

# Synthesis and Study of Silver Nanoparticles

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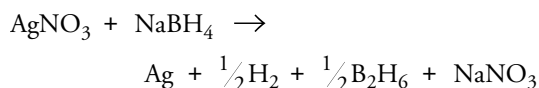
A laboratory experiment is described in which students synthesize yellow colloidal silver, estimate particle size using visible spectroscopy, and study aggregation effects. This experiment, which can be included in the general chemistry laboratory course, introduces students to nanotechnology while reinforcing topics such as redox chemistry, limiting and excess reactants, spectroscopy, and atomic size. The experiment has also been made available for advanced high school classes through the Science in Motion outreach program.<sup>1</sup>

## 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, 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 make ruby-colored glass. In performing the experiment described here, students will observe the bright yellow color of silver nanoparticles compared to colorless silver nitrate solution and metallic bulk silver.

The determination of an optimal set of conditions for the synthesis of silver nanoparticles is described in the sections that follow. The easy and convenient method uses dilute aqueous solutions, can be done on the bench top, and requires simple equipment such as the Spectronic-20 spectrophotometer and a magnetic stir plate.

The chemical reaction is the sodium borohydride reduction of silver nitrate:



The method produces  $12 \pm 2$  nm particles. The plasmon absorbance is near 400 nm and the peak width at half maximum (PWHM) is 50–70 nm. How the student experiment was developed is described below in detail, including the use of transmission electron microscopy (TEM) to find the size of particles that corresponded to the visible spectrum of the product. (Depending on the availability of the instrument, the TEM material could be expanded in an experiment for an upper-level course.) The relationship between aggregation and optical properties was determined along with a method to protect the particles using polyvinylpyrrolidone. Results obtained in two general chemistry laboratory classes (25 student pairs) are given along with student reactions to the experiment.

## Synthesis of Yellow Colloidal Silver

Studies of wine-red colloidal gold have been described in this *Journal* (1, 2). In designing an experiment involving the synthesis of noble metal nanoparticles for a multi-section general chemistry class, cost was an important consideration. Since the hydrogen tetrachloroaurate(III) trihydrate,  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  used to prepare colloidal gold is about 25 times more expensive than silver nitrate<sup>2</sup> the experiment chosen for development was the synthesis and study of colloidal silver.

A multitude of chemical reduction methods have been used to synthesize silver nanoparticles from silver salts. The reactions considered here were limited to those using silver nitrate as the starting material. They vary in the choice of reducing agent, the relative quantities and concentrations of reagents, temperature, duration of reaction, as well as the diameters of the nanoparticles produced. In nearly all of them the colloidal silver products are described as turbid and greenish-yellow or brown (3–5). Yellow colloidal silver has been reported upon reaction with ice-cold sodium borohydride (6) and is the basis for the method used in the experiment described next.

The synthetic method developed for this experiment consistently produces a stable yellow colloidal silver,<sup>3</sup> provided the conditions are properly controlled. The silver nitrate (>99%  $\text{AgNO}_3$ ) and sodium borohydride (99%  $\text{NaBH}_4$ ) were purchased from Aldrich Chemical Company. Distilled water was used. Glassware was cleaned by soaking in alcoholic KOH.

A large excess of sodium borohydride is needed both to reduce the ionic silver and to stabilize the silver nanoparticles that form. A 10-mL volume of 1.0 mM silver nitrate was added dropwise (about 1 drop/second) to 30 mL of 2.0 mM sodium borohydride solution that had been chilled in an ice-bath. The reaction mixture was stirred vigorously on a magnetic stir plate. The solution turned light yellow after the addition of 2 mL of silver nitrate and a brighter yellow (Figure 1A) when all of the silver nitrate had been added. The entire addition took about three minutes, after which the stirring was stopped and the stir bar removed. The clear yellow colloidal silver shown on the left in the photograph in Figure 1, is stable at room temperature stored in a transparent vial for as long as several weeks or months.

Reaction conditions including stirring time and relative quantities of reagents (both the absolute number of moles of each reactant as well as their relative molarities) must be carefully controlled to obtain stable yellow colloidal silver. If stirring is continued once all of the silver nitrate has been added, aggregation begins as the yellow sol first turns a darker yellow.

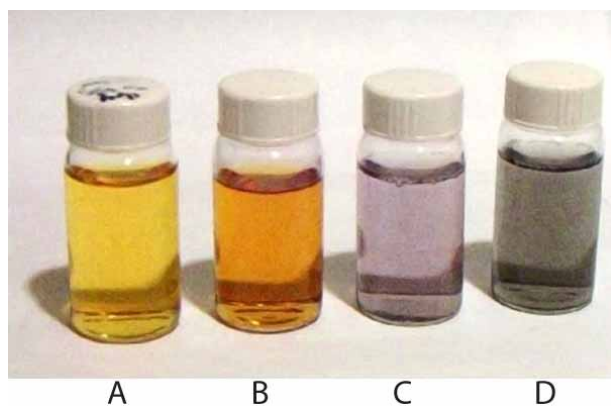


Figure 1. Colloidal silver in various stages of aggregation, (A) clear yellow sol, (B) dark yellow sol, (C) violet sol, and (D) grayish sol, as aggregation proceeds.

