Synthesis of Silver Nanoprisms with Variable Size and Investigation of Their Optical Properties: A First-Year Undergraduate Experiment Exploring Plasmonic Nanoparticles

Andrew J. Frank, Nicole Cathcart, Kenneth E. Maly, and Vladimir Kitaev*
Chemistry Department, Wilfrid Laurier University, Waterloo, Ontario, Canada N2L 3C5
*vkitaev@wlu.ca

In recent years, there has been great interest and significant progress in the synthesis of various shapes and sizes of metal nanoparticles (NPs) *(1)*. An undergraduate laboratory experiment in which nanoparticles are synthesized and characterized is therefore both relevant to modern chemistry and appealing to students. Synthesis of both semiconductor *(2, 3)* and metal *(4–6)* NPs in an undergraduate laboratory have been described in this *Journal*. The proposed experiment allows students to prepare defined anisotropic nanostructures: nanoprismatic silver nanoparticles (AgNPs) with size control. NP size control can be readily visualized through variations in localized surface plasmon resonance (LSPR) *(7–9)*, which produces color changes that can be monitored by UV–vis spectroscopy.

The physical properties of nanoscale-sized metal particles differ from those of the corresponding bulk material because of dimensional confinement of electron density in the nanoparticle. The variation in physical properties caused by this confinement is known as a quantum-size effect. An important example of such size effects in metal NPs is LSPR, which describes the collective interaction of geometrically constrained, delocalized electrons with light *(7)*. Confinement of delocalized electrons is different from a more familiar quantum-size effect in semiconductors, where an excited delocalized electron can be visualized as "a particle in a box", and nanocrystals serve as a "box" *(3)*.

With LSPR, the conducting electron cloud of the nanoparticle oscillates as quantized waves and absorb electromagnetic radiation of a particular energy. Mie theory has been successfully used to account for LSPR and the origin of color in spherical metal particles, whereas more general approaches based on the calculation of scattering and absorbance of electromagnetic waves are used to account for colors of general anisotropic shapes, such as prisms *(8)*. Readers are referred to the article by Campbell and Xia in this *Journal* that is devoted to the description of plasmons in the context of teaching chemistry *(7)*.

Nanoparticles of different sizes and shapes display different plasmon resonances and as a consequence absorb light of different wavelengths, thereby giving rise to different colors of NP dispersions. Most commonly prepared silver nanoparticles are nonshape-selected quasi-spherical particles with a plasmon resonance maxima around 400 nm and a characteristic yellow color. Controlling the shape and size of the particles in one or two dimensions, as in rods and platelets, respectively, enables maneuvering of plasmon resonances through the entire visible and near IR spectrum *(9)*. Herein, we demonstrate a novel approach with substantial advancement in size and shape control of 2-D silver nanoprisms and provide a procedure suitable and proven for use in a first-year undergraduate chemistry lab.

Experimental Section

Chemicals

The water used for this experiment ideally should be Millipore grade (with >18.2 MΩ cm resistivity); however, good results are attainable with water purified by high-quality reverse osmosis. The following chemicals were used for this experiment: sodium citrate tribasic dihydrate (99%, Caledon Laboratory Chemicals), silver nitrate (99%, BDH), hydrogen peroxide (29–32 wt %, Caledon Laboratory Chemicals), potassium bromide (99%, Sigma-Aldrich), and sodium borohydride (98%, Sigma-Aldrich). All chemicals were used as received. Students should prepare or be supplied with the following solutions: 1.25×10^{-2} M sodium citrate, 3.75×10^{-4} M silver nitrate, 5.0×10^{-2} M hydrogen peroxide, 1.0×10^{-3} M potassium bromide, and 5.0×10^{-3} M sodium borohydride.

Experimental Procedure

With the exception of potassium bromide, all reagents may be added using graduated cylinders or bottle top dispensers. The volume of bromide added is critical for nanoprism size control with this experiment and consequently must be precisely added using a calibrated micropipet. Bromide importance is evident in that even a difference of a few microliters in concentration of bromide ions will produce substantial deviations in nanoprism size.

