Gold Nanoparticles Absorbance

Purpose

To investigate principles of colloids and nanoparticle aggregation.

Learning Objectives

- Construct scientific explanations about absorbance of gold nanoparticles.
- Apply spectrophotometer to measure absorbance of gold nanoparticles.
- Align a molecular scheme to dimerization behavior of gold nanoparticles.

Introduction

Metallic Bonding

Most metals have very compact crystal structures involving close-packed atoms. Owing to this close-packed structure, bonding in metals is unlike ordinary ionic or covalent bonding. A valuable clue to the nature of bonding in metals is provided by their ability to conduct electricity. Electrons can be fed into one end of a metal wire and removed from the other end without causing any obvious change in the physical and chemical properties of the metal.

To account for this freedom of movement, modern theories of metallic bonding assume that the valence electrons are completely **delocalized**; that is, they occupy orbitals belonging to the entire metallic crystal instead of being constrained to the orbitals around a single atom. These delocalized electrons are often referred to as an **electron gas** or an **electron sea**. Positive metal ions produced by the loss of these valence electrons can then be thought of as "floating" in this three-dimensional sea (see Figure 1). Each ion is held in place by the attraction of the negatively charged electron sea and the repulsion of its fellow positive ions. The electron-sea model of metals not only explains their electrical properties but their malleability and ductility as well.

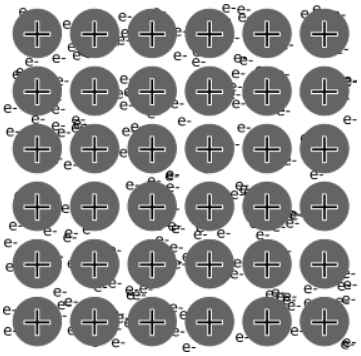

Figure 1. Lattice of metal atoms surrounded by an "electron sea"; net charge is neutral, but electrons have high freedom of motion. Image Credit: Steven Legg (Sjlegg) / Public domain via Wikimedia Commons.

Surface Plasmon Resonance (SPR)

When considering the electron sea model for metals, it is convenient to think of the electrons behaving in a manner like flowing liquid. The liquid-like movement of electrons on the surface of an atom causes fluctuations in charge much like waves in the sea. These wave-like fluctuations in the electron behavior are called plasmons or surface plasmons.

Surface plasmon resonance (SPR) refers to the electromagnetic response that occurs when plasmons are oscillating with the same frequency on the surface of a material. The interactions are similar to the photoelectric effect in which photons of light are absorbed by an atom when the frequency of the incoming light matches the electronic transition between energy levels. By comparison, in SPR, incoming light interacts with the electrons on the surface of the particle and the light can be absorbed when the frequencies match.

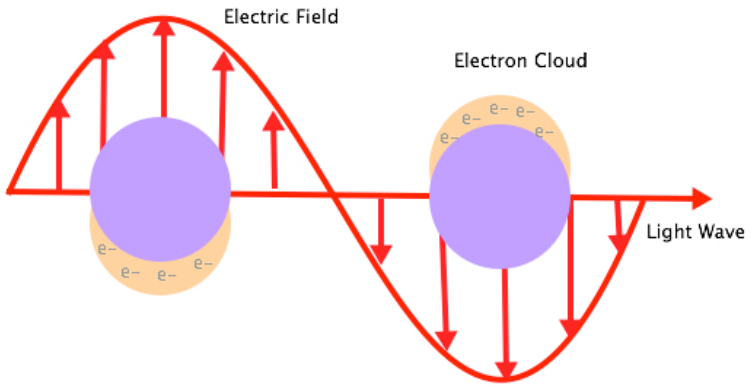

Figure 2. As a light wave passes through a metal particle, the "electron sea" fluctuating along the surface of the metal atom responds and can absorb light.

Surface Plasmon Resonance and Nanoparticles

One of the important properties of nanoparticles is that they exhibit surface plasmon resonance (SPR).

When light is directed at nanoparticles, SPR leads to absorption of the incident light. This light absorption behavior is dependent on the properties of the particle, including the shape, structure, metal type, size, and surrounding medium (such as air or water). For instance, if nanoparticles are allowed to agglomerate in a solution, becoming larger, their surface electrons will begin to behave differently, notably the frequency of light that is absorbed by the material will change and therefore the color of the solution of nanoparticles will also change. At the nanoscale, the absorption process is capable of being rigorously observed through spectrophotometric techniques. Since the absorbance behavior is readily measured, metal nanoparticles of gold and silver are commonly investigated, especially in biological applications.

Procedure

Activity I – Initial Ideas

Do not look up, reference, or copy someone else's ideas – all these responses should be your own original ideas.

