# Part 1: Silver Nanoparticle Synthesis and Spectroscopy

**Introduction:** This lesson is designed to familiarize students with the reduction synthesis of silver nanoparticles and to gain experience with characterization tools used in nanoscale science and engineering.

**Purpose and Objectives:** Students will learn about the differences in physical propoerties at the nanoscale as compared to the same materials at the macroscale. The students will demonstrate the appropriate use of a spectrophotometer and will convert between different units of measurement. This unit assists students in working with scale and unit conversion.

**Time required:**
Time: Two 50 minute classes. Part I can easily be completed in a 40 minute period. An additional 40 minute period will be necessary for Part II.

**Level:** High School Chemistry. This lab is designed for an advanced chemistry class, but may also be done with first year students. Prior experience with spectroscopy is recommended. Part 2 can also be used in biology classes.

**Big Ideas of Nanoscale Science:** Size Dependent Properties; Tools and Instrumentation

**Teacher Background:**
Nanoparticles are made of thousands of atoms of an element and are extremely small, ranging from1 to 100 nanometers (nm) in size. A nanometer is 1 billionth of a meter or $1x10^{-9}$. Nanoparticles often have different properties than those associated with the element at the macroscale. For example, silver, gold, and copper interact with light differently at the nanoscale which in turn affects the color. Nanoscale silver has been used as an antibacterial agent, and can even kill harmful strains of bacteria which are resistant to antibiotics. Silver nanoparticles have been used in the dressing of wounds, surgical masks, food packaging, water treatment, and even socks which prevent the growth of bacteria that cause foul odor. Because of the widespread us of nanosilver, it is important for students to understand its applications as well as potential problems. See the resource section for general information on Ag nanoparticles as well as the environmental implications.

Silver nanoparticles (AgNPs), or colloidal silver, will be synthesized in the presence of starch according to the following redox reaction:

$$2AgNO_{3\,(aq)} + C_6H_{12}O_{6(aq)} + H_2O_{(l)} \longrightarrow 2Ag_{(s)} + 2HNO_{3(aq)} + C_6H_{12}O_{7(aq)}$$

In this reaction, glucose ($C_6H_{12}O_6$) reduces the silver cations from the silver nitrate. As the silver metal forms, starch coats the outsides of the particles, preventing them from aggregating and forming larger particles. Nano-sized materials often have different properties than the bulk materials; for example, silver nanoparticles appear yellow. A visible spectrum of AgNP solution will be determined. This lab will help students understand that not only are nanoparticles extremely small but that their properties differ from the bulk material.



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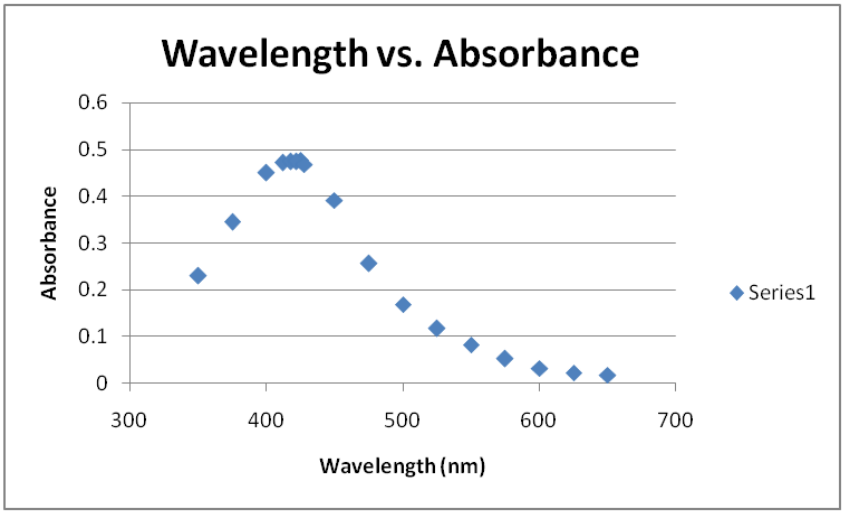


