GOLD NANOPARTICLES

A Tool for Single Molecule Spectroscopic Detection

INTRODUCTION

As you have seen in the SAM’s lab, thiolated molecules have a strong affinity for gold films binding to form self-assembled monolayers. The hydrophobicity of molecules on this bulk material was analyzed using a water droplet contact angle measurement. SAMs are not the only interesting example of gold chemical species. Research on gold nanomaterials is a growing field. Why? The physical properties of nanomaterials often differ from bulk material. Although the focus on gold nanoparticles is a modern trend, the synthesis of metallic nanoparticles is not entirely a novel procedure. Nanoparticle synthesis dates back to ancient Roman decorative artifacts. One of the most famous of these artifacts is the Lycurgis Cup. This relic, dating back to 4AD, was produced by synthesizing gold-silver alloy nanoparticles in solution. Such a nanoparticle solution is known as a colloid. This colloid was diluted in glass and hardened to produce the rich color shown in the glass of the cup. In this lab, you will look at the chemistry of colloidal gold.

We will use Raman spectroscopy to investigate an interesting property of nanoparticles – single molecule detection. The supplemental reading on vibrational spectroscopy has provided a basic background of the interaction between light and chemical substances in Raman spectroscopy. As stated in the reading, when a laser beam interacts with a sample, radiation is scattered (Rayleigh, Anti-Rayleigh, and Stokes Scattering). Unlike bulk of typical samples, the energy (wavelength) of the laser is resonant with the natural oscillation frequency of electrons in the nanoparticles. This resonant energy produces an electric field as the nanoparticle’s electron cloud to oscillates back and forth. This oscillation is known as surface plasmon resonance (see Figure 1).
Figure 1: Surface plasmon resonance.

As a result of surface plasmon resonance, the electric field of the light scattered by the particles is enhanced. In other words, the intensity of the radiation scattered by a nanoparticle is greater than the intensity of the laser beam that caused the scattering. This increase in intensity allows for detection of chemicals at lower concentrations than possible for a Raman measurement of a bulk substance. This type of spectroscopy is known as SERS (Surface Enhanced Raman Spectroscopy).

The intensity of the scattered radiation (i.e., the intensities recorded on a Raman spectrum) is defined by the following equation:

$$I = \frac{c\varepsilon_0}{2}|E|^2 = \beta(I_0)$$

Where $I$ is the scattered intensity, $c$ is the speed of light, $n$ is the refractive index of the material, $\varepsilon_0$ is the dielectric constant of the material, $E$ is the electric field of the incoming beam, $I_0$ is the initial intensity of the laser hitting the nanoparticles, and $\beta$ is the enhancement factor of the electric field. The enhancement factor causes the detected scattering to be several orders of magnitude greater than bulk Raman measurements, meaning a signal at concentrations otherwise undetectable becomes visible with the SERS effect. Interestingly, if the nanoparticles aggregate into dimer and trimer geometries in solution, it is found that the enhanced electric field focuses between the particles, further enhancing the scattered signal. This allows for single molecule vibrational and electronic Raman measurements. These single molecule measurements may be marked by small shifts in the vibrational spectrum to a higher frequency from bulk measurements depending on the bound molecule found in the focus of the field. These shifts are due to fundamental physical processes such as charge transfer between the gold nanoparticle aggregates and the bound molecule that are not well understood. This phenomenon, known as a Stark shift, has direct implications in the design of desired nano-electronic device components.

Taking advantage of these techniques, the Potma/Apkarian Labs have been able to design advanced nanosystems for better understanding a variety of fundamental electron transfer processes at the single-molecule scale. In addition, by pulsing the lasers used in measurements to time scales on the order of femtoseconds, electron transfer dynamics may be observed on time-resolved scales. This means such electron transfer processes as described above can be studied on the time scale of the electrons so they may be better controlled. This research will allow for better fundamental understanding of the physical nature of the electron at the quantum level, which in turn allows for more efficient design of nano-scale molecular information transfer systems.
This lab uses the *MORE* (Model, Observe, Reflect, and Explain) approach.

**Model:** Your prelab assignment is to use your current knowledge to construct a nano- and/or macroscale understanding of the chemistry you are about to perform.

**Observe:** While completing the procedures below, make detailed observations thinking about the model you created in the prelab.

**Reflect & Explain:** Do your observations prove or disprove your model? Construct a short written report based on your observations that supports or refutes your initial model.

Before starting the experiment, the TA will asks you to do a quick demonstration or talk-through one of the following:

1) How to use a stir bar with a stir plate.
2) Show how to use a volumetric flask, specifically: how do you get to the correct volume you want?

**SAFETY**

WHEN WORKING WITH ALL CHEMICALS, HANDLE WITH GLOVES AND PROPER PERSONAL PROTECTIVE EQUIPMENT (PROTECTIVE EYEWEAR, APPROPRIATE CLOTHING, AND LAB APRON). Place all waste in appropriately labeled containers under fume hood.

**PROCEDURE**

**Part A: Synthesis and Characterization of Gold Nanoparticles**

To synthesize gold nanoparticles, a reducing agent is added to boiling chloroauric acid. The gold cation from the acid is reduced from a positive to a zero charge state, allowing the gold in solution to form metallic bonds. As the reaction proceeds, spherical nanoparticles are suspended in solution forming a colloid. Once the reaction is complete, the colloid’s surface is covered by excess reducing agent molecules. These capping molecules keep the particles homogeneously dispersed in solution, preventing aggregation. In this experiment, you will synthesize gold nanoparticles in solution ~20 nm in diameter that are ruby red in color [1]. These particles resonantly scatter light that is centered around 785 nm in wavelength. However, if the synthesis is not complete or aggregation occurs due to the introduction of a salt or new binding ligand, this color will
change. If the system changes in such a way that a molecule finds its way into the focus point of the Electric field during aggregation, a particularly important observation will occur. The ultimate goal of this lab is to use the MORE approach to discover the chemical single molecule sensing using the gold nanoparticles you synthesize in Part A below.

