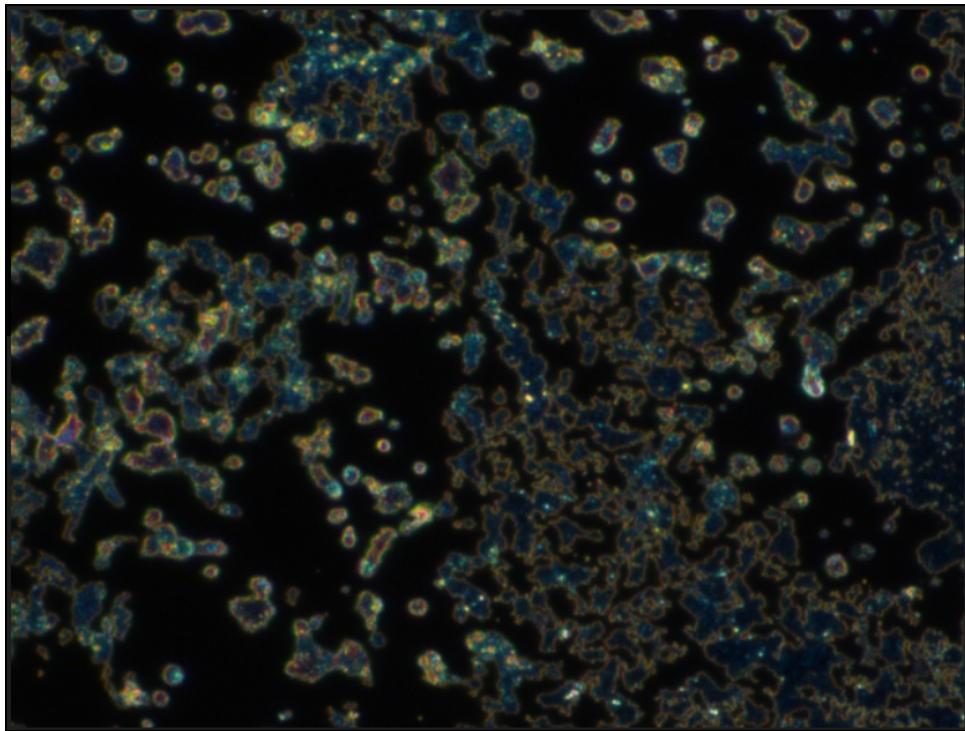


Lab Report: **Metal Nanoparticle Synthesis and Assembly**



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Purpose

Metal nanoparticles, specifically silver and gold, have localized surface plasmon resonances that are dependent on their size and shape and can be excited in the optical range, making them suitable for LSPR-based biosensing in various fields. LSPR sensors are optical devices that detect changes in refractive index at the metal surface, allowing for ultrasensitive detection of molecular events such as protein binding. This module focuses on the synthesis of metal nanoparticles using solution-based methods and assembling them into films for large-scale applications.

Background and Research Motivation

Plasmonics is a field of science and technology that uses metal nanostructures as antennas or waveguides to manipulate light with high precision (Rycenga). Plasmonic metal nanostructures can be categorized into two types: localized surface plasmons (LSPs) and propagating surface plasmons (PSPs). LSPs occur when the negatively charged electrons in the metal collectively oscillate in response to the electric field of light, resulting in an LSPR mode at a resonant frequency. Silver (Ag) is a suitable metal for plasmonic technologies due to its ability to support a strong surface plasmon at a broad spectrum range. Single-particle spectroscopy can be used to examine the relationship between shape, size, and the LSPR wavelength of nanoparticles (Willets). UV-Vis spectroscopy is typically utilized to detect LSPR, and the Langmuir-Blodgett technique can offer several benefits for depositing nanoparticles with precise control over orientation (Tao).

The unique optical and electronic properties of metal nanoparticles, which can be tuned by controlling their size, shape, and surface chemistry, have motivated researchers to investigate their properties and potential applications in a wide range of fields, including biosensing, catalysis, and medical imaging and therapy.

LSPR-based biosensors, in particular, offer ultrasensitive detection capabilities that could significantly improve medical diagnosis and treatment by enabling early disease detection and real-time monitoring of biological processes. Thus, exploring the synthesis, properties, and applications of metal nanoparticles has significant research potential for the development of innovative technologies with widespread benefits.