Discuss ideas with your lab partner and answer the following in your lab notebook:

1. Hypothesize about what you expect to see in the absorbance spectra of each of the nanoparticle mixtures you have studied for the past two labs (mixtures A, B, and C). To answer this question, generate a completed table in your lab notebook with this format:

	Brief description of expected peak height	**Brief description of expected peak width**	**Approximate λ_{max}**
Mixture A			
Mixture B			
Mixture C			

   Take a picture of your original table from your lab notebook and insert it into your lab report submission.

2. Recall your observations of color and light scattering from the last experiment. Describe what changes you expect to see (if any) in the absorbance spectra of mixture C upon addition of NaCl. Directly address any expected shifts in λ_{max} related to changes in the color observed for this system. Explain why you expect those changes in the spectrum.

3. Describe what changes you expect to see (if any) in the absorbance spectra of mixture C upon addition of dextrose. Directly address any expected shifts in λ_{max} related to changes in the color observed for this system. Explain why you expect those changes in the spectrum.

Activity II – Experiment

Before running any experiments, pre-clean the cuvettes at your lab bench. Use cotton-tipped applicators and warm, soapy water to gently wipe the inside walls of the cuvettes to remove any residue left behind from other lab classes. After wiping the inside of the cuvettes, rinse them well with tap water and one final rinse with DI H_2O.

**Refresher: Reopen the TEM images from the previous lab and refresh your memory of the particle structure and size distribution for each solution.*

1. Place eight **(8)** clean, empty cuvettes into the holder sitting at your lab bench. Sample organization is very important throughout the experiment today, so pay careful attention to the location of different cuvettes as you put them in the holder. It may be helpful to use a paper towel or sheet of paper under the holder to write labels about what sample is in which sample holder spot. DO NOT write directly on the cuvettes.
2. In the first cuvette, place DI H_2O. This cuvette will be used to calibrate the SpectroVis.

3. In the second cuvette, add 35 drops of mixtures A. In the third cuvette, add 35 drops of mixture B.
4. In the five (5) remaining cuvettes, add 35 drops of mixture C to each cuvette.
5. In your lab notebook, make an observation table that looks like the following (keep the table on one page of your notebook):

	General mixture visual observations	**Laser pointer observations**
Mixture A		
Mixture B		
Mixture C		

6. Record visual and laser scattering observations of mixtures A, B, and C in a similar manner as the previous labs. Note: These observations may be slightly different from the previous lab when the mixtures were first synthesized, which is why it is worthwhile to record them again.
7. To record absorbance spectra, follow the same steps as in previous labs (a-c below). This lab uses semi-micro cuvettes, the same kind utilized in earlier labs, make sure to place the cuvette into the spectrometer with the correct orientation (1 cm pathlength) to collect proper spectra. To collect:
    - Use the DI H_2O 'blank' to calibrate the SpectroVis (*'Experiment> Calibrate > Spectrometer: 1'*).
    - Measure samples using the '*Collect'* and *'Stop'* buttons.
    - Store the spectrum of each individual sample by selecting '*Experiment > Store Latest Run.'*
8. When you are done collecting the spectra, stop data collection in LoggerPro. Keep your cuvettes of A, B, and C for reference.
9. Use text annotation to add useful labels to the graph to remember which spectrum matches which mixture.
10. <u>Print/Save:</u>
    - Once you are done labeling, use '*File > Print Graph'* to print a copy for your lab notebook.
    - Also, print a PDF copy and save/send yourself the file for online report submission.
    - You are also strongly encouraged to save your LoggerPro raw data file for analysis later/outside of class.

Activity III – Analysis

Consider your observations of the absorbance spectra for mixtures A, B, and C. Discuss and write responses to the following in your lab notebook:

1. What specific similarities and differences do you notice among the absorbance spectra for the nanoparticle mixtures (A, B, and C)? Specifically address the shapes of the spectra and λ_{max} values.
2. Look back in your notebook at the data from the imaging lab. What is the **<u>range</u>** of particle sizes in each nanoparticle mixture?
3. How do you think the size of the nanoparticles relates to the observed spectrum for each mixture?

Activity IV – Experiment

1. In your lab notebook, make an observation table that looks like the following (keep the table on one page of your notebook):

	Visual observations – immediately after mixing	**Visual observations – ~10 min after mixing**	**Laser observations – ~10 min after mixing**
Mixture C with NaCl			
Mixture C with dextrose			
Mixture C with cysteine			

2. Into three of the cuvettes that contain mixture C, prepare separate mixtures by adding 5 drops of NaCl, dextrose, and cysteine solutions (C + NaCl, C + dextrose, and C + cysteine). Remember to use an organization system to identify each sample without writing on the cuvettes.
3. Carefully cap the cuvettes, and gently shake them to fully mix the solutions.
4. **Record the clock time** at which you prepared these cuvette solutions and record visual observations of these new mixtures.
5. Wait at least 10 minutes, during which time you should continue observing the solutions. Record any visual changes that occur over this time.