To four 20 mL borosilicate vials (VWR), the following were added in order: 2.0 mL of 1.25×10^{-2} M sodium citrate, 5.0 mL of 3.75×10^{-4} M silver nitrate, and 5.0 mL of 5.0×10^{-2} M hydrogen peroxide. Then, to each vial a different volume of 1.0×10^{-3} M potassium bromide was added as follows: 0 μL, 20 μL, 25 μL, 40 μL. For the silver reduction step, 2.5 mL of freshly prepared 5.0×10^{-3} M sodium borohydride was added. Once all reagents were combined, the caps were placed on the vials and they were carefully swirled to fully mix the reactants. Almost immediately, the progression of the reaction becomes evident through the visual changes consistent with the growth of silver nanoprisms. Typically, the sequence of color changes is from yellow to orange to red to purple to violet to blue to pale greenish blue for the largest nanoprisms. It takes approximately 3 min to reach a stable color that students can use to make qualitative observations, measure the UV–vis spectra, and perform Beer's law experiments.

10.1021/ed100166g

Hazards

Sodium citrate may cause irritation to skin, eyes, and respiratory tract. Silver nitrate is poisonous, corrosive, and a strong oxidizer. As a strong oxidizer, hydrogen peroxide is corrosive, causing burns to the eyes, skin, and respiratory tract. Potassium bromide is harmful if swallowed or inhaled. Sodium borohydride is a corrosive, flammable solid that is dangerous when wet and may release hydrogen gas. Solutions of borohydride should not be kept in tightly sealed vessels to avoid possible explosions. The vials with the freshly synthesized nanoprisms should not be tightly capped because of possible gas release from unreacted borohydride and hydrogen peroxide. The experiment described in this work uses dilute solutions, which are suggested to be prepared ahead of time to minimize the risk that the solids and concentrated solutions pose to students.

Results and Discussion

The starting point for this experiment was a work by Mirkin and co-workers, where silver nanoprisms were prepared thermally using hydrogen peroxide *(10, 11)*. In their article, variation in the volume of sodium borohydride was employed for size control, which we found to be much too unreliable for an undergraduate laboratory setting, especially considering borohydride decomposition in aqueous solutions. Photochemical methods can also be used to control the size of nanoprisms produced *(12, 13)*, but this is not convenient for an undergraduate laboratory experiment because of time constraints. To make the procedure more robust, we developed a novel approach that uses a substantial excess of sodium borohydride and instead relies on the addition of bromide ions to tailor the size of the silver nanoprisms. Bromide has been previously used to some extent as a shape-modifying agent for AgNPs in several research reports, for example, nanobars and singly twinned right bipyramids *(14)*. We were also able to exclude polyvinylpyrrolidone *(11)* to shorten the development time of the nanoprisms from original 20−30 min *(11)* down to 3 min. Furthermore, the resulting nanoprisms are stable and remain intact for at least several days so that all necessary optical and other characterization can be easily performed.

With the method used in this experiment, sodium borohydride is added to reduce silver nitrate:

$$\begin{aligned}&\mathrm{NaBH_4(aq) + 8AgNO_3(aq) + 4H_2O(l)}\\ &\rightleftharpoons \mathrm{Na[B(OH)_4](aq) + 8Ag(s) + 8HNO_3(aq)}\end{aligned} \tag{1a}$$

As the silver ions are reduced, silver atoms begin to aggregate, forming a well-defined nanoparticle in the presence of surface-stabilizing (capping) and shape- and size-modifying agents. Excess sodium citrate acts as a buffer to maintain neutral or weakly basic pH of the solution by reaction with the nitric acid as it is generated:

$$\begin{aligned}&\mathrm{Na_3C_3H_5O(COO)_3(aq) + HNO_3(aq)}\\ &\rightleftharpoons \mathrm{Na_2HC_3H_5O(COO)_3(aq) + NaNO_3(aq)}\end{aligned} \tag{1b}$$

In addition to acting as a buffer, sodium citrate charge stabilizes the silver nanoprisms. First, citrate complexes silver, then associates with Ag^+ on a surface of a growing nanoparticle, rendering the surface negatively charged and electrostatically preventing nanoparticles from aggregating. Without proper stabilization, reduction of silver ions leads either to a bulk metal (e.g., the well-known silver mirror reaction*(15)*) or heavily aggregated nanoparticles (a blackish precipitate). Two other roles attributed to citrate include the complexation of silver ions and possible stabilization of close-packed (111) planes in silver and gold nanostructures.

