#29   Synthesis and Study of Colloidal Silver

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Purpose: Colloidal silver is synthesized and its visible spectrum used to find the size of the silver nanoparticles.

Background:

Nanotechnology deals with processes that take place on the nanometer scale, that is, from approximately 1 to 100 nm. Properties of metal nanoparticles are different from those of bulk materials made from the same atoms. For example, silver metal is grayish, but colloidal silver from this synthesis is a clear yellow. The striking effect of nanoparticles on color has been known since antiquity when tiny metal particles were used to color glass in church windows. Silver particles stained the glass yellow, while gold particles were used to produce ruby glass.

Synthesis of Colloidal Ag
Colloidal silver is made by adding an excess of the reducing agent sodium borohydride, $NaBH_4$ to silver nitrate, $AgNO_3$.

$$AgNO_3 \ + \ NaBH_4 \ \rightarrow \ Ag \ + \ 1/2H_2 \ + \ 1/2B_2H_6 \ + \ NaNO_3$$
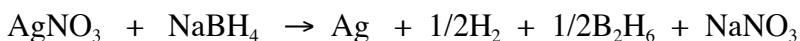
The method used in the procedure for this experiment produces nanoparticles that are about 10-14 nm in diameter. The transmission electron microscope (TEM) image shown corresponds to a sample of silver nanoparticles with diameters that are 12 ± 2 nm. (The length bar is 20 nm.) Particle size can also be determined using visible spectroscopy.
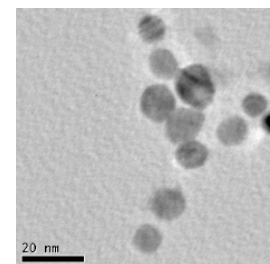
Spectroscopy and Size of Nanoparticles
For the 12 nm Ag nanoparticles, the maximum wavelength is near 400 nm. In general, as the particles become larger the absorption maximum shifts to longer wavelengths

Apparatus: You will be taking a spectrum of the colloidal silver sol. (Colloidal dispersions of insoluble materials (e.g. silver nanoparticles) are called sols).   Refer to the operating instructions. If you are using a Spectronic-20, record %T (easier to read) and convert to A.

Safety and Waste Disposal: Safety glasses are _always_ required in the laboratory. Gloves _must_ be worn throughout this experiment. Silver nitrate is caustic and stains the skin. A container will be made available for any waste solutions.

Procedure:
Glassware was cleaned by soaking in an alcoholic KOH bath, and is ready to use.
Part A   Synthesis of Colloidal Silver
1. Two solutions will be available.
0.0010 M $AgNO_3$(aq) and 0.0020 M $NaBH_4$ (aq)

2. Using a graduated cylinder, pour 30 mL 0.0020 M sodium borohydride into the 250 mL Erlenmeyer. Place the Erlenmeyer into an ice bath. Allow to cool for 20 minutes.

3. Place a stir bar in the Erlenmeyer, center the assembly on the stir plate and begin the stirring.

4. Pour 10 mL 0.0010 M $AgNO_3$ in a buret supported with a clamp and a ring stand. Add the solution dropwise, about 1 drop/second, until it is all used up. After 2 mL has been added, the solution should turn light yellow. When all (or most) of the silver nitrate has been added, the solution should be a darker, medium yellow. This should take around 3 minutes.

5. *Stop the stirring as soon as the silver nitrate solution is added* and remove the stir bar. **CAUTION**: If the stirring is continued once all the silver nitrate has been added, aggregation is likely to occur; the yellow darkens, turns violet, then grayish as the particles settle out.

6. The product should be clear yellow once the reaction is completed and should remain yellow, although it may darken somewhat. Record the appearance of your product as soon as the stirring is stopped and after waiting for about 5 minutes. If your product has aggregated and turned gray---repeat the synthesis if possible. Otherwise, a sample will be provided for you to complete part B.

Part B. Taking the Spectrum of Colloidal Silver
1. The peak absorbance (A) near 400 nm should be between 0.5 and 1. Start by testing your sample at 400. If A is less than 1, continue and take the whole spectrum from 350 to 600 nm (See Step B.**2**). If A at 400 nm is > 1, dilute your sample, starting with 1 part water to 1 part sample. You can do this by pouring out half the sample (into a marked waste bottle) and replacing it with distilled water then swirling the cuvette to mix. *You can estimate half the amount by eye*. Measure the value of A at 400 again. If A is still > 1, dilute again by removing half the sample and replacing with water. Describe the dilution process you used on the data sheet.

2. When A is < 1, you can measure the % transmittance (Spectronic-20) every 10 nm between 350 nm and 600 nm, except near 400 nm, where you should record %T every 5 nm. Pour the diluted colloidal Ag solution into the marked waste bottle.

 3. Convert % T to A. Make a plot of absorbance (A) vs. wavelength (λ), by drawing a smooth curve through the points .

4. Record the wavelength of the peak absorbance, λmax.

Data and Results (Colloidal Ag)

Name(s) _____   Date _____

Part A   Synthesis of Colloidal Silver

Record appearance of your product.

