Expt. 17: Investigating Silver Nanoparticles

INTRODUCTION

Nanomaterials are materials which typically have length scales on the order of 1-100 nm in at least one dimension. Examples include nanoparticles, nanowires, and thin films. The observed properties of materials change as their sizes approach nano-scale. An easily observable example is color change between bulk-scale and nano-scale materials. One historically relevant case is the production of gold stained glass in medieval architecture. Artisans would create red glass by mixing in small amounts of nanoscale gold particles during the manufacturing process, resulting in a ruby color [1].

Silver nanoparticles (AgNPs) are another widely studied nanomaterial. AgNPs are known for their antibacterial properties, which is of interest in the health industry, textiles, food-storage, and several environmental applications. The electrochemical properties of AgNPs are also useful for the development of faster and more sensitive nanoscale sensors [2]. As you will see in this lab, silver nanoparticles can be used to create yellow glass.

This lab analyzes a colloidal silver solution synthesized via chemical reduction using silver nitrate and sodium borohydride, which is given by the following chemical equation:

$$AgNO_3 + NaBH_4 \rightarrow Ag + \frac{1}{2} H_2 + \frac{1}{2} B_2H_6 + NaNO_3$$

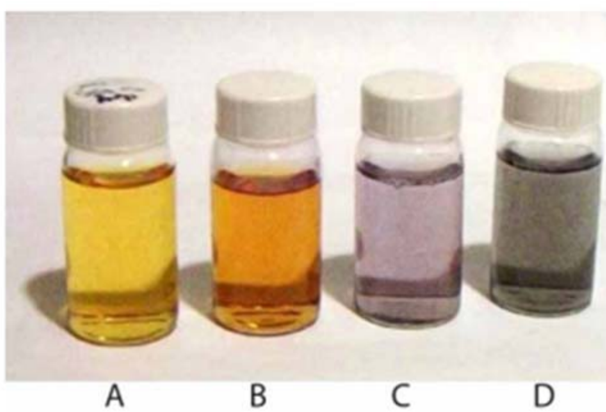

Figure 1. Colloidal silver in various stages of aggregation, (A) clear yellow, (B) dark yellow, (C) violet, and (D) gray solutions, as aggregation proceeds from a colloidal to aggregated solution. [1]

As AgNPs begin to form, the solution turns yellow. As the particles aggregate together to form larger and larger particles, the solution will begin to turn violet and eventually gray (Figure 1). To prevent aggregation, the silver nanoparticles can be stabilized, i.e. kept from precipitating out of solution, by a protective layer of borohydride ions. Particles can also be stabilized with a polymer coating such as polyvinyl pyrrolidone (PVP).

Absorption measurements can be used to determine the size of the nanoparticles. Using a spectrophotometer, the wavelength at the maximum absorbance can be determined, as can the peak full width at half the absorption maximum (FWHM). This can then be compared to literature values to estimate the size of the nanoparticles. An example of how to determine FWHM is shown in Figure 2.

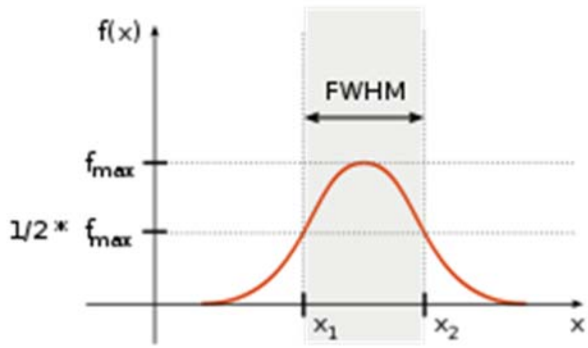

Figure 2. Determination of full peak width at half peak maximum. [3]

Typically, spectrophotometers measure % Transmittance, which can be correlated to absorbance using the equation $A = 2 - \log_{10} \%T$.

PROCEDURE

Part 1 Synthesis of Colloidal Silver

1. Pour 30 mL 0.002 M $NaBH_4$ into 250 mL Erlenmeyer flask in an ice bath, allow to cool for 20 min.
2. Begin stirring the solution using a stir bar and stir plate
3. Add 10 mL 0.0010 M $AgNO_3$ dropwise at about 1 drop/second (~3 minutes). Solution should be yellow after approx. 2mL.
4. Stop stirring immediately and remove stir bar.
5. Record appearance after stirring is stopped and again after 5 minutes.
6. After the silver particle solution is prepared, store it in an ice bath to slow down the aggregation process and keep your particle size constant.