Hydrogen peroxide is employed to facilitate formation of shape-selected nanoparticles. It serves as an etching agent. Less stable newly formed silver nanoparticles are etched by hydrogen peroxide, establishing equilibrium between sodium borohydride reduction and hydrogen peroxide oxidation of silver:

$$\mathrm{2Ag^0(s) + H_2O_2(aq) + 2H^+(aq) \rightleftharpoons 2Ag^+(aq) + 2H_2O(l)} \tag{2}$$

In the absence of peroxide, uncontrolled growth of all the nuclei results in yellow quasi-spherical nanoparticles with large number of structural defects, as commonly observed in most silver nanoparticle formations. Borohydride is an anion, so it reacts with silver cations quickly. On the other hand, hydrogen peroxide molecules are neutral and their reaction with silver nanoparticles is appreciably slower, so larger peroxide concentrations are required. Using peroxide as an etching agent ensures that only the least reactive (or faster growing) of nanoparticle shapes survive and grow at the expense of more reactive shapes *(10, 14)*. Under the conditions outlined in this experiment, the surviving most stable shape is a prism (triangular or truncated triangular platelets) *(11)*. It is instructive to mention that the platelets selection is largely due to the kinetic factors of their fast growth along their planar twinning defects *(16)*. Upon thermal or photochemical treatments, platelets convert to more stable 3-D shapes, such as cubes, bipyramids, and decahedra *(17, 18)*.

In the approach developed in our laboratory *(19)*, bromide is added to the reaction to alter the size at which the particle stops growing, thus overcoming the limitations of using borohydride for size control. Potassium bromide limits the growth of the silver nanoparticles, leading to smaller sizes of nanoprisms being produced and allowing size control. Bromide is known to strongly bind to the silver surface, forming silver bromide that arrests growth of the silver particle surfaces. This strong binding of bromide ions can be rationalized in terms of the low K_{sp} of silver bromide (5.4×10^{-13}) and that silver nanoparticles always have some Ag^+ on their surface *(20)*. Therefore, using different concentrations of bromide in the reaction media enables variation of the size of silver nanoprisms and, as a result, the colors of their dispersion. Typical UV−vis absorption spectra of the four nanoparticle dispersions of different-sized prisms produced in this experiment are shown in Figure 1. When no potassium bromide is added, the largest nanoprism size is achieved, yielding a transparent blue dispersion with an absorbance maximum at 690−750 nm. A typical 705 nm absorbance maximum (Figure 1D) corresponds to an average nanoprism lateral dimension of 64 ± 10 nm and average thickness of 5.3 ± 0.7 nm. A photograph of the dispersions and a transmission electron microscopy (TEM) image of these nanoprisms are shown in Figures 2D and 3D, respectively.

Addition of 20 μL of potassium bromide yields a violet solution upon reduction (Figure 2C), with an observed absorbance maximum at around 575 nm (Figure 1C). The nanoprisms have an average lateral dimension of 40 ± 5 nm and average thickness of 8.5 ± 1.4 nm (Figure 3C). Addition of a larger volume of potassium bromide (25 μL) further restrains nanoparticles growth. The solution typically becomes orange (Figure 2B), with an absorbance

