## Teacher's Preparatory Guide

# *Synthesis and Stability of Silver Nanoplates*

**Purpose:** The purpose of this experiment is to conduct synthesis of silver nanoplates and explore their shape stability that affects optical property (referred to as localized surface plasmon resonance (LSPR). Students will learn about the differences in physical properties and behavior at the nanoscale as compared to the same materials at the macroscale. This lesson assists students in working with scale and unit conversion.

**Time required:** 8 hours

**Level:** Undergraduate Chemistry

**Teacher Background:** 'Nano' means small, very small; But, why is this special? At the nanometer scale, the properties of matter, such as optical and electrical properties, change. This is a direct consequence of the size of nanomaterials, physically explained as quantum confinement. The consequence is that a material (e.g. a metal) when in a nano-sized form can assume properties, which are very different from those when the same material is in a bulk form. For instance, bulk silver is non-toxic, whereas silver nanoparticles (AgNPs) are capable of killing viruses upon contact. Properties like electrical conductivity, color, strength, and weight can change when the nanoscale level is reached.

Because of these unique properties, silver nanostructures have been heavily researched in an attempt to leverage the benefits of their use. Silver nanoparticles are useful for their plasmonic properties, especially with improvements to Surface Enhanced Raman Scattering (SERS) that can be obtained from their use. Two areas of focus have come to great attention; the control of shape and size as both of these have an effect on their properties including physical appearance along with behavior of the particle.

Silver nanoparticles can take the shape of cubes, spheres, bars, wires, bi-pyramids, beams, plates, and discs depending upon the seed it forms from. As long as the nanostructure retains its respective shape, it will retain its unique optical properties. If the particle loses shape, or stability, it will lose its exhibited properties.

The distinct properties of nanoscale silver have afforded its use in many everyday items. Silver nanoparticles can be used as biological tags for quantitative detection and in biosensors. It's used as an antibacterial/antifungal agent, and can kill harmful strains of bacteria, which are resistant to antibiotics. Some of these products have been incorporated in apparel, footwear, paints, appliances, cosmetics, food packaging, and plastics. There are several medical uses of silver nanoparticles, which include the dressing of wounds, surgical masks, and surgical instruments. Silver nanoparticles are used to efficiently harvest light and for enhanced optical spectroscopies including metal-enhanced fluorescence (MEF) and surface-enhanced Raman scattering (SERS).



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In this lesson, silver nanoplates will be synthesized through a redox reaction-involving Poly (vinylpyrrolidone) (PVP) as a capping/mild reducing agent in ethanol (EtOH) at 80$^{o}$C.

$AgNO_3$
PVP-29K -----------------------------> Ag Nanoplates
EtOH        80$^{o}$ C Solvothermal oven

*(note: Solvothermal reduction at 80$^{o}$C)

In this reaction, PVP-29K, combined with ethanol (EtOH) reduces the silver cations from the silver nitrate. As the silver metal forms, PVP coats the outside of the particles, preventing them from aggregating and forming larger particles. Because the nano sized particles have different properties than bulk materials, the silver nanoparticles appear yellow. When mixed with certain chemicals, AgNPs can either red or blue shift, causing color appearance changes. If this occurs, the nanoparticle has lost stability and may be truncated at its corners or edges. Once stability is lost in shape, it affects the function of the particle and may cause it to loose special properties. This lab will allow students to synthesize silver nanoplates and observe either red or blue shift changes that affect its stability.

**Materials:**

**For Synthesis**

- 0.01M Silver nitrate ($AgNO_3$ CAS 7761-88-8)
- 0.001M Poly(vinyl pyrrolidone) (PVP-29K) Sigma Aldrich product #773147
- Ethanol (EtOH) (200 proof)
- 20mL vial
- (4) 100mL vials
- Aluminum foil
- Pipettes (1mL, 10mL)
- Conventional oven to perform solvothermal reaction at 80$^{o}$C
- Acid digest reaction vessel (used Parr Instrument Co. vessel # 4745)
- Oven mitt
- Googles
- Nitrile/vinyl gloves
- Plastic container to hold vessel

**For Stability**

- Prepared Ag nanoparticles (see synthesis section)
- Cuvettes
- 500 mL tap water
- Droppers

**For Spectroscopy**

- Spectrometer

- Cuvettes
- Ethanol (EtOH) (200 proof)
- Droppers

**Advance Preparation:**
To prepare .01M $AgNO_3$, dilute 0.0066g $AgNO_3$ (CAS 7761-88-8) to 3.89mL with ethanol.
To prepare .001M Poly (vinyl pyrrolidone), dilute .3752g to 12.9mL with ethanol.