Several research publications have explored the synthesis, properties, and applications of metal nanoparticles. For instance, a study by Chen et al. (2021) demonstrated the use of gold nanoparticles as a catalyst for the

electrochemical reduction of CO₂, highlighting their potential for sustainable energy conversion. In another study, Yan et al. (2022) investigated the effect of particle size on the plasmonic properties of silver nanoparticles and their performance as LSPR-based biosensors for the detection of DNA molecules. Moreover, Wang et al. (2020) reported the development of a novel biosensing platform based on LSPR of gold nanorods for the detection of circulating tumor cells in cancer patients. These examples illustrate the diverse and innovative applications of metal nanoparticles, emphasizing the importance of continued research.

Computational Details and Methods

Use the materials list found in the appendix. First, Reduce Ag⁺ in silver nitrate to Ag⁰ using polyvinylpyrrolidone (PVP) as a polymer capping agent to synthesize Ag nanoparticles in solution via a redox reaction.

- Prepare a PVP solution and an AgNO₃ solution
- To prepare the PVP solution, dissolve 1.287g (we measured **1.2875 g**) PVP in ~50mL ethylene glycol in a 100mL round-bottom flask with a magnetic stir bar
- To prepare the AgNO₃ solution, dissolve 0.200g (**.202g used**) AgNO₃ in 1mL deionized water in a glass vial using sonication
- Preheat an oil bath to 150C using a hotplate with a stirring rod and a thermometer
- Place the PVP solution in the oil bath with a moderately fast stir rate and preheat for at least 10 minutes until the temperature is stable
- Add 1.0 mL of the AgNO₃ solution using a pipet and let the reaction continue for up to 30 minutes

- Stop the reaction once the desired color is achieved and allow the solution to cool



Figure 1: Desired Solution Color

- Transfer 10ml of the nanoparticle solution to two 15ml centrifuge tubes and label them with group number, date, and contents
- Store the remaining nanoparticle solution in a 50ml centrifuge tube labeled with the group number, date, and contents
- If more solution is required, use the stored 50ml tube
- Add 5mL of ethanol to both 15ml centrifuge tubes containing the nanoparticle solution and mix well using a sonicator



Figure 2: Sonication Process

To prepare the ethylene glycol-ethanol nanoparticle solutions for centrifugation, follow these steps:

- Prepare a water counterbalance in a separate centrifuge tube that weighs within 50mg of the nanoparticle solution.

- Centrifuge the tubes at approximately 3500 rpm for 25 minutes, placing the tubes and counterweight opposite each other in the centrifuge.
- Repeat the centrifugation process until a substantial 'pellet' of nanoparticles has formed at the bottom of the tube and the liquid above the pellet (supernatant) is adequately clear.
- Discard the clear supernatant while preserving the pellet of nanoparticles.
- If the supernatant isn't clear but there is still a pellet, collect and store the supernatant for potential future use.
- Wash and re-disperse the nanoparticles by adding 15mL of ethanol to the nanoparticle tubes and sonicate.
- Centrifuge the tube again, remove the supernatant, add 15 mL of ethanol, and sonicate to wash the nanoparticles **THREE** (took one extra time for our team) more times.
- Store the solution for the following lab day.

Next, we create a thin film of the nanoparticles using the LB (Langmuir Blodgett) technique...

Here are the steps to prepare Ag nanoparticles for LB assembly:

- Add 5mL of the ethanolic nanoparticle solution to a 15mL centrifuge tube.
- Make the appropriate counterbalance and centrifuge the sample at 2500 rpm for 20 minutes.
- Repeat the centrifugation process until the supernatant is clear and mostly colorless.
- Discard the supernatant and re-disperse the nanoparticles in 200 μ L ethanol using the sonicator.
- Add 2 mL of chloroform to the vial, sonicate, and transfer the solution into a glass scintillation vial.

Here are the steps to fabricate the nanoparticle thin-film:

- Set up the LB trough using the SOP. Ensure **3mm meniscus** and retain through process
- Add the sample dropwise to the top of the water near the center of the bath until $\frac{3}{4}$ of the surface area has nanoparticles.