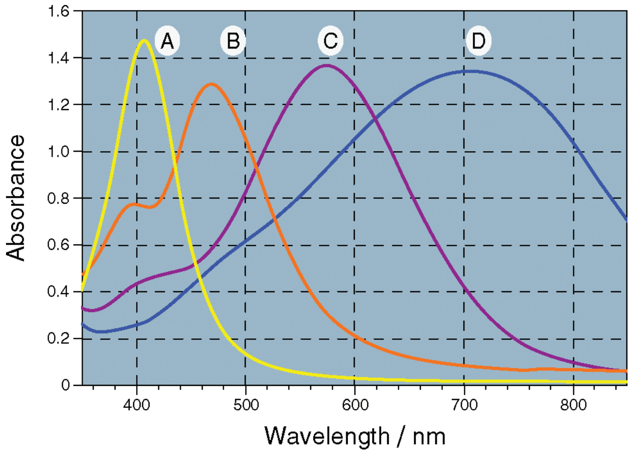

Figure 1. UV–vis absorbance spectrum of silver nanoprisms synthesized using different volumes of 1.0×10^{-3} M potassium bromide. (A) 40 μL KBr, yellow solution; (B) 25 μL KBr, violet solution; (C) 20 μL KBr, orange solution; and (D) 0 μL KBr, blue solution.

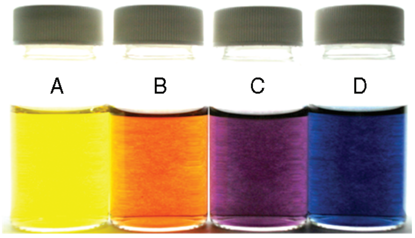

Figure 2. Optical images of the aqueous dispersions of the silver nanoprisms of four different sizes. The letters are the same as given for the absorbance spectra (Figure 1).

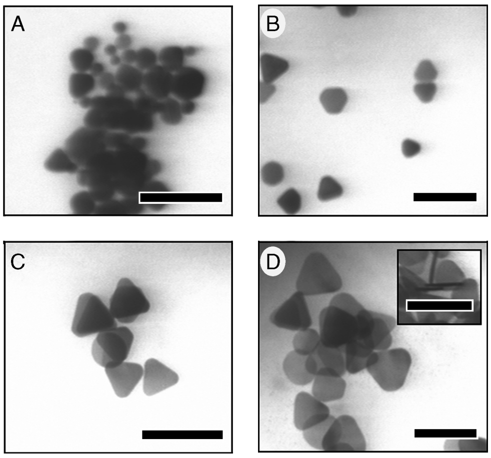

Figure 3. Transmission electron microscopy (TEM) images of silver nanoprisms. The letters are the same as given for the absorbance spectra (Figure 1) and optical images (Figure 2). (A) yellow (10–30 nm polydisperse quasispherical particles); (B) orange (35 ± 4 nm average lateral dimension); (C) violet (40 ± 5 nm average lateral dimension; 8.5 ± 1.4 nm average thickness); and (D) blue (64 ± 10 nm average lateral dimension; 5.3 ± 0.7 nm average thickness), the inset is the side view of the nanoprisms. The bar in each image corresponds to 100 nm.

maximum of around 470 nm (Figure 1B) and average lateral prism dimension of 35 ± 4 nm (Figure 3B). Finally, when 40 μL of potassium bromide is used, the nanoprisms virtually do not develop, resulting in fairly isotropic AgNP shapes, so that a yellow solution typical for quasispherical silver particles can be observed (Figure 2A). The absorbance maximum is around 400–420 nm (Figure 1A). The particles are polydisperse with the sizes ranging from typical 10 nm up to 30 nm (Figure 3A).

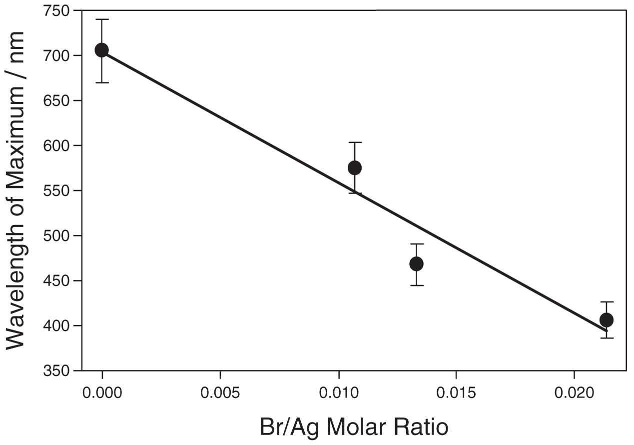

Figure 4. Wavelength of the maxima of optical absorption of the silver nanoprisms as a function of the Br/Ag molar ratio.