**Part A. Nanoparticle Synthesis.**

**Model. (Prelab)**

1.) Draw three models of a nanoparticle colloid solution. (Draw cartoons representing a set of nanoparticles as you believe they would appear if you could see them at a molecular level.)
   a. Model 1: unaggregated
   b. Model 2: aggregated
   c. Model 3: aggregated with molecules bound to nanoparticle surface

2.) How is sodium citrate involved in the synthesis? What about chloroauric acid? Draw the structures of these compounds. What would you expect the geometry of chloroauric acid to be? Draw where you would expect the reaction to take place with respect to the central gold atom?

**Procedure/Obsere.**

1.) Fill an Erlenmeyer flask with 20 mL of 1mM chloroauric acid solution. Add a stir bar.
2.) Bring to boil on hot plate while stirring at a moderate rate. *The setting on the hotplate and stirrer should not exceed 5, and may need to be reduced during the course of the reaction.*
3.) Slowly add 2 mL of 1% sodium citrate using a disposable pipette.
4.) Boil for 10 minutes. *Be careful not splatter the solution or boil it to dryness.*
5.) Cool the solution to room temperature.
6.) Using a graduated pipet, fill Cuvette A, with a known volume of the cooled solution.

**Part B: Raman Spectroscopic Analysis of KSCN**

**Model. (Prelab)**

1.) Model the IR spectrum of SCN\(^-\) with Spartan (Equilibrium Geometry, Hartee-Fock, 3-21G, see instructions on the last page of this document). Draw cartoons showing the different vibrations for the peaks in the spectrum. Use arrows to represent the directionality of any movements.
2.) In IR, electromagnetic energy from the source is absorbed by the chemical being studied. In Raman, energy from the source is scattered by the chemical being studied. Creating a drawing or sequence of drawings representing the difference. Your drawing can have representations of chemical species involved, arrows to representing the energy coming in and out of the sample, and/or energy level diagrams.

3.) What frequency range would you expect a Raman signal of KSCN?

4.) How might concentration or binding affect the Raman signal of KSCN?

Procedure/Observe.

1.) Fill Cuvette B with 1 mL of 2M KSCN standard. Take a Raman spectrum.
2.) Record the frequencies of your spectral peaks
3.) Using the 2M standard, prepare a $1.0 \times 10^{-3}$ M KSCN solution. The calculations for this step must be performed before lab. Use a micropipet pipet to transfer the appropriate volume of KSCN from the standard into a 5 mL volumetric flask. Fill to the mark with nanopure water.
4.) Fill Cuvette C with $1.0 \times 10^{-3}$ M KSCN. Take a Raman spectrum.

Part C: Raman Spectroscopic Analysis of KSCN with AuNPs

Model. *(Prelab... answer after finishing Part B in lab)*

Using your observations from Part B, how do you think the two Raman spectra taken below will differ.

1.) What happens when KSCN and the gold nanoparticles synthesized in Part A are combined? Draw a picture of this. How does the addition of $K^+$ in solution affect the particles? What do you think happens to the $–SCN$ group? Draw a picture of this as well.

2.) Does the spectra change noticeably? If so, how? Explain your answer.

Procedure/Observe.

1.) Collect a Raman spectrum of the gold nanoparticles in Cuvette A.
2.) Using a microliter pipet add enough of the 2M KSCN solution to Cuvette A to create a $1.0 \times 10^{-3}$ M M KSCN concentration. Securely cap the cuvette and shake well. Let solution stand for at least 10 min.
3.) Collect a Raman spectrum.
Reflect & Explain:

Do your results match your initial model? Write a brief paragraph explaining your observations and supporting your conclusions. If your results differ from your model, be sure to explain why you believe this is the case. Be sure to answer all points brought up in the modeling section questions. You may notice that some concepts of this experiment are not covered in the standard textbooks for your courses. When this is the case, you are encouraged to perform scientific literature searches to aid in your answers. This is a crucial skill to develop in furthering your education in the sciences. Papers from journals such as Science and Nature, can provide a wealth of understanding in such cases. These resources can be obtained online as a service for being a UCI student. In addition, many YouTube videos exist to explain scientific concepts not covered by traditional textbooks. Be sure to properly cite any sources you use in preparing your paragraphs. You will use this approach to finish the rest of the lab through the MORE approach.

REFERENCES CITED


Spartan Instructions for Part B.

1. Build SCN with the Inorganic Model Kit. Click on the ** button and then choose S (sulfur). Click anywhere in the workspace area to add the sulfur. Click on the ** button, choose C (carbon), and then add bond to the sulfur in the Workspace area. Click on the ** button, choose N (nitrogen), and then add bond to the carbon in the Workspace area. Because two significant resonance structures exist for SCN, double or triple bonds will not be added here. We will let Spartan decide the real structure (which is an unequal average of the two resonance structures). Click Build, and then Minimize.
2. Perform an Equilibrium Geometry calculation with the Hartree-Fock 3-21G method. Before submitting the calculation, click on the boxes to the left of Infrared Spectra and Vibrational Modes in the Calculation window.
3. Go to the Display menu and choose Spectra. Click on + and select IR calculated. Click on the peaks in the Spectra window. Record the frequencies that result in stretching vibrations of the sulfur-carbon and the carbon-nitrogen bonds.