- Wait for the chloroform to evaporate before adding more solution to prevent the nanoparticles sinking to the bottom.
- Prepare a glass slide with cleaner (Kim wipe and Alcohol)
- Place the glass slide in the glassware oven until it is dry.
- Insert the glass slide into the water subphase using the dip coating apparatus.
- Compress the nanoparticle film at 5 mm/min until the surface pressure is $\Pi > 20$ mN/m.
- Deposit the nanoparticles onto the clean glass slide using the LB trough dip-coater with speeds ranging from 1-5 mm/min.

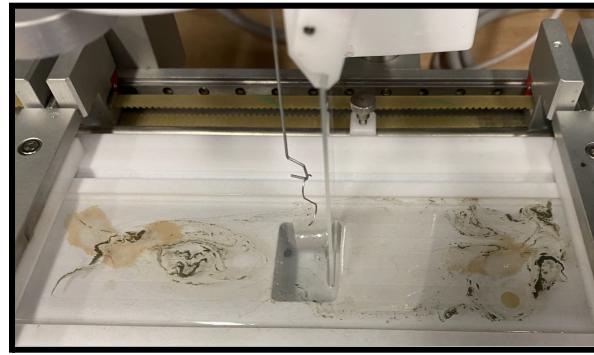


Figure 3: Solution applied to LB trough.

- Let the film dry before collecting optical microscope images and UV-Vis data.

Results and Discussion

UV-Vis gave a peak of 463 nm and an absorbance of .32199 AU. This is consistent with the expected absorbance wavelength.

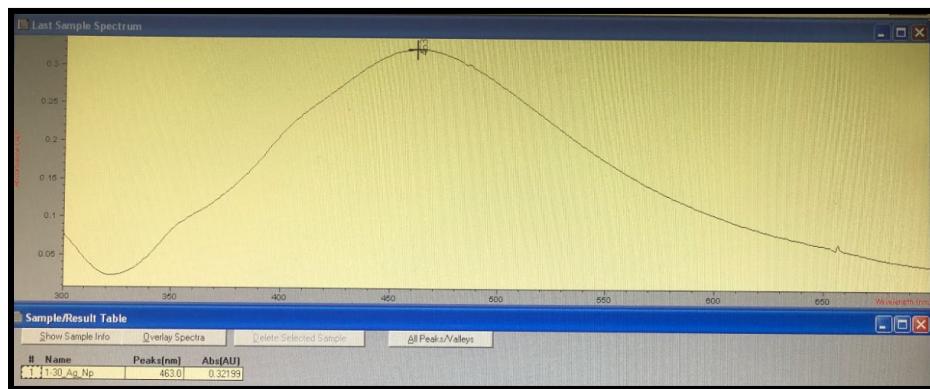


Figure 4: UV-Vis Spectra of NP Dilution

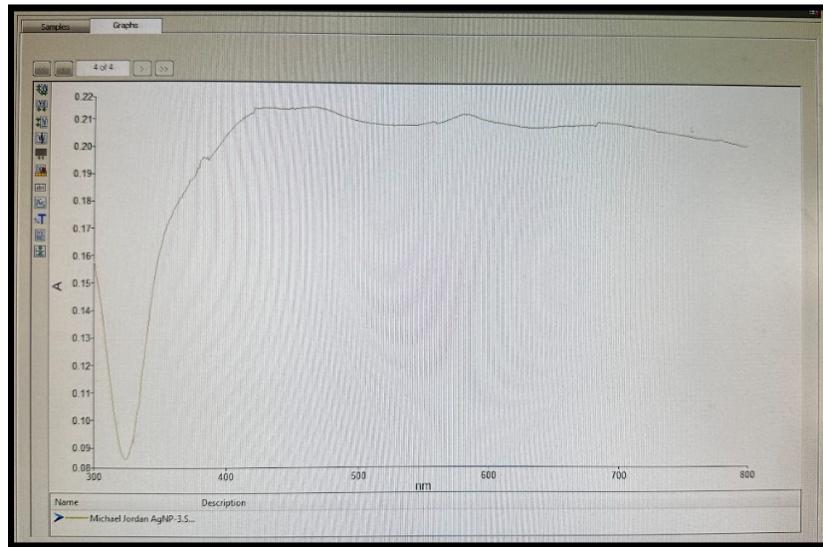


Figure X: Absorbance graph of Ag NP Film

Various factors, including the dimensions and morphology of nanoparticles, the dielectric properties of the surrounding medium, and the spacing between particles, can impact the widths of the UV-VIS peaks. We can use Beer-Lambert law to find that the molar absorptivity and using out length of light path and absorbance plus concentration. Our absorption peak is 463 nm and from Ref [4]. We conclude the nanoparticle size is between 80~90nm. This result is backed by the optical microscopy estimations. We can complete calculations for the percent yield and concentration as follows. Starting with Beer Lambert's law (equation 1) ...