A plot of maximum absorbance wavelength of the set of the prepared silver nanoprisms as a function of molar ratio of bromide to silver is presented in Figure 4. An approximately linear inverse relationship exists between the amount of bromide added at constant silver concentrations and the maximum of the nanoprism absorbance. This graph illustrates the role of bromide in controlling the nanoprism size. As more bromide is added to the reaction, the resulting nanoprisms become smaller, as evidenced by a decrease in the wavelength of their maximum absorbance. The wavelength of the plasmon resonance maxima correlates well with the largest dimension of the silver nanoprisms consistent with visualization of plasmon as a standing wave of oscillating free electron density. It should be noted that near linear dependence of plasmon maximum versus bromide concentration holds well for the conditions and the range of bromide concentrations described but is not a universal phenomenon in nanoprism formation that is influenced by strongly binding anions. More details on effect of halides on AgNP preparation and postmodification can be found in ref *19*.

With proper care, the AgNP preparation is reliable, and the prepared reagents will last several days to months with the exception of sodium borohydride, which must be replaced daily. To address the concern of borohydride decomposition, we optimized the procedure to conduct the reaction at the highest reasonable borohydride concentration. This assures that issues associated with its decomposition are alleviated as much as possible. Sodium borohydride decomposes in water as follows:

$$\mathrm{NaBH_4(aq) + 4H_2O(l) \rightleftharpoons Na[B(OH)_4](aq) + 4H_2(g)} \qquad (3)$$

The effect of sodium borohydride decomposition over time on the quality of the largest size of nanoprism produced is illustrated in Figure 5. The formation of larger nanoprisms is robust and stable; however, a rapid decrease occurs after ca. 20 h. Thus, a sodium borohydride solution prepared in the morning can be safely used in the evening (in fact we have successfully performed the experiments for 9 different daytime and evening laboratory sections using borohydride solutions prepared the morning of

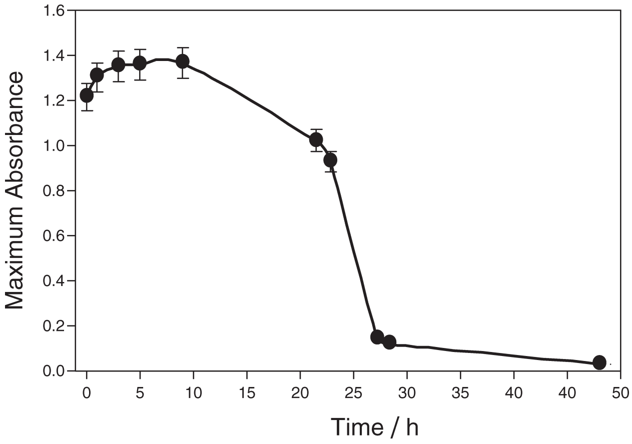

Figure 5. Effect of the decomposition of sodium borohydride on effectiveness of the silver nanoprism preparation. Absorption maximum of the blue silver nanoprisms at 650–700 nm region is plotted against the aging time of borohydride solution used for the reduction.

the experiment). Borohydride solutions still have to be prepared on a daily basis, because using old borohydride will not achieve reduction necessary to produce larger nanoprisms.

Important Observations for Successfully Conducting the Experiment

The volume of potassium bromide added to the solution proved to be critical. Some first-year students may need to be supervised on use of micropipets, which was successfully done by properly trained teaching assistants. The most common student mistake is to press the micropipet button all the way in when drawing up the solution, which leads to dispensing larger volumes of bromide and results in yellow nanoparticle solutions produced in all the vials where bromide was added. Despite all the pitfalls of usually sensitive nanoparticle preparations, the overall rate of the student success in producing more than three solutions of different colors was better than 85%.

For the Beer's law experiment, if high purity distilled water is not used, larger nanoprisms may quickly fragment into smaller particles resulting in a characteristic yellow solution regardless of the starting shape and size. To overcome this issue, high-quality reverse osmosis water or better must be used for all aspects of the experiment.