**Table 1. Effect on the Stability of Ag Nanoparticles when  $[\text{NaBH}_4]$  Is Varied**

| $[\text{NaBH}_4]/[\text{AgNO}_3]^a$ | Time for Breakdown of Colloid/min |
|-------------------------------------|-----------------------------------|
| 2.0                                 | stable                            |
| 2.1                                 | ~ 30                              |
| 1.9                                 | ~ 20                              |
| 1.8                                 | ~ 5                               |

<sup>a</sup> $[\text{AgNO}_3]$  is constant at 1.0 mM.

low (Figure 1B), then violet (Figure 1C), and eventually grayish (Figure 1D), after which the colloid breaks down and particles settle out. Similar aggregation may also occur if the reaction is interrupted before all of the silver salt has been added.

It was also found that the initial concentration of sodium borohydride must be twice that of silver nitrate:  $[\text{NaBH}_4]/[\text{AgNO}_3] = 2.0$ . When  $[\text{NaBH}_4]$  was varied from 2.0 mM while using 1.0 mM  $[\text{AgNO}_3]$ , breakdown of the product took place in less than an hour (Table 1).

### Optical Properties

The distinctive colors of colloidal gold and silver are due to a phenomenon known as plasmon absorbance. Incident light creates oscillations in conduction electrons on the surface of the nanoparticles and electromagnetic radiation is absorbed. The spectrum of the clear yellow colloidal silver from the synthesis above is shown in Figure 2. To adjust the absorption maximum between 0.5 and 0.7, the product sol was diluted with distilled water. The plasmon resonance produces a peak near 400 nm with PWHM of 50 to 70 nm.

The wavelength of the plasmon absorption maximum in a given solvent can be used to indicate particle size. Silver nanoparticles that produced the spectrum in Figure 3 ( $\lambda_{\text{max}}$

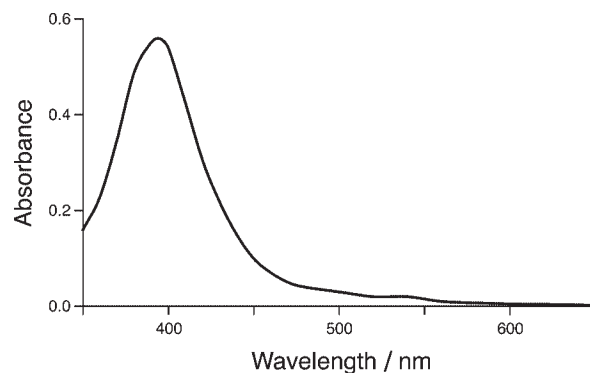


Figure 2. UV-vis absorption spectrum of clear yellow colloidal Ag.

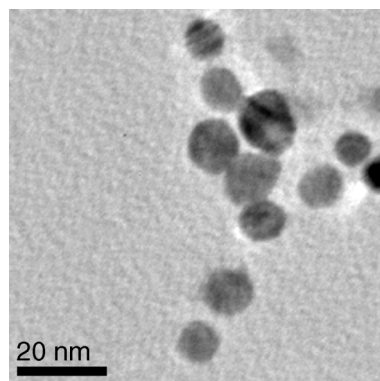


Figure 3. TEM image of silver nanoparticles.

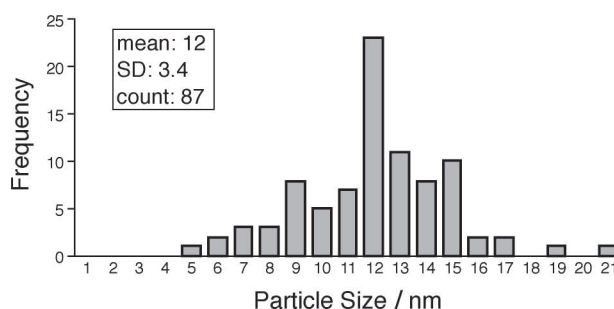


Figure 4. TEM-derived Ag nanoparticle size distribution.

= 400 nm) were examined using transmission electron microscopy (TEM). A sample of silver nanoparticles from a freshly synthesized clear yellow sol was prepared by drying a small drop on a carbon-coated 200-mesh copper grid. The TEM image of a region of the sample is shown in Figure 3, and the size distribution is shown in Figure 4. In general, as

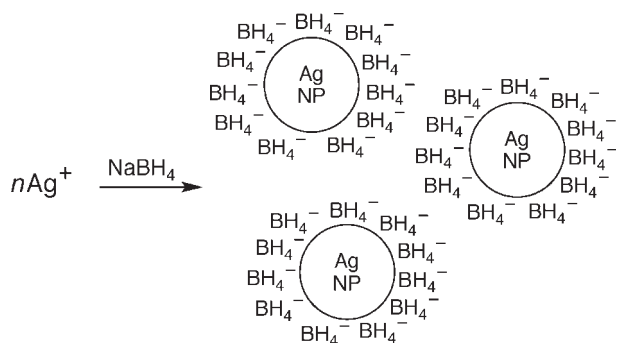


Figure 5. Repulsive forces separate Ag nanoparticles (NP) with adsorbed borohydride.

