conducts the following:

- scans your sample (between 200 and 900 nanometers).
- records the absorbance values at each of these wavelengths in a data file.
- generates a graphical representation (spectrum) of the data on the computer screen.
- sends this file to the ICN server in order to place a copy in your account.

The ICN program automatically saves your files, so you do not need to re-draw or record wavelengths and absorbances at this time.

III – The effect of NaCl on silver nanoparticles.

1. **To your remaining solution from Part I, step 6, add 1 mL of 1M sodium chloride. Mix thoroughly.**
2. **Measure out 5 mL of this solution into a graduated cylinder. Add 5 mL of distilled water to the graduated cylinder and mix thoroughly. Use this 1:1 dilution for the next step.**
3. UV-Vis spectrum: record the UV-vis spectrum in a plastic cuvette following the directions given above.
4. **Compare this spectrum to that obtained in Part II, step 2.**

3. Observe the Tyndall effect for your silver nanoparticles colloidal suspensions.

From Wikipedia: "The Tyndall effect, also known as Willis-Tyndall scattering, is light scattering by particles in a colloid or else particles in a very fine suspension. It is named after the 19th-century physicist John Tyndall." (https://en.wikipedia.org/wiki/Tyndall_effect accessed 11/8/2019).

a. To measure the Tyndall effect, obtain an infrared thermometer like the one shown here. Each thermometer has a built-in laser, that is used to align your measurement. We will only be using this feature of the infrared thermometer. When the trigger is depressed, the laser is activated. Avoid any eye contact with the laser; this can cause serious eye damage.

b. Fill a small glass vial with the silver nanoparticle solution. Using the laser pointer, direct the beam through the vial. The appearance of particles in solution are characterized by the laser beam being highlighted as a line as it goes through the vial. It may be helpful to view against a dark background.

c. Test for the Tyndall effect on a solution of yellow dye (that does not contain fine particles). Repeat the laser measurement. Record any differences you see between your silver nanoparticles solution and the yellow dye solution.

3. Design experiments to test the effect of starch, glucose and sodium citrate on the synthesis of silver nanoparticles. For example, repeat the synthesis of the silver nanoparticles omitting starch from the procedure. Note the color of the solution, record the UV-vis spectrum and test for the Tyndall effect. Then add a measured amount of 1 M NaCl, and observe the effect on the color of the solution, the UV-is spectrum and the Tyndall effect. Compare the results to the synthesis in the presence of starch.

Record your procedures and observations in your lab notebook for each experimental variation that you do. Discuss the possible role that each ingredient plays in the synthesis. You should discuss your results when you present the information to the rest of the class.

Rubric for the PowerPoint Presentation (your group can also present a poster – Ask your TA if your group interested in this option)

Title and Team Member Names (10 pts)	Your PowerPoint should contain: • Contains title • Authors (Team member names) • Date of experiment/presentation • Overview: brief statement/introduction about the poster

Data, Results, Evidence:
 	
Scientific data that supports the claim.
 	
(25 pts total)
	Your PowerPoint presentation should include a section that organizes data, results, and evidence. The goal of the section is to describe what your team did and what data was collected. Observations are important data to present.
	• **Questions – answer the following questions:**
	  o What is a nanoparticle?
	  o What is a colloidal suspension and how does it differ from a solution?
	• What is the Tyndall effect? **Investigation details, evidence for the silver nanoparticles:**
	  o Observations about any suspension of silver nanoparticles
	  o The effect of NaCl
	  o Evidence for synthesizing silver nanoparticles
	• **Size of silver nanoparticle:**
	  o Present any evidence that could be used to determine the size of the silver nanoparticle

Analysis of Evidence (Reasoning): **(30 pts total)**	Your presentation should address/analyze and discuss the results of the silver nanoparticles, including: • **Colloidal Suspensions:** Discuss how colloidal suspensions are different than solutions • **Tyndall effect**: Discuss how the Tyndall effect was used to characterize a colloidal suspension containing nanoparticles • **Nanoparticle:** Discuss the estimate of the size of the nanoparticle. What does average size mean? Discuss the error in the measurement. • **NaCl:** Discuss any evidence obtained about the effect of NaCl on the silver nanoparticles? • **Role of ingredients:** speculate on the role of different ingredients in making the silver nanoparticle
Claim(s): Statement(s), derived from evidence, using scientific reasoning. **(15 pts total)**	Your PowerPoint slides should present: • Any claims or conclusions