Part B. Taking the Spectrum of Colloidal Silver

1. Dilution:

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

λmax   _____ nm

Questions

1. Write the half reaction for the reduction of silver ion to elemental silver.

2. Estimate the number of silver atoms in a 12-nm Ag nanoparticle. Assume that each silver atom occupies the volume of a cube with an edge of 0.3 nm. (Volume of a sphere = $4/3 \, \pi \, r^3$)

3. Which reactant, silver nitrate or sodium borohydride, is in excess? Give a reason for this. Find the relative number of moles of excess to limiting reactant.

$$AgNO_3 \; + \; NaBH_4 \; \rightarrow \; Ag \; + \; 1/2H_2 \; + \; 1/2B_2H_6 \; + \; NaNO_3$$

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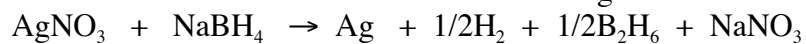
Instructor Notes
(Synthesis and Study of Colloidal Ag)

Time: 1.5 to 2 h (2 h if the synthesis needs to be repeated)

Equipment and Materials (assuming that students work in groups of 2)

Items	per group	Comment
250-mL Erlenmeyer	1	Reaction vessel (precleaned)
Buret, clamp ,ring stand	1	For adding silver nitrate
50-mL graduate	2	To measure 30-mL borohydride solution and prepare dilutions of product and PVP
Stir plate/bar	1	Heating will not be needed.
0.0010 M$AgNO_3$(aq)	10 mL	For one synthesis reaction
0.0020 M $NaBH_4$ (aq)	30 mL	For one synthesis reaction
ice		
Spectronic-20	1 *	* if there are not enough spectrometers, groups can share; one group can work on aggregation while the other takes a spectrum
Cuvettes	2	1 for sample and 1 for blank
Beaker or test tube rack	1	if needed--to hold the cuvettes upright

All solutions will be provided.
0.0010 M $AgNO_3$: Add 0.170 g $AgNO_3$ to a 1-L volumetric and dilute to the mark with distilled water. (Molar mass of $AgNO_3$ is 170).
0.0020 M $NaBH_4$ (aq): Add 0.0378 g sodium borohydride* to a 500 mL volumetric and dilute to the mark with distilled water. (Molar mass of $NaBH_4$ is 37.8).

*   Occasionally the purity of "99% sodium borohydride" could be lower for a particular batch #. Using a newly purchased bottle of sodium borohydride, we found that every attempt to repeat the synthesis failed and resulted in aggregated product. When we contacted Aldrich we were informed that the purity of that particular batch was only 98.39, compared to all other batches that we used which were 98.9%. Instead, you can use the somewhat more expensive 99.995% sodium borohydride.
To purchase from Aldrich:
48,088-6 sodium borohydride granules 99.995%   25 g $45
21,346-2 sodium borohydride 99%   25 g $27
Cleaning Glassware
Alcoholic KOH bath: 1 L 95% ethanol + 120 mL water + 120 g KOH.
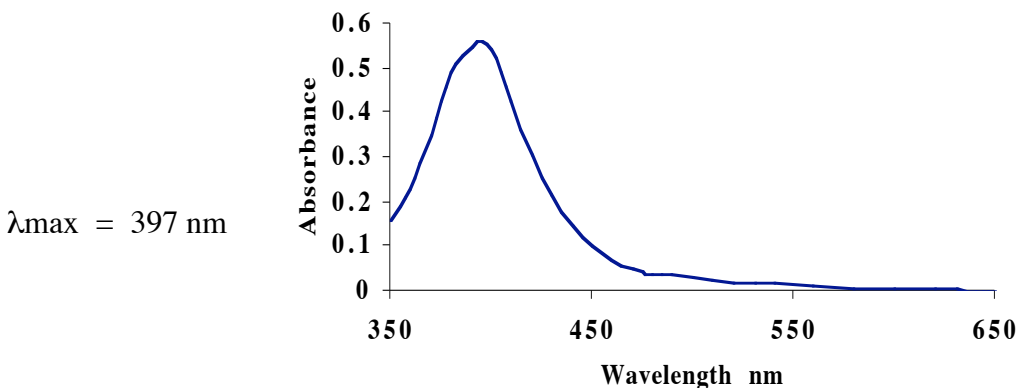
Typical Results:

Part A   Clear yellow colloidal silver will keep for weeks, even months, when stored in a transparent vial.
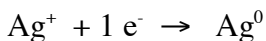
Part B. Taking the Spectrum of Colloidal Silver

Dilution: Could be anywhere from 1:1 to as much as 8:1 (water: AgNP sample)

Spectrum:

λmax = 397 nm

Answers to Questions

1. Write the half reaction for the reduction of silver ion to elemental silver.
$Ag^+ + 1\ e^- \rightarrow Ag^0$

2. Estimate the number of silver atoms in a 12-nm Ag nanoparticle. Assume that each silver atom occupies the volume of a cube with an edge of 0.3 nm. (Volume of a sphere = $4/3\ \pi\ r^3$)

Volume spherical nanoparticle = $4/3\ \pi\ 6^3$ nm^3; Volume of a gold atom is about 0.3 nm^3
Number of atoms = $\dfrac{4/3\ \pi\ 6^3\ nm^3}{0.3^3\ nm^3}$ = 33,000   or about 30,000 to 35,000 atoms

(Note: The diameter of a gold atom is 0.288 nm)

3. Which reactant, silver nitrate or sodium borohydride, is in excess?   Give a reason for this. Find the relative number of moles of excess to limiting reactant.

$AgNO_3 + NaBH_4 \rightarrow Ag + 1/2H_2 + 1/2B_2H_6 + NaNO_3$
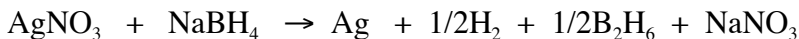
2.0 mmol NaBH$_4$/L x 0.030 L = 0.060 mmol NaBH$_4$
1.0 mmol AgNO$_3$/L x 0.010 L = 0.010 mmol AgNO$_3$

Sodium borohydride is in excess. This is needed to stabilize the Ag nanoparticles. There is a 6-fold excess of sodium borohydride.