**Table 2. Particle Size and Spectral Features of Ag Nanoparticles**

| Particle Size/nm   | $\lambda_{\text{max}}$ /nm | PWHM/nm |
|--------------------|----------------------------|---------|
| 10–14 <sup>a</sup> | 395–405                    | 50–70   |
| 35–50 <sup>b</sup> | 420                        | 100–110 |
| 60–80 <sup>c</sup> | 438                        | 140–150 |

<sup>a</sup>Data from this work. <sup>b</sup>Data from ref 4. <sup>c</sup>Data from ref 5.

the particles become larger the plasmon peak shifts to longer wavelengths and broadens. Values for Ag particle size, plasmon maxima, and PWHM that have been reported are listed in Table 2.

### Aggregation

The possibility of aggregation during the synthesis was discussed above. Adsorption of borohydride plays a key role in stabilizing growing silver nanoparticles by providing a particle surface charge as shown in the schematic diagram in Figure 5. There must be enough borohydride to stabilize the particles as the reaction proceeds. However, later in the reaction too much sodium borohydride increases the overall ionic strength and aggregation will occur (7, 8).

The aggregation can also be brought about by addition of electrolytes such as NaCl. Nanoparticles are kept in suspension by repulsive electrostatic forces between the particles owing to adsorbed borohydride (Figure 5). Salt shields the charges allowing the particles to clump together to form aggregates. The colloidal silver solution turns darker yellow, violet, then grayish (See Figure 1). The visible spectrum of the violet solution pictured in Figure 1C is shown in Figure 6. A new broad peak around 525 nm appears along with a decrease in the intensity of the plasmon absorbance.

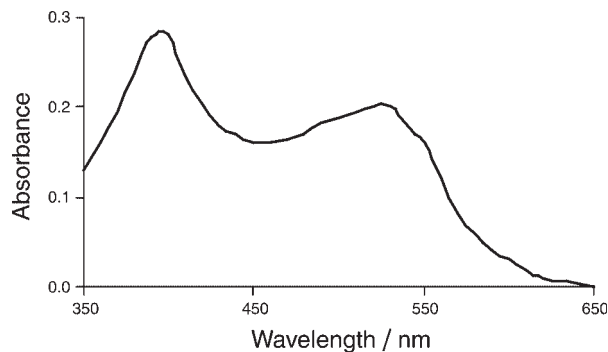


Figure 6. UV-vis absorption spectrum of violet sol.

Nanoparticles in colloidal sols can also be stabilized by adsorbed polyvinylpyrrolidone (PVP) (9, 10). The concentration of PVP needed to prevent the aggregation can be found by adding one drop of aqueous PVP (Aldrich  $M_r = 10,000$ ) to a 5-mL volume of yellow silver sol, then testing for stabilization by adding 1–2 drops of 1.5 M NaCl. Using 0.3% PVP the sol remains yellow and stable. The procedure is repeated with diluted PVP until aggregation is observed upon addition of salt. The minimum concentration of PVP required to stabilize the sol synthesized according to the method described here was 0.01%.

### Student Results

This experiment was performed by 25 pairs of general chemistry students. Students described the appearance of their product as “yellow” or “golden” and found a value for  $\lambda_{\text{max}}$  (using a Spectronic-20) near 400 nm. In one instance, aggregation took place and the product was described as “black with gray particles”.

Students enjoyed the experiment and were particularly impressed by the color of the silver nanoparticles. “I thought the experiment was very interesting”, said one student, “because I never knew that elements could have different properties when their size is changed.” And from others, “I found it interesting that properties of matter can change on a nano-level” and “it was certainly intriguing to see the color change from silver to yellow. This was definitely a worthwhile experiment.”

### Hazards

Silver nitrate is corrosive, causing burns in contact with the skin and eyes. Sodium borohydride is flammable and toxic. The dilute aqueous solutions of silver nitrate (1.0 mM) and sodium borohydride (2.0 mM) can be made available for the students who need not handle either of the solids. Labeled waste containers should be made available for any waste colloidal silver and unused borohydride solution (which must be freshly made every day).

Flammable and corrosive alcoholic KOH used to clean glassware should be handled with care and done ahead for the students. Gloves and safety glasses should be worn throughout the experiment.

### Acknowledgments

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### <sup>W</sup>Supplemental Material

Instructions for the students and notes for the instructor are available in this issue of *JCE Online*.

### Notes

1. Science in Motion is a program that transports equipment and expertise as requested by teachers in Pennsylvania public schools.
2. A 25 g quantity of hydrogen tetrachloroaurate(III) trihydrate (0.063 mol) costs \$650 compared to \$27 for the same

mass of silver nitrate (0.15 mol). Per mole, the gold salt is more than 50 times more expensive.

3. Colloidal dispersions of insoluble materials (e.g., silver nanoparticles) are called sols.

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