Lab Module 2: Synthesis of Hollow Gold-Silver Nanoparticles and Investigation of Their Optical Properties

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Prerequisite Student Knowledge: Chemistry and Materials Science background at the level of PHYS 2074 (University Physics II), CHEM 1123/1121L (University Chemistry II) or MEEG 2303 (Introduction to Materials), or equivalent

Student Learning Objectives

1. Introduce students to the control of composition/morphology for the nanoparticles with programmable physical and chemical properties.
2. Introduce the solution-phase synthesis of nanoparticles with the emphasis on the galvanic replacement reaction.
3. Demonstrate how composition and morphology of the nanoparticles influence their optical properties.
4. The end goal is to give students an introductory knowledge of chemical synthesis of nanoparticles and how the properties change with composition and morphology of the nanoparticles

Safety Rules

1. Safety information must be reviewed prior to experiments. This includes lab safety training, safety data sheets (e.g. MSDS) for chemicals used, and lab procedures.
2. Personal protective equipment is required at all times. These include lab coats, safety glasses, gloves, close-toed shoes, and long pants.
3. Used chemicals and materials should be captured in appropriate waste receptacles and not sent to the sewer.
4. Caution should be taken around heating mantles and reaction flasks to minimize risk of accidental burns.

Introduction

Nanomaterials composed of coinage metals (Cu, Ag, and Au) have many attractive biological applications due to their unique optical properties.[1-3] When their size is comparable or smaller to the wavelength of light, their free electrons in the conduction band collectively oscillate with the electric field generated by the incident light and give rise to an extinction peak at the resonant wavelength (Fig. 1). This phenomenon is called localized surface plasmon resonance (LSPR). The extinction peak is the sum of absorption and scattering. In 1908, Gustav Mie developed a theory to describe the light extinction and scattering of spherical metal nanoparticles. The Mie theory is the exact solution to Maxwell’s electromagnetic field equations which describe a plane wave interacts with a metal sphere of radius R having the same dielectric functions as its

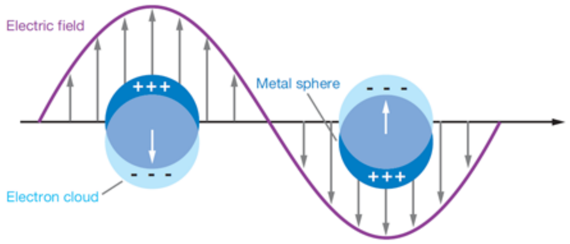


***Figure 1**. Schematic illustration of a localized surface plasmon. (Reproduced from reference 2).*

bulk counterpart. If the boundary conditions are specified, the extinction cross-section (σ_{ext}) of a sphere can be obtained, and thus the extinction efficiency factor (Q_{ext}) which is defined as ratio of the extinction cross section to the physical cross-sectional area (πR^2). For example, when $R \ll \lambda$, one can neglect the phase retardation and effects of higher multipoles and only consider the dipole oscillation contribution. The extinction cross-section is then derived as eqn. 1.

$$\sigma_{ext}(\lambda) = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_i(\lambda)}{[\varepsilon_r(\lambda) + 2\varepsilon_m]^2 + \varepsilon_i(\lambda)^2} \qquad (1)$$

where ε_m is the dielectric constant of the embedding medium and the ε_r and ε_i are the real and imaginary components of the metal dielectric function, respectively. A resonance peak occurs when the condition of $\varepsilon_r(\lambda) = -2\varepsilon_m$ is satisfied. In the case of Cu, Ag, and Au, this condition is met in the visible region of the electromagnetic spectrum. For a given material, the position, height, and width of resonance peak depend on the size and shape of the nanoparticle.

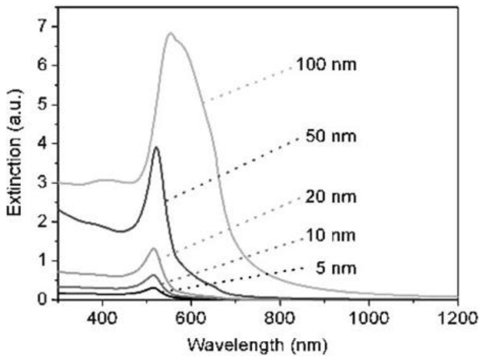


***Figure 2**. Extinction spectra calculated using Mie theory for Au nanoparticles of different diameters. (Reproduced from reference 3).*

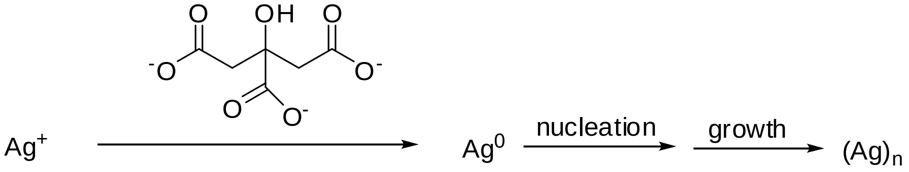
In addition to size and shape, the dielectric constant ε_m of the embedding medium (or refractive index, n; $\varepsilon_m = n^2$) also influence the wavelength maximum of the resonance (λ_m). The shift of this wavelength is dependent on the change in the local environment such as the solvent and the surface coating. For example, the relationship between the shift and the surface adsorbate is shown in eqn. 2.[2]

$$\Delta\lambda_{\max} = m\Delta n[1 - \exp(-\frac{2d}{l_d})] \qquad (2)$$

where m is the bulk refractive-index of the nanoparticle; Δn is the change in the refractive index induced by the adsorbate; d is the effective thickness of adsorbate layer; and l_d is the characteristic electromagnetic field decay length. The sensitivity of the LSPR to the local environment provides a useful tool for chemical and biological sensing and indirect validation of the success of the surface modification.