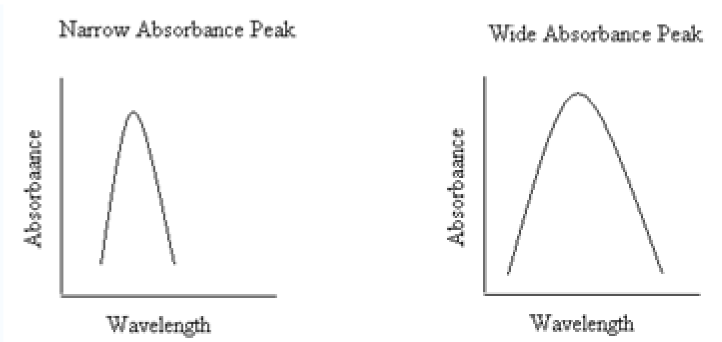


**Materials:**

**For Synthesis:**

- 0.1M $AgNO_3$ ($AgNO_3$ CAS 7761-88-8)
- 0.1M α-D-glucose (α-D-glucose CAS 50-99-7)
- 0.2% wt. soluble starch (soluble starch CAS 9005-84-9)
- 200 µL pipet
- 1000 µL pipet
- 10 mL pipet or graduated cylinder
- Hot plate
- Small Erlenmeyer flask or beaker
- Glass vials

**For Spectroscopy:**

- Droppers
- Spectrophotometer
- Cuvettes
- Kimwipes
- 0.2% wt. soluble starch for blank

**Advance Preparation:**

- To prepare 0.1M $AgNO_3$, dilute 1.6988g $AgNO_3$ (CAS 7761-88-8) to 100mL with deionized water.
- To prepare 0.1M glucose, dilute 1.8016g of glucose (CAS 50-99-7) to 100mL with deionized water.
- To prepare 0.2%wt. soluble starch, dissolve 0.4g soluble starch (9005-84-9) in 200mL deionized water.
- Schedule and arrange remote access to the AFM and Spectrophotometer

**Safety Information:**

- Wear safety goggles and chemical gloves when handling the chemicals
- Do not use a magnetic stir bar during the synthesis
- Have all MSDS printed and in the classroom

**Directions for the Activity:**

- Have students complete the activity following the steps outlined in the procedure section (in student guide with answers below)
- Remotely characterize the samples with the students using the facility at Pennsylvania State University (access information at end of lesson)
- Have the students record results on their worksheet
- Have students write a paragraph to describe the results of the experiment and their reflections on their experiences during this activity

**Cleanup:**

- Let hot plates cool before putting away
- Solutions can be disposed of according to local waste regulation

**Extensions:**

Add 1M NaOH dropwise to aggregate the particles, if desired. The synthesized silver nanoparticles may be used to do experiments on *E. coli* inhibition (Part 2). Students may also research practical uses of silver nanoparticles; they are currently used for their antimicrobial properties in products such as socks, food containers, and washing machines.

**Assessment**

- Work sheet answers should be correct and complete.

**Remote Characterization can be arranged:**

Visit: http://www.nano4me.org/educators.php for more information

**References:**

Kalaugher, L. (2004, January 12). *Green Technique Makes Silver Nanoparticles.* Retrieved July 3, 2007, from Nanotechweb.org: http://nanotechweb.org/articles/news/3/1/1/1

Liu, X., Atwater, M., Wang, J., & Huo, Q. (2006). Extinction coefficient of gold nanoparticles with different sizes and different capping ligands. *Colloids and Surfaces B: Biointerfaces*.

Raveendran, P. F. (2006). A Simple and "Green" Method for the Synthesis of Au, Ag, and Au-Ag Alloy Nanoparticles. *Green Chemistry* , 34-38.
Raveendran, P., Fu, J., & Wallen, S. L. (2003). Completely "Green" Synthesis and Stabilization of Metal Nanoparticles. *J. Am. Chem. Soc.* , 13040-13041.
*Silver Nanoparticles S-MITE*. (n.d.). Retrieved July 31, 2007, from American Elements: Silver Nanoparticles Supplier & Tech Info: www. americanelements.com/agnp.html#MSDS
Solomon, S. D., Bahadory, M., Jeyarajasingam, A. V., Rutkowsky, S. A., Boritz, C., & Mulfinger, L. (2007). Synthesis and Study of Silver Nanoparticles. *Journal of Chemical Education* , 322-325.