> ***Note: Not all chemistry happens instantly! If you are expecting an 'instant reaction/lack of reaction,' then you will miss most of the science taking place in the world. The mixing behaviors you will be observing today are not instant and require you to have patience and use the scientific skills you have been practicing and developing throughout this course. Consider what the terms 'careful observation' and 'patience' mean with respect to practicing rigorous, high-quality science.***

6. While you are waiting, hold the cuvettes of A, B, and C side-by-side with the new mixtures to make visual comparisons of the colors and any other noteworthy observations. Record any similarities and differences you notice (that aren't already recorded) in your lab notebook.
7. After 10 minutes has elapsed, record another set of visual observations and laser scattering in your observation table.
8. Start a new graph on the Spectrovis. If you still have the spectra for mixtures A-C, you should save the data before creating a new graph.
9. Measure the absorbance of the three mixtures on one graph in LoggerPro (C + NaCl, C + dextrose, and C + cysteine).
10. Use text annotation to add useful labels to the graph to remember which spectrum matches which mixture.
11. Print/Save:
    - Once you are done labeling, use '*File > Print Graph'* to print a copy for your lab notebook.
    - Also, print a PDF copy and save/send yourself the file for online report submission.
    - You are also strongly encouraged to save your LoggerPro raw data file for analysis later/outside of class.

Activity V – Analysis

Consider your observations of what you see changing in the absorbance spectra for these mixtures in comparison to the spectra of just mixtures A, B, and C. Discuss and write responses to the following in your lab notebook:

1. What similarities and differences do you notice among the absorbance spectra for these new mixtures of C (with the different substances) as compared to the original mixtures A, B, and C? Specifically address the shapes of the spectra and λ_{max} values.
2. For any differences in the spectra that you see occurring upon addition of NaCl, dextrose, or cysteine, provide a molecular-level explanation for what you think is occurring with the nanoparticles that can explain the observed differences.
3. Sketch a picture to accompany the explanation in the previous question. Take a picture of your lab notebook page containing the original sketch so you can insert it into your lab report submission.

Activity VI – Predict

In the next activity, you will add a solution of copper(II) nitrate to the mixtures you just prepared (C + NaCl, C + dextrose, and C + cysteine). Based on your current molecular-level thinking of what is happening in these systems, predict what you expect to observe upon addition of copper(II) nitrate to these previously prepared mixtures (C + NaCl, C + dextrose, and C + cysteine).

Complete your predictions by making a prediction table in your lab notebook. For this table, split the width of the lab notebook in half with the following:

- Left side: mixture label and macroscopic prediction column
- Right side: absorbance spectrum simple sketch, label with approximate predicted λ_{max}

	Predicted changes – macroscopic level (color, light scattering, visual observations?)	**Sketch of predicted absorbance spectrum – clearly show features (peak height, peak width, λ_{max})**
Mixture C + NaCl		
Mixture C + dextrose		
Mixture C + cysteine		

Take a picture of your lab notebook page containing the prediction table so you can insert it into your lab report submission.

Activity VII – Experiment

WARNING: Your experiment will fail if you try to perform this activity too soon. You should have spent a reasonable amount of time on the previous activities. This lab manual procedure assumes that AT LEAST 30 minutes has passed since you first mixed the solutions in Activity IV. If it has been less time than that, this experiment will fail.

Test your predictions by completing the following experiment:

1. In your lab notebook, make an observation table that looks like the following (keep the table on one page of your notebook):

	Visual observations – immediately after mixing	**Visual observations – ~5 min after mixing**	**Laser observations – ~5 min after mixing**
Mixture C with NaCl + copper			
Mixture C with dextrose + copper			
Mixture C with cysteine + copper			

