Semiconductor Lab - *Metal Nanoparticles and Surface Plasmon Resonance*

Objectives Synthesize gold nanoparticles of various sizes and relate size to synthetic conditions and surface plasmon resonance.

Background Colloidal gold has been used for centuries in glass for its brilliant red color.[1]

Figure 1: the Lycurgas cup, stained red with colloidal gold[1]

Gold and other metal nanoparticles have enhanced optical properties due to the collective oscillations of surface electrons excited by visible light. For example, they absorb light orders of magnitude more effectively than strongly absorbing organic dyes. Their enhanced optical properties make them useful for applications such as sensing of biological analytes and enhancement of Raman scattering for molecule detection.[2] This effect is not limited to metal nanoparticles, as recently many examples have been demonstrated in semiconductor nanoparticles.[3]

This enhancement in optical properties is caused by collective oscillations of electrons at the surface of nanoparticles, otherwise known as **surface plasmon resonance (SPR)**, presented schematically in Figure 1. SPR occurs because the electric field of light (electromagnetic radiation) polarizes the particle's conduction electrons to one side of the particle. The electrons are then pulled back to their nuclei by Coulombic attraction with a specific frequency determined by the size and shape of the metal nanoparticle as well as the dielectric constant of the metal and surrounding media. When incident light is in resonance with this specific frequency, the electron cloud oscillates.[2,4] This effect is only visible in small particles because the surface alters the polarizability of the material, shifting the resonance frequency to the visible light regime. Furthermore, the radius of the particle must be much smaller than the wavelength of incident light for the surface plasmon to be excited.[5]

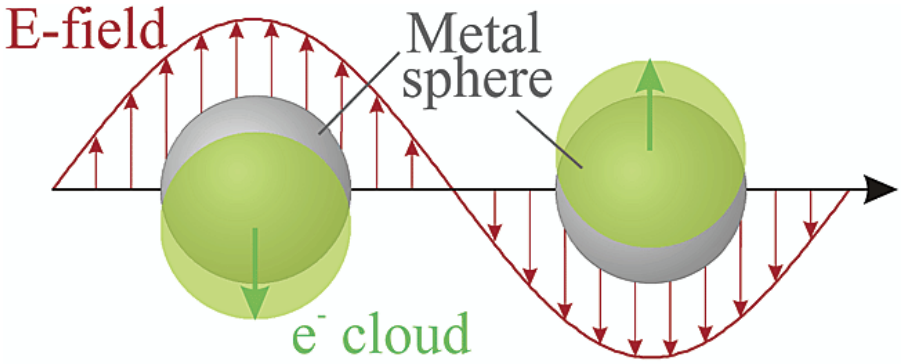

Figure 2: Surface plasmon resonance in metal nanospheres[4]

Varying synthetic conditions can significantly affect particle size and shape, which can drastically affect the optical properties and therefore the end use. Gold nanoparticles are classically synthesized by reducing a Au(III) salt with sodium citrate.[6] Initially, the gold salt is dissolved in water. When the reducing agent is added, the Au(III) is reduced to Au metal (oxidation state of zero), which quickly nucleates and grows into nanoparticles. These particles are capped by the citrate molecules and are therefore stabilized against aggregation. In this lab we will explore the effects of varying citrate concentration on particle size, and we will characterize the variable optical properties and particle size by absorption spectroscopy and dynamic light scattering (DLS). The effects of particle size on surface plasmon resonance frequency have been theoretically determined by Mie in 1908, who solved Maxwell's equations for light interacting with small metal spheres. His solution dictates that for gold nanoparticles above 20 nm in diameter, the surface plasmon resonance frequency shifts to lower energies as particle size increases,[5] which we expect to observe as a redshift in absorbance as particle size increases.

Figure 3: gold nanospheres of variable size and color[7]

Discussion

- Describe how surface plasmon resonance works, especially related to nanoparticles
- Discuss how synthetic protocol affects size
- Discuss characterization techniques (DLS and absorption spectroscopy)

- What are some potential applications of surface plasmon resonance in metal nanoparticles?

Materials

- Tetrachloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$)
- Sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$)
- 20 mL scintillation vials
- Small magnetic stirrers
- DI water

Equipment

- Dynamic Light Scattering Spectrometer, Absorption Spectrometer, Hot plate, 100-1000 µL micropipette, hand clamp

Procedure

1. Prepare gold and citrate solutions
    a. Measure about 40 mg tetrachloroaurate trihydrate into a scintillation vial (must be at least 40 mg).
    b. Add the gold salt to a 250 mL beaker by dissolving in water and pouring into the beaker. Follow with washing to ensure all gold is in the beaker. Do not use more than 100 mL water for this process.
    c. Dilute the solution to 0.4 mg/mL by adding the appropriate amount of DI water
    d. Add 10 mL of gold solution to 7 separate scintillation vials with stir bars
    e. Measure about 100 mg sodium citrate dihydrate to a scintillation vial
    f. Dilute to 10 mg/mL by adding the appropriate amount of DI water
2. Boil gold solution
    a. Set one scintillation vial on the hot plate
    b. Set heat to 290 ˚C and stirring to 1000 rpm. These settings will vary depending on the hot plate and stir bar being used.
    c. Observe when the solution boils. It may be necessary to stop stirring briefly, as stirring disrupts formation of bubbles.
3. Add citrate
    a. Have a labmate hold the scintillation vial with the hand clamp. This is important, as if your hand slips while adding the citrate you will spill boiling acid in the fume hood.
    b. Carefully inject the appropriate amount of 10 mg/mL sodium citrate solution to the scintillation vial while it is stirring. For the first sample, inject 250 µL.
    c. Allow the solution to stir while boiling for 5 minutes and observe changes in the solution
    d. Using the hand clamp, carefully remove the scintillation vial and close it when it is sufficiently cool
4. Repeat steps 2 and 3 but inject the following volumes of sodium citrate solution
    a. 375, 500, 625, 750, 875, and 1000 µL
5. Characterize by DLS and UV-Vis

References

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