**Resources:**

- Silver as an antimicrobial agent: http://microbewiki.kenyon.edu/index.php/Silver_as_an_Antimicrobial_Agent#Current_uses
- Silver nanoparticles and the environment: http://pubs.acs.org/doi/abs/10.1021/es2001248
- Properties and Applications: http://www.sigmaaldrich.com/materials-science/nanomaterials/silver-nanoparticles.html
- Nanoparticles information: http://www.nanoparticles.org/
- Synthesis and Applications: http://www.sciencedirect.com/science/article/pii/S1878535210000377
- Environmental Impacts: http://cohesion.rice.edu/centersandinst/icon/emplibrary/ICON-Backgrounder_NanoSilver-in-the-Environment-v4.pdf and http://www.empa.ch/plugin/template/empa/*/70057/---/l

**Acknowledgements:**
National Nanotechnology Infrastructure Network
For more information, visit www.nnin.org.
Penn State Center for Nanotechnology Education and Utilization
For more information, visit www.cneu.psu.edu
Penn State Center for Science and the Schools
For more information, contact Bill Carlson at wsc10@psu.edu.
Science in Motion at Juniata College
For more information, contact Tara Fitzsimmons at fitzsit@juniata.edu

# Student Guide
# (with answers)

## *Silver Nanoparticle Synthesis and Spectroscopy*

**Introduction:** In this lab you will synthesize silver nanoparticles one of the most commonly used nanoparticles found in consumer products. Nanoparticles are made of thousands of atoms of an element and are extremely small, ranging from1 to 100 nanometers (nm) in size. A nanometer is 1 billionth of a meter or $1x10^{-9}$. Nanoparticles often have different properties than those associated with the element at the macroscale. For example, silver, gold, and copper interact with light differently at the nanoscale which in turn affects the color. Nanoscale silver has been used as an antibacterial agent, and can even kill harmful strains of bacteria which are resistant to antibiotics. Silver nanoparticles have been used in the dressing of wounds, surgical masks, food packaging, water treatment, and even socks which prevent the growth of bacteria that cause foul odor.

## Silver Nanoparticle Activity:

**Materials:**
**For Synthesis:**

- 0.1M $AgNO_3$ ($AgNO_3$ CAS 7761-88-8)
- 0.1M α-D-glucose (α-D-glucose CAS 50-99-7)
- 0.2% wt. soluble starch (soluble starch CAS 9005-84-9)
- 200 µL pipet
- 1000 µL pipet
- 10 mL pipet or graduated cylinder
- Hot plate
- Small Erlenmeyer flask or beaker
- Glass vials

**For Spectroscopy:**

- Droppers
- Spectrophotometer
- Cuvettes
- Kimwipes
- 0.2% wt. soluble starch for blank

**Procedure**
**Part 1. Synthesis of Ag Nanoparticles:**

1. Place 200 µL of 0.1M $AgNO_3$ into a small Erlenmeyer flask or beaker.
2. Add 500 µL of 0.1M glucose, making sure that it comes into contact with the $AgNO_3$.

3. Invert the starch solution several times. Add 10mL of the starch solution.
4. Heat the solution on a hot plate on a high setting until it is boiling vigorously. **Do not stir the solution!**
5. Boil the solution for 10 minutes. The solution should turn yellow.
6. Remove the sample from the hot plate, and let it cool.

**Part 2. Spectropshotometric Analysis of Ag Nanoparticles**

1. Turn on the spectrophotometer and allow it to warm up for the recommended length of time.
2. Put the instrument in Transmittance mode. With the sample compartment empty, set the dark current to zero.
3. Invert the starch solution several times. Fill a clean cuvette with the starch solution. Wipe the outside with a Kimwipe, then insert it into the sample compartment.
4. Set the wavelength at 350nm and zero the absorbance.
5. Insert a clean cuvette filled with the AgNP solution, and record the absorbance in the data section in Table 1.
6. Repeat steps 4 and 5 for different wavelengths; increasing the wavelength by 25nm each time until a reading is obtained for 650nm. Remember to zero the machine each time you change the wavelength. Record the data in **Table 1** of the data section.
7. Identify the wavelength from Table 1 with the highest absorbance. Use the spectrophotometer to collect additional absorbance readings by varying the wavelengths in that specific area of the spectrum to determine which gives the wavelength of maximum absorbance ($\lambda_{max}$). Record these observations in **Table 2** of the data section. (For example, if the maximum absorbance in Table 1 is at 500 nm, then test the absorbance of the AgNPs at 490, 495, 500, 505, and 510 nm, looking for the wavelength that gives the maximum absorbance).
8. Divide the absorbance at the $\lambda_{max}$ by 2 and record in **Table 3** of the data section as absorbance at ½ max.
9. Graph the data from Table 2 on a separate sheet of graph paper or in Excel.
10. Using the graph created in step 9, mark the maximum absorbance on the y-axis. Mark the ½ max. absorbance on the y-axis and find the corresponding wavelength on the x-axis.
11. Zero the spectrophotometer at the interpolated $\lambda_{1/2max}$ from step 10. Compare the absorbance of the AgNPs at the interpolated $\lambda_{1/2max}$ to the absorbance calculated in step 8. Adjust the wavelength on the spectrophotometer and record the absorbance of the AgNPs until a value close to the calculated value of the absorbance at $\lambda_{1/2max}$ from step 8 is obtained. Record this wavelength in **Table 3** as wavelength at ½ max.