1. You should have two cuvettes that still contain mixture C alone (with nothing added). Keep one of these cuvettes as a control. Into the other cuvette of mixture C, add 5 drops of copper(II) nitrate solution.
2. Similarly, add 5 drops of copper (II) nitrate solution into each of the three mixtures containing C that have already been mixed with other substances (C + NaCl, C + dextrose, and C + cysteine).
3. Carefully cap the cuvettes, and gently shake them to fully mix the solutions.
4. Immediately record visual observations on the mixtures that now contain copper(II) nitrate.
5. Continue observing the solutions for approximately 5 minutes, recording any visual changes that occur over this time in your lab notebook.
6. While you are waiting, hold the cuvettes of A, B, and C side-by-side with the new mixtures to make visual comparisons of the colors and any other noteworthy observations. Record any similarities and differences you notice (that aren't already recorded) in your lab notebook.
7. After 5 minutes has elapsed, record another set of visual observations as well as laser scattering in your observation table.
8. Use the Spectrovis to measure the absorbance of the four mixtures that contain copper(II) nitrate on one graph in LoggerPro:
    - C + NaCl + $Cu(NO_3)_2$
    - C + dextrose + $Cu(NO_3)_2$
    - C + cysteine + $Cu(NO_3)_2$
    - C + $Cu(NO_3)_2$
9. Use text annotation to add useful labels to the graph to remember which spectrum matches which mixture.
10. <u>Print/Save:</u>
    - Once you are done labeling, use '*File > Print Graph'* to print a copy for your lab notebook.
    - Also, print a PDF copy and save/send yourself the file for online report submission.
    - You are also strongly encouraged to save your LoggerPro raw data file for analysis later/outside of class.

Activity VIII – Analysis

Your TA will provide you with a molecular scheme representing the chemical reaction you just completed. In the scheme, there are three stages in the reaction scheme separated by arrows.

Consider your observations in conjunction with the scheme your TA has provided and the chemical structures of each substance present in the mixtures (NaCl, dextrose, and cysteine). If needed, the chemical structures of the different substances can be looked up online. Discuss and complete the following:

1. Label the scheme with the following:
    - Chemical identities of each unmarked symbol
    - Observable color at each of the three stages in the scheme

    Take a picture of your labeled scheme to include in your lab report submission.

2. Provide a molecular-level explanation for what is happening at:
    a. First stage in scheme (with only the circles alone)
    b. Second stage in scheme (circles surrounded by wavy lines)
    c. Third stage in scheme (circles surround by wavy lines closer together connected by small dots)

3. In this lab, a minimum wait time of 30 minutes was required between the steps done between two of the experimental activities.
    a. Describe which part of the scheme corresponds to this wait time.
    b. Provide a scientifically-logical hypothesis for why the molecular-level process taking place in the scheme requires this wait time.

Before Leaving Lab

- Properly dispose of all lab waste
- Thoroughly clean your workspace area
- Sanitize all equipment as directed
- Check to make sure you have the necessary data and files for your lab report submission. In addition to the observations and written responses collected in your notebook, for this lab you should have:
    - Picture of your lab notebook page containing the prediction table from Activity I
    - PDF file containing the spectra from Activity II
    - PDF file containing the spectra from Activity IV
    - Picture of your lab notebook page containing the original sketch from Activity V
    - Picture of your lab notebook page containing the prediction table from Activity VI
    - PDF file containing the spectra from Activity VII
    - Picture of your labeled molecular scheme from Activity VIII

Post-Lab Additional Questions (20 pts)

Do not look up, reference, or copy ideas from any other sources besides your own thinking.
All responses given on these questions should be your own original ideas.

Based on your experimental observations from this lab and evidence from previous labs, consider each of the chemical systems listed in the questions below and complete the questions for each.

You are STRONGLY encouraged to review your prior labs as the quality of your responses on this post-lab will be graded based on cumulative knowledge and experimentation completed throughout the semester. This would include reading grading feedback and incorporating that into revised ideas about these different chemical systems.

When asked for sketches, be sure to include a key or labels to identify any symbols used in your picture. For each sketch, take a separate digital picture to insert into your lab report submission. Be sure your photo is clear/in focus and appropriately sized so details will be easy to read.

1. Gold nanoparticles

    a. (2 pts) At the molecular-level, describe the chemical structure of gold nanoparticles.
    b. (2 pts) In your lab notebook, sketch a molecular-level picture of gold nanoparticles.

2. Aqueous solutions produced from placing food dye in water

    a. (2 pts) At the molecular-level, describe how this system is similar and different from gold nanoparticles.
    b. (2 pts) In your lab notebook, sketch a molecular-level picture of this system.

3. Aqueous solutions produced from placing NaCl in water

    a. (2 pts) At the molecular-level, describe how this system is similar and different from gold nanoparticles.
    b. (2 pts) In your lab notebook, sketch a molecular-level picture of this system.

4. Aqueous solutions produced from placing sugar in water

    a. (2 pts) At the molecular-level, describe how this system is similar and different from gold nanoparticles.
    b. (2 pts) In your lab notebook, sketch a molecular-level picture of this system.

5. Solid precipitates formed by reacting hydroxide salts with iron or copper solutions

    a. (2 pts) At the molecular-level, describe how this system is similar and different from gold nanoparticles.
    b. (2 pts) In your lab notebook, sketch a molecular-level picture of this system.