Finally, this experiment has been successfully introduced in 2009 in an introductory university chemistry class, with 500+ students (groups of 20–24 students working in pairs) successfully performing it to date. The students found the experiment to be fairly challenging, yet rewarding.

Conclusion

The experiment described herein presents a simple, effective method for undergraduate students to synthesize and characterize silver nanoprisms of different colors within a 3-h laboratory. The colors of the dispersions are due to size-dependence of the plasmon resonance of AgNPs. As a result, students are introduced to nanochemistry and nanoscience in a manner that is readily perceived and understood. In first-year laboratory settings, the proposed experiment can nicely reinforce concepts of colorimetry, UV–vis spectroscopy, and Beer's law. In more advanced laboratories, measurements by scanning probe microscopy, light scattering, electron microscopy, and so forth can be performed based on the proposed synthetic procedures.

Acknowledgment

The authors gratefully acknowledge financial support by the Natural Science and Engineering Research Council of Canada and Research Corporation for Science Advancement. The Centre for Nanostructure Imaging, University of Toronto is greatly appreciated for access to Electron Microscopy facilities.

Literature Cited

1. Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. *Angew. Chem., Int. Ed.* **2009**, *48*, 60.
2. Winkelmann, K.; Noviello, T.; Brooks, S. *J. Chem. Educ.* **2007**, *84*, 709.
3. Boatman, E. M.; Lisensky, G. C.; Nordell, K. J. *J. Chem. Educ.* **2005**, *82*, 949.
4. Keating, C. D.; Musick., M. D.; Keefe, M. H.; Natan, M. J. *J. Chem. Educ.* **1999**, *76*, 949.
5. McFarland, A. D.; Haynes, C. L.; Mirkin, C. A.; Van Duyne, R. P.; Godwin, H. A. *J. Chem. Educ.* **2004**, *81*, 544A.
6. Solomon, S. D.; Bahadory, M.; Jeyarajasingam, A. V.; Rutkowsky, S. A. *J. Chem. Educ.* **2007**, *84*, 322.
7. Campbell, D. J.; Xia, Y. *J. Chem. Educ.* **2007**, *84*, 91.
8. Liz-Marzán, L. M. *Mater. Today* **2004**, *7*, 26.
9. Sun, Y.; Xia, Y. *Analyst* **2003**, *128*, 686.
10. Millstone, J. E.; Hurst, S. J.; Metraux, G. S.; Cutler, J. I.; Mirkin, C. A. *Small* **2009**, *5*, 464.
11. Metraux, G. S.; Mirkin, C. A. *Adv. Mater.* **2005**, *17*, 412.
12. Jin, R.; Cao, Y.; Mirkin, C. A.; Kelly, K. L.; Schatz, G. C.; Zheng, J. G. *Science* **2001**, *294*, 1901.
13. Jin, R.; Cao, Y.; Hao, E.; Metraux, G. S.; Schatz, G. C.; Mirkin, C. A. *Nature* **2003**, *425*, 487.
14. Wiley, B.; Sun, Y.; Xia, Y. *Acc. Chem. Res.* **2007**, *40*, 1067.
15. Kemp, M. *J. Chem. Educ.* **1981**, *58*, 655.
16. Aherne, D.; Ledwith, D. M.; Gara, M.; Kelly, J. M. *Adv. Funct. Mater.* **2008**, *18*, 2005.
17. McEachran, M.; Kitaev, V. *Chem. Commun.* **2008**, *44*, 5737.
18. Pietrobon, B.; Kitaev, V. *Chem. Mater.* **2008**, *20*, 5186.
19. Cathcart, N.; Frank, A. J.; Kitaev, V. *Chem. Commun.* **2009**, *46*, 7170–7172.
20. Xiong, Y.; Washio, I.; Chen, J.; Sadilek, M.; Xia, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 4917.

Supporting Information Available

Description of the experimental procedure; preparation of materials provided to students; instructor notes; results of a typical student lab; CAS registry numbers. This material is available via the Internet at http://pubs.acs.org.