$$A = \epsilon b C \quad (\text{equation 1})$$

Absorbance of Dispersed NPs = 0.32199

Absorbance of Film NPs = 0.201

From Ref [4] we know Molar Absorptivity = $5.37 \times 10 M^{-1} cm^{-1}$

Density of Ag = 10.49 g/cm

Molecular Weight of Ag = 107.97 g/mol

Molecular Weight of AgNO₃ = 169.87 g/mol

Path Length = 1cm (given)

Concentration of Dispersed NP using B-L:

$$\frac{0.32199}{\varepsilon L} = 5.99 \cdot 10^{-12} M$$

Concentration of Film NP using B-L:

$$\frac{0.201}{\varepsilon L} = 3.74 \cdot 10^{-12} M$$

Nanoparticle Density:

$$\text{Dispersed: } 5.99 \cdot 10^{-12} \frac{\text{mol}}{\text{L}} \cdot \frac{107.8\text{g}}{\text{mol}} \cdot \frac{\text{L}}{1000\text{mL}} \cdot \frac{\text{cm}^3}{10.49\text{g}} \cdot \frac{1}{65.4 \cdot 10^{-18} \text{cm}^3} = 940 \text{ NP per mL}$$

$$\text{Film: } 3.74 \cdot 10^{-12} \frac{\text{mol}}{\text{L}} \cdot \frac{107.8\text{g}}{\text{mol}} \cdot \frac{\text{L}}{1000\text{mL}} \cdot \frac{\text{cm}^3}{10.49\text{g}} \cdot \frac{1}{65.4 \cdot 10^{-18} \text{cm}^3} = 590 \text{ NP per mL}$$

Theoretical Yield

$$\frac{0.2\text{g}}{51\text{mL}} \cdot \frac{\text{mol}}{169.8\text{g}} \cdot \frac{1000\text{mL}}{\text{L}} = 0.02332 \text{ M}$$

Dispersed Yield

$$\frac{5.99 \cdot 10^{-12}}{0.02332} \cdot 100 = 2.57 \cdot 10^{-8} \text{ Percent}$$

Film Yield

$$\frac{3.74 \cdot 10^{-12}}{0.02332} \cdot 100 = 1.61 \cdot 10^{-8} \text{ Percent}$$

The Langmuir trough provided a graph of surface pressure vs. trough area, seen in the figure below.

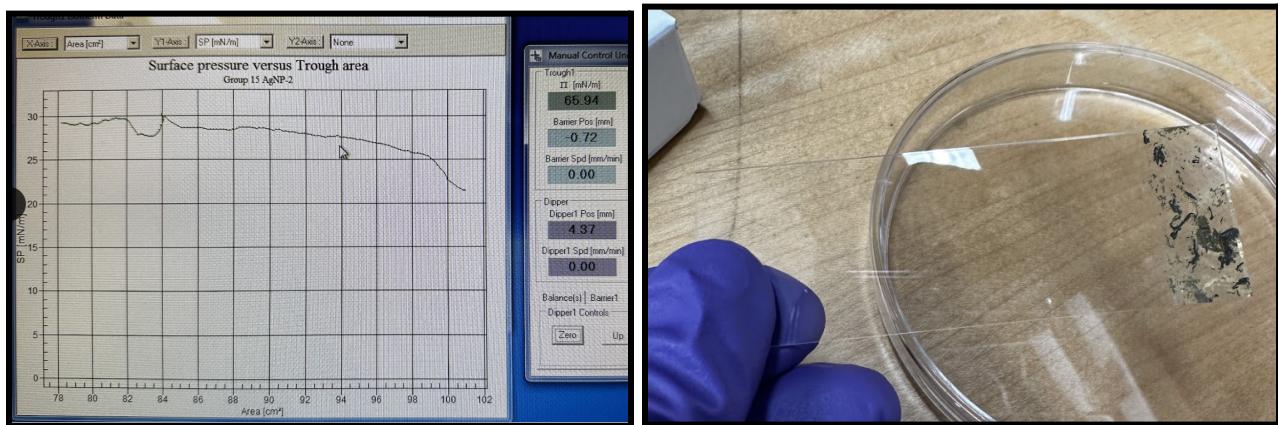


Figure 5 & 6: Surface Pressure Isotherm from LB Trough and Image of Sample respectively.