## Calculations:

1. To determine the Peak Width at Half Max (PWHM), first subtract the $\lambda_{max}$ from the $\lambda_{1/2max}$. The difference is half the peak width. Multiply by 2 to get the PWHM.

   *PWHM = ($\lambda_{1/2max}$ - $\lambda_{max}$)*2*
   *PWHM = (480nm-425nm)*2*
   *PWHM = 110nm*

2. How many silver atoms are in one nanoparticle?
   Determine the average number of atoms per nanoparticle using the following formula:

$$N = \frac{\pi \rho D^3}{6\ M} N_A$$

N = number of atoms per nanoparticle

ρ = density of face centered cubic (fcc) silver = $10.5 g/cm^3$ (convert to $g/nm^3$)
D = average diameter of nanoparticles = 11nm
M = atomic mass of silver
$N_A$ = number of atoms per mole
Note: This equation is taken from Liu, Atwater, Wang, and Huo (see References.) It assumes that the nanoparticles have a spherical shape and a uniform fcc crystaline structure. **Be sure your units are consistent!**

*ρ must be converted to $g/nm^3$; $\rho = 1.05x10^{-20} g/nm^3$*
*D = 11nm*
*M = 108g/mol*
*$N_A = 6.022x10^{23}$ atoms/mol*
$N = [(\pi\rho D^3)/(6M)] * N_A$
$N = [(\pi (1.05 \times 10^{-20}) (11)^3) / (6(108))] * 6.022 \times 10^{23}$
$N = 4.08 \times 10^4$ atoms/NP

3. What is the concentration of your silver nanoparticle solution?

Determine the molar concentration of the nanoparticle solution using the following formula:

$$C = \frac{N_T}{NVN_A}$$

C = molar concentration of nanoparticle solution
$N_T$ = Total number of silver atoms added in $AgNO_3$
N = number of atoms per nanoparticle (determined in Calculation 2)
V = volume of the reaction solution in L
$N_A$ = number of nanoparticles per mole

$$N_T = 200\mu L AgNO_3 \left(\frac{1x10^{-6} L\ AgNO_3}{1\mu L\ AgNO_3}\right)\left(\frac{0.1 mol\ AgNO_3}{1L\ AgNO_3}\right)\left(\frac{1 mol\ Ag}{1 mol\ AgNO_3}\right)\left(\frac{6.022x10^{23} atoms\ Ag}{1 mol\ Ag}\right)$$

$N_T = 1.20 \times 10^{19}$ atoms Ag

Note: This equation is also taken from Liu, Atwater, Wang, and Huo (see References.) It assumes that the reduction of $Ag^+$ to $Ag^0$ was complete.

4. What effect might a large variance in particle size have on the width of the absorbance peak in the visible spectrum?

   *Different sized nanoparticles will absorb different wavelengths of light. A large variance in particle size will result in a wider absorbance peak. A Peak Width at Half Max (PWHM) of 100 or less would indicate a fairly uniform distribution of particle sizes.*

5. Name a physical property of silver that changes at the nanoscale.

   *The color of silver changes; this procedure produces yellow silver nanoparticles (AgNPs). The melting point of silver also drops at the nanoscale.*

## Sample Data:

**Table 1**

| Wavelength (λ) (nm) | Absorbance |
|---|---|
| 350 | 0.230 |
| 375 | 0.345 |
| 400 | 0.450 |
| 425 | 0.478 |
| 450 | 0.392 |
| 475 | 0.257 |
| 500 | 0.169 |
| 525 | 0.118 |
| 550 | 0.083 |
| 575 | 0.053 |
| 600 | 0.033 |
| 625 | 0.023 |
| 650 | 0.018 |

**Table 2**

| | Wavelength (nm) | Absorbance |
|---|---|---|
| $\lambda_{max}$ | 425 | 0.478 |
| $\lambda_{1/2max}$ | 480 | 0.239 |

**Table 3**

| Wavelength (λ) (nm) | Absorbance |
|---|---|
| 412 | 0.472 |
| 418 | 0.474 |
| 422 | 0.474 |
| 428 | 0.468 |
| | |
| | |
| 480 | 0.243 |
| 483 | 0.232 |
| 481 | 0.236 |
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