Part 2 Measuring size of Silver Particles

1. Place 1 mL of distilled water into a cuvette (it's a bit like a test tube) and measure % transmittance (%T) at a wavelength of 400 nm. This number is used to calibrate the machine and will be subtracted from your other measurements.
2. Place 1 mL of colloidal silver into a cuvette and take a new %T measurement at 400 nm and convert to absorbance. If this number is not between 0.5 and 1, dilute the product with distilled water and repeat until the absorbance is between 0.5 and 1. (Like the class demo)

a. *Example: if the absorbance of 1 mL of solution is 2, and the desired absorbance is between 0.5 and 1, the solution needs to be diluted by at least 100%. This means you add 1-3 mL to achieve the correct dilution.*

3. Measure %T of the diluted colloidal silver solution in 5 nm wavelength increments from 350 to 430 nm, and in 10 nm increments from 430 to 640 nm.

4. Convert %T to absorbance (A) and record in the table below.

Silver solution			**Silver solution**			**Silver solution**		
λ nm	%T	A	λ nm	%T	A	λ nm	%T	A
350			415			530		
355			420			540		
360			425			550		
365			430			560		
370			440			570		
375			450			580		
380			460			590		
385			470			600		
390			480			610		
395			490			620		
400			500			630		
405			510			640		
410			520					

Part 3 Aggregation and stabilization

1. Pour 2 mL of yellow nanoparticle solution into test tube then add **1 drop** of 1.5M NaCl and record any change.

2. Place 1 mL of solution from step 1 into a cuvette, measure %T at 400 nm, and convert to absorbance. If this number is not between 0.5 and 1, dilute with the distilled water using the same procedure as in Part 2.

a. *Example: if the absorbance of 1 mL of solution is 2, and the desired absorbance is between 0.5 and 1, the solution needs to be diluted by at least 100%. This means you add 1-3 mL to achieve the correct dilution.*

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365			430			560		
370			440			570		
375			450			580		
380			460			590		
385			470			600		
390			480			610		
395			490			620		
400			500			630		
405			510			640		
410			520					

5. Using another test tube, **add 1 drop** of 0.3% polyvinyl pyrrolidone solution and then pour 2 mL of yellow nanoparticle solution into test tube then add **1 drop** of 1.5M NaCl and record any change in the table below.

6. Using another test tube, **add 1 drop** of 0.3% polyvinyl pyrrolidone solution and **1 drop** distilled water and then pour 2 mL of yellow nanoparticle solution into test tube then add **1 drop** of 1.5M NaCl and record any change in the table below.

7. Using another test tube, **add 1 drop** of 0.3% polyvinyl pyrrolidone solution and **2 drops** distilled water and then pour 2 mL of yellow nanoparticle solution into test tube then add **1 drop** of 1.5M NaCl and record any change in the table below.

8. Repeat step 7, increasing the number of drops of water until an observable change occurs. Record the final number of drops of water added. This number corresponds to the minimum concentration of polyvinyl pyrrolidone required to stabilize the silver nanoparticles.

PVP Concentration (Mass %)	Color upon addition of 1.5 M NaCl, and other observations
0	
0.3%	
0.15%	
0.075%	
0.0375%	
0.001875%	

What is the minimum stabilizing concentration of PVP? ____________ %

POSTLAB QUESTIONS

1. Write the REDOX half-reactions for the synthesis of silver nanoparticles, shown below (note: more than one element may be oxidized or reduced). When writing the REDOX reactions note that because hydrogen is more electronegative than boron it takes on a negative oxidation number.

$$AgNO_3 + NaBH_4 \rightarrow Ag + \frac{1}{2} H_2 + \frac{1}{2} B_2H_6 + NaNO_3$$

OX:
RED:

2. What is the limiting reactant?

3. a) Use Excel to plot two absorbance vs wavelength graphs from the tables you completed in Part 1 and Part 3.

b) Determine λ_{max} from the tables you completed in Part 1 and Part 3.

c) Determine full peak width at half maximum height (FWHM) from each of your graphs.

d) Comparing your results to the table below, which particle size (nm) correlates best to your λ_{max} and FWHM for your solutions from Part 1 and Part 3?

Part 1:
Part 3:

Comparing particle size to λ_{max} and FWHM [1]:

Particle Size (nm)	λ_{max} (nm)	FWHM (nm)
10-14	395-405	50-70
35-50	420	100-110
60-80	438	140-150

4. Did you see any change in the appearance of your experiment after Part 3 Step 1? What did this change mean?

5. What is a reason for different colors being observed in the same nanoparticle solutions?

BONUS QUESTION

6. Comment on why you see different properties in the same material just by changing from bulk to nano-scale?

REFERENCES

[1] L. Mulfinger, S.D. Solomon, M. Bahadory, A.V. Jeyarajasingam, S.A. Rutkowsky, and C. Boritz, Journal of Chemical Education 84, 322 (2007).

[2] K.M.M. Abou El-Nour, A. Eftaiha, A. Al-Warthan, and R.A.A. Ammar, Arabian Journal of Chemistry 3, 135 (2010).

[3] http://en.wikipedia.org/wiki/Full_width_at_half_maximum