UV-Vis spectra was recorded and used to record the absorbance of the sample and can be seen above in the report. The absorbance peak is seen at ~450 nm with a second peak farther along in the spectra. The presence of plasmon coupling is confirmed by the addition of a second peak, which indicates a response in the LSPR.

Under optical dark-field microscopy, we observe the nanoparticles

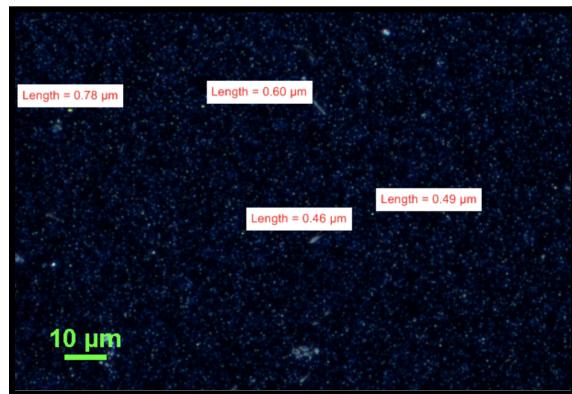


Figure 7: Ag Nanoparticle 5 μ L Solution in Dark-Field Imaging Mode

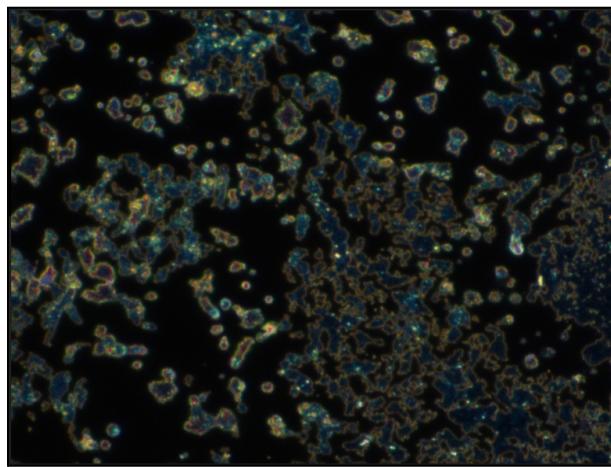


Figure 8: Ag Nanoparticle 5 μ L Film in Dark-Field Imaging Mode (50x)

According to the UV-Vis and optical microscopy findings, the Ag nanoparticles in the dispersed solution are more uniform and smaller in size, in contrast to the Ag nanoparticles in the film which exhibit varied shapes and sizes without uniformity. This difference is expected because PVP is present in the dispersed Ag nanoparticles, which prevents the particles from aggregating. Conversely, during the formation of the film, PVP is removed via chloroform, causing the Ag NPs to aggregate, resulting in a variety of sizes. The UV-Vis

analysis revealed a clear peak for the dispersed Ag NPs, while the compressed Ag NPs film exhibited no discernible peak, suggesting a lack of size uniformity among the Ag NPs.

The SEM images of the dispersed nanoparticle solution helped illustrate the size and topography of the sample we synthesized:

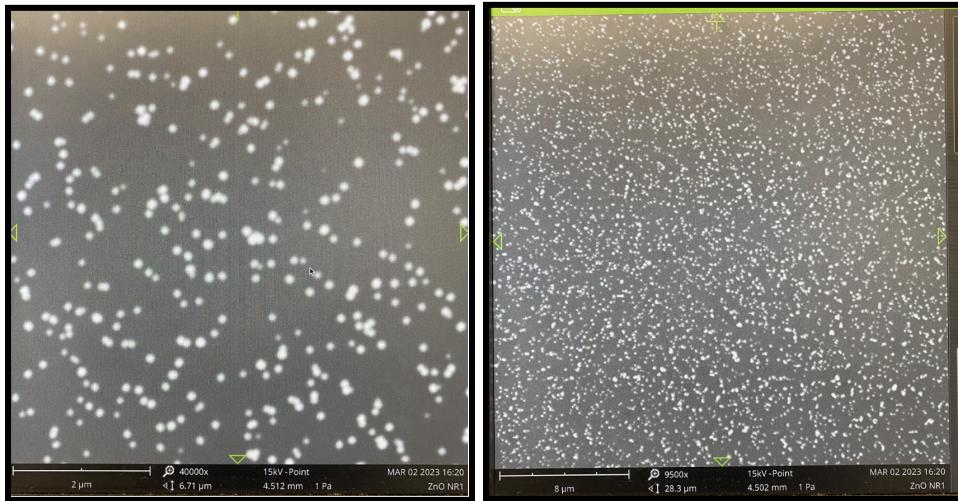


Figure 9 & 10: SEM Images of Ag NP under 40,000x and 9500x magnification respectively

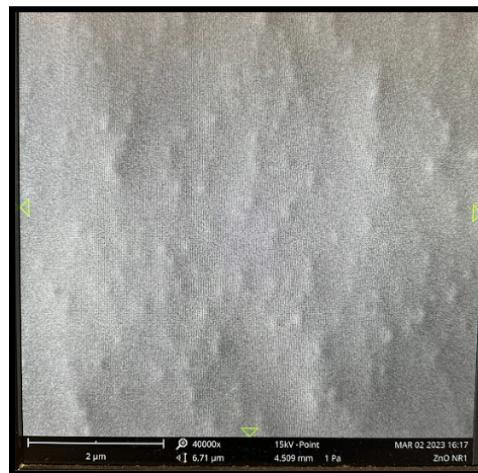


Figure 11: Dispersed Ag NP Topology @ 40,000x Mag

The SEM images provided further evidence of the size and uniformity of the Ag nanoparticles in the dispersed solution, confirming that they are all approximately 100 nm in size and uniform in shape. This conclusion is also supported by the single peak observed in the UV-Vis analysis, indicating that the Ag nanoparticles appear

smaller in optical microscopy. Thus, the dispersed Ag nanoparticles are consistently found to be nearly 100 nm in size, circular in shape, and with minimal clustering.

Module Questions

See Appendix

Conclusion

In this study, a synthesis and characterization process was carried out on a thin film of Ag nanoparticles to gain insights into the LSPR response. The bottom-up approach of Langmuir-Blodgett deposition was utilized to fabricate thin films on glass substrates. The characterization process involved the use of UV-vis spectroscopy, dark field microscopy, and scanning electron microscopy to determine key parameters such as size, shape, and scattering properties of the Ag nanoparticles and thin films. The UV-vis results were used to confirm the effects of plasmon coupling on the LSPR response. The findings suggest that thin films fabricated using Langmuir-Blodgett deposition technique can be used to study LSPR response in Ag nanoparticles. These techniques will be important for the future of many technical nanotechnology applications.

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Appendix

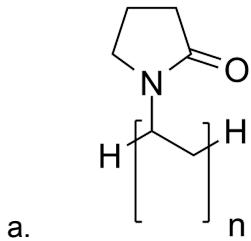
Pre Lab Questions:

1. LSPR is Localized Surface Plasmon Resonance. It is an effect in which an external electromagnetic field excites a resonance of the collective oscillation of electrons on the surface of a metal nanoparticle. This resonance is strongly influenced by various factors such as the size, shape, and composition of the nanoparticle.
2. It has dependencies of conformation and properties. For example: an increase in size would result in a lower frequency. Resonant frequencies would go up in value for higher electron density.
3. These metals have low losses in the NIR-Vis light ranges and their electron densities are flexible to migrate. They also have low damping effects. Other metals are often used to excite LSPRs... some examples would be Al, Ti, and Cu.
4. Dark field provides high contrast, with good resolution. It allowed the viewer to see electron-surface effects of scattering.
5.
 - a. A Langmuir-Blodgett trough is a device for creating monolayer films on a liquid surface.
 - b. This technique is used for synthesizing nanostructures, especially nanoparticles.
 - c. The process involves compressing nanoparticle precursors on the liquid surface to form a condensed phase, which is then transferred to a solid substrate.
 - d. The surface pressure can be precisely controlled to regulate the density and organization of the nanoparticles in the film.
6. Surface pressure is the measurement of the force per unit length at a liquid interface on a stationary or movable barrier. In Langmuir Blodgett troughs, surface pressure is regulated by compressing or expanding a monolayer of molecules at the liquid-air or liquid-substrate interface. This process enables the transfer of the compressed molecules onto a substrate to form a thin film.