Gold nanoparticles are the well-studied materials due to their chemical and biological inertness. The LSPR of the spherical nanoparticles is in the visible region and slightly varies with the size of the nanoparticles (Fig. 2). For biomedical applications, the LSPR of the nanoparticles need to be shifted to the near-infrared (NIR) region (650-900 nm), which is the “transparent” window for the light, enabling deeper tissue penetration. There are several ways to shift the LSPR of the nanoparticles to NIR: 1) aggregation of individual particles to nanoparticle clusters; 2) coating of SiO_2 particles with metal shells; 3) elongation of the spherical particles into rod-shaped particles; and 4) hollowing out the interior of the metal nanoparticles. The color change in the first scenario is often used for biological sensing.[4] The latter three types of nanostructures can be used as contrast agents for optical imaging, therapeutic agents for photothermal therapy, and controlled-release drug delivery.[5] In this module, we will synthesize the hollow Au-Ag nanoparticles and characterize their optical properties.

Hollow Au-Ag nanoparticles are synthesized using the galvanic replacement reaction between the Ag nanoparticles and chloroauric acid ($HAuCl_4$). Initially, Ag nanoparticles are prepared through the chemical reduction using sodium citrate as a reducing agent (eqn. 3).[6] Citrate also serves as a capping agent that protects the nanoparticles from aggregation.



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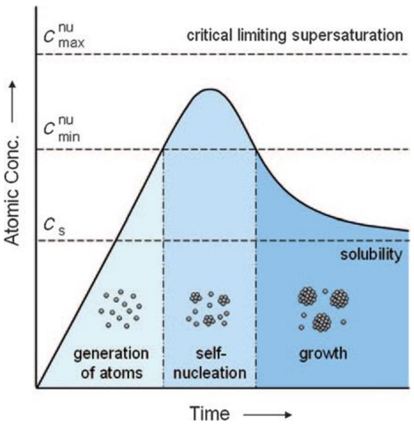

Figure 3*. Schematic illustration of nucleation and growth of nanoparticles. (Reproduced from reference 4).*

After the Ag reduces, two major processes will occur in the reaction: nucleation and growth (Fig. 3).[7-8] Once the atomic concentration of Ag has reached a critical threshold it becomes supersaturated, and the atoms independently self-nucleate. Nucleation creates small nanoclusters of atoms lowering the atomic concentration below the critical nucleation threshold. Metal atoms still persist at a concentration sufficient to grow onto the preformed nuclei during the growth phase. It requires significantly more energy to self-nucleate than to join an existing nucleus, so nuclei grow larger. Thus, as long as the atomic concentration remains below the nucleation threshold growth will occur. If the atomic concentration crosses the nucleation threshold again, then additional nucleation events can occur, which results in a broader distribution of sizes as the older and younger nuclei are not at the same point in the growth process. There are different means to control the size distribution of the nanoparticles in the citrate reduction method.[9-12] In this context, a strong Ag capping agent, poly(vinyl pyrrolidone) (PVP), will be added to the reaction.

In the second step, the Ag nanoparticles will serve as a sacrificial template for the generation of the hollow Au-Ag nanoparticles via the galvanic replacement reaction (Eqn. 4).[13-14]

$$3Ag\ (s) + AuCl_4^-\ (aq) \xrightarrow{heat} Au\ (s) + 3Ag^+\ (aq) + 4Cl^-\ (aq) \qquad (4)$$

The driving force of the reaction is the reduction potential difference between the redox pairs. The reduction potential for the $AuCl_4^-/Au$ pair (0.99 V vs SHE) is higher than the Ag^+/Ag pair (0.80 V vs SHE), resulting in the spontaneous reaction of eqn. 5 (Gibbs energy change: $\Delta G = -nFE < 0$). The reaction is carried out by titrating different volumes of the $HAuCl_4$ solution to the Ag nanoparticle suspension. The morphological change of the nanoparticles is illustrated in Figure 4. The replacement reaction is initiated stochastically from the surface of the nanoparticles through a pitting process (A). As the reaction proceeded, nanoboxes are formed through a combination of replacement and alloying between Ag and Au (B-C). By the end of the reaction, Au-Ag nanocages with hollow interiors and porous walls evolved as a result of dealloying of Ag from the Au-Ag alloyed walls (D-F). The formation of the hollow

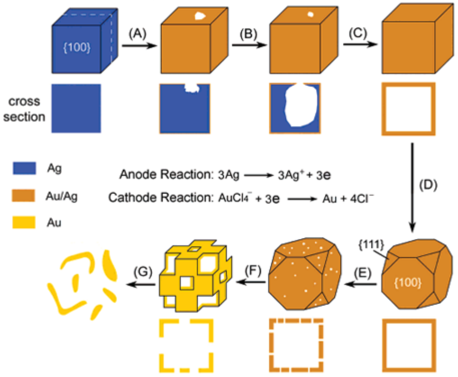

Figure 4*. Schematic illustration of morphological evolution of galvanic replacement reaction. (Reproduced from reference 12).*

structures is attributed to difference in the diffusion rates between the Au and Ag, known as the Kirkendall effect.[15-16] The 3 to 1 stoichiometry of Ag to Au in the reaction leads to fewer atoms in the final nanoparticles