**Synthesis of Ag Nanoplates:**

The Ag nanoplates were prepared by heating a mixture of $AgNO_3$ and PVP in ethanol to 80 $^oC$ in acid digest vessels (Parr Instrument Company, vessel number 4745). In a standard procedure, $AgNO_3$ and PVP-29K were separately dissolved in ethanol at concentrations of 10.0 mM and 1.0 mM (in terms of the molecular weight of PVP), respectively. Next, 12 mL of the prepared PVP solution was added into a Teflon liner, followed by the addition of 0.3 mL of the $AgNO_3$ solution to the same liner. The Teflon liner was then sealed, placed in a stainless steel vessel, and heated in an oven at 80 $^oC$. The acid digest vessel was heated for 5 hours. Upon completion, the vessel was water-cooled to room temperature for about 20 minutes prior to disassembly. The product was then transferred into a 20-mL glass vial and stored for future use. The final solution should appear blue. After spectrometry, the UV-vis should show the highest peak around 650-730nm as shown in Figure 1.

**Stability of Ag Nanoplates:**

The stability of the freshly synthesized Ag nanoplates was tested using tap water. 500 mL of the prepared Ag nanoparticles were transferred to a cuvette. The initial color (should be blue) was recorded and observed. 500 mL of tap water was added to the cuvette of Ag nanoplates. The solution was placed on the lab table and observed for color change. Results were recorded at 0, 30, and 60-minute intervals.

**Spectroscopy of Ag Nanoplates:**

Spectroscopy was taken of the freshly synthesized Ag nanoplates using a Cary 50 UV-Vis Spectrophotometer. Following the protocols explained on the student guide, a cuvette of 500mL of the Ag nanoplates was initially scanned. After adding 500 mL of tap water, another scan was completed at 0 minutes and again at 120 minutes to compare the changes in wavelength and observe either a red or blue shift from the initial scan. Fig. 1 shows the results acquired from spectroscopy.



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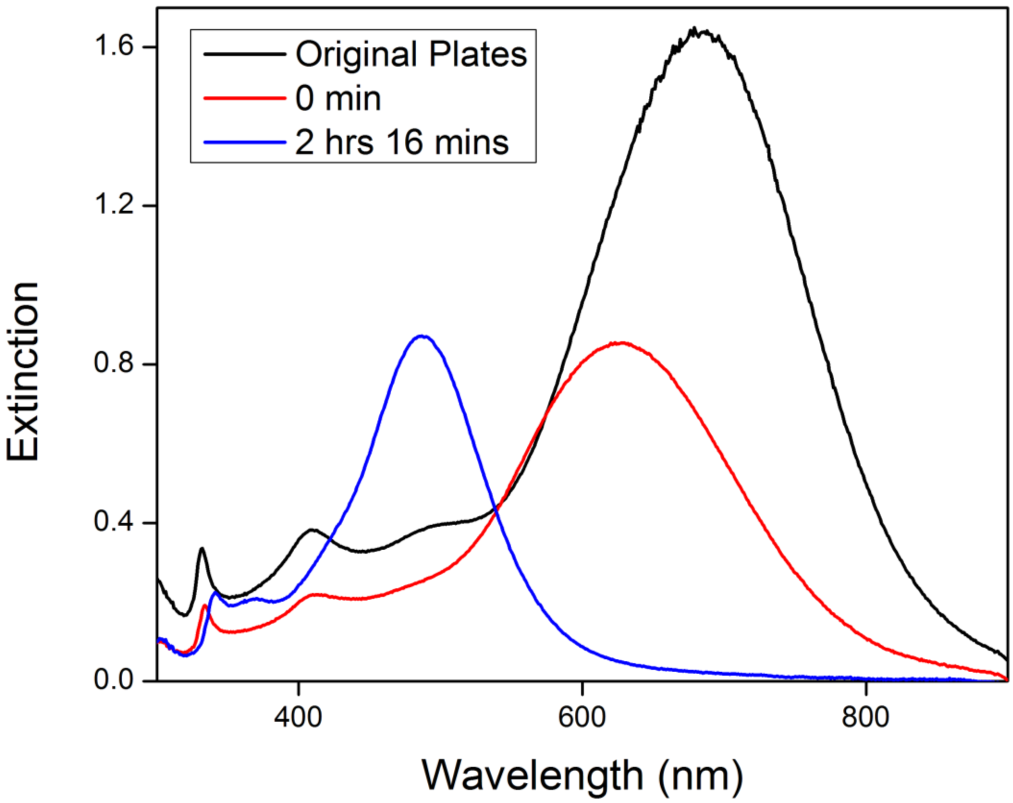


**Fig. 1 UV-vis Spectra of Ag Nanoplates**

**Safety Information:**
All individuals in the lab should be wearing safety goggles and closed-toed shoes. Students should wear nitrile gloves since they may come in contact with silver nitrate. Students, per the teacher's discretion, may also wear a lab coat. When heating solutions, students should use caution when working with hot glassware, as hot and cold glassware look the same. Download the appropriate MSDS for the chemicals.

**Instructional Strategies:**
The silver nitrate solution must be prepared fresh when conducting this experiment. Because the production of Ag nanoplates is not 100% reproducible, you may consider making 2 separate batches at once. Have students complete the activity following the steps outlined in the procedure section (In student guide with answers). Students should record results on their worksheet. Part 3 of the experiment is optional if you have access to a spectrophotometer. The spectrometry procedure described in the student guide is specific for a Cary 50 UV-Vis Spectrophotometer. Directions may differ from spectrophotometer to spectrophotometer.

**Cleanup:**
Solutions should be disposed of in properly labeled waste container. All glassware and plastic ware should be disposed of in the designated waste container. The instructor should properly clean Teflon liners using nitric acid.



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**Assessment:** The students should observe the following changes in the solution and answer the questions. Correct answers are in red.

| TIME (MIN.) | COLOR |
|---|---|
| 0 minutes Ag nanoparticles only | (Blue) |
| 0 minutes with tap | (Purple/blue violet) |
| 30 minutes with tap | (Pink) |
| 60 minutes with tap | (Orange) |

1. Name a physical property of silver that changes at the nanoscale.
*The color of silver changes at the nanoscale. In this experiment, silver nanoplates were created and appeared blue until they lost stability due to the addition of tap water.*

2. Given the observed color changes over the course of 60 minutes, did the Ag nanoparticles experience a blue shift or a red shift change? Does the shift indicate an increase or decrease in the wavelength?
*There was a blue shift of the curve. A blue shift indicates a decrease in the wavelength.*

3. If the observed shift trend witnessed in your results continues from where your observations ended, what color do you predict would be observed next?
*Yellow/yellow orange*

**Resources:**

- Silver Nanoparticles: Physical Properties http://nanocomposix.com/kb/silver/physical-properties
- Optical Properties of Self-Assembled 2D and 3D Superlattices of Silver Nanoparticles http://pubs.acs.org/doi/abs/10.1021/jp972807s
- The Extinction Spectra of Silver Nanoparticle Arrays: Influence of Array Structure on Plasmon Resonance Wavelength and Width http://pubs.acs.org/doi/abs/10.1021/jp034235j
- UV-Vis-NIR Spectroscopy Tutorial http://www.chem.agilent.com/en-US/products-services/Instruments-Systems/Molecular-Spectroscopy/Pages/tutorial.aspx



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**References**

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Qiang Zhang, Y. Y. (2013). Citrate-Free Synthesis of Silver Nanoplates and the Mechanistic Study . *ACS Applied Materials & Interfaces* , 6333-6345.

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