Discussion Questions:

- Initially, the solution was clear in the absence of PVP, but turned yellow upon adding AgNO₃. Upon heating, the solution changed to an orange hue, followed by dark brown/orange and then a slightly green/grey-brown color. The color is due to the Ag⁺ ions and eventually subsides because of the reduction to Ag atoms (the NPs). The final green-brown hue is due to the reflection of light, which appears green, while the transmission of light through the solution results in a (dark) red color due to LSPR.

- Polyvinylpyrrolidone



- a. 111.15 g/mol
- b. The addition of PVP to the reaction serves as a stabilizer for Ag nanoparticles, preventing them from aggregating and growing into larger particles by adsorbing onto their surface through van der Waals and electrostatic forces, ultimately forming a protective layer that stabilizes the nanoparticles in solution (Kowal)
- c. The size and shape of nanoparticles are affected by the concentration of PVP, as lower concentrations result in smaller nanoparticles with octahedral morphology and higher concentrations lead to larger nanoparticles with a cubic morphology due to the degree of capping.
- $\lambda_{\text{max}} = 463.0 \text{ nm}$ $A = 0.32199$; $\text{FWHM } A = 0.160995$; Corresponding $\lambda_s = 386 \text{ nm}$, 559 nm. The nanoparticle spacing can affect the peak width, with wider spacing resulting in broader peaks for free nanoparticles, while a closer spacing in a thin film can lead to narrower peaks. (Y.K.)
4. .
- a. Paramelle gives d between 80 and 90 nm for the Ag NP in correlation with $\lambda_{\text{max}} = 463.0 \text{ nm}$. This is quite close to our visual estimates from SEM/Optical Microscopy.

d / nm	$\lambda_{\text{max}} / \text{nm}$	$\varepsilon /$ $\text{M}^{-1} \text{cm}^{-1}$ $\cdot 10^8$
56	427.0	658
58	429.2	699
60	431.5	739
62	433.8	779
64	436.2	820
66	438.7	860
68	441.3	900
70	443.8	941
72	446.7	981
74	449.5	1021
76	452.3	1062
78	455.3	1102
80	458.3	1142
82	461.4	1183
84	464.6	1223
86	467.9	1263
88	471.2	1304
90	474.6	1344
92	478.1	1384
94	481.6	1425
96	485.3	1465
98	489.0	1505
100	492.8	1546

- b. The optical extinction spectrum of Ag nanoparticles exhibits varying SPR wavelengths and extinction coefficients according to their size, whereby larger nanoparticles exhibit a red shift in the SPR wavelength and an increase in the extinction coefficient.
5. The UV-Vis and optical microscopy findings demonstrate that the Ag nanoparticles in the dispersed solution exhibit a higher degree of uniformity but are smaller in size, while the Ag nanoparticles in the film display variances in size and shape without uniformity. This can be attributed to the presence of PVP in the dispersed Ag nanoparticles, which inhibits the aggregation of the Ag NPs. In contrast, during the formation of the film, the PVP is removed via chloroform, and the Ag NPs tend to aggregate, resulting in multiple sizes. The UV-Vis analysis

revealed a distinctive peak for the dispersed Ag NPs, whereas there was no distinctive peak observed for the compressed Ag NPs film, indicating non-uniformity in size for the Ag NPs.

6. The results make apparent the dispersed solution is more uniform throughout but with lesser sized NPs. The film has carried size and conformation with less uniformity throughout when compared to the solution. The PVP keeps the silver from aggregating in the solution, when in the absence of this the conformation can vary more and the particles can bunch together.
 7. The solution had a peak as the size in the dispersed solution appears smaller than physical in microscopy. The double peak seen in our UV-Vis spectra of the film indicates the formation of a monolayer (much shorter distance) creating a plasmon coupling effect – no distinct resonance frequency but in this case two of them..
 8. Yes, these could be used in many sensor types (horizontal nanowires).
 9. The Biacore system is a protein sensor that relies on the detection of changes in the metal's refractive index resulting from surface binding, and for effective operation, the nanoparticle surface must have the capability to bind with the ligand, which can subsequently attach to the target protein, while the deposition of the nanoparticles through spin-coating on the substrate is adequate for the fabrication process.
10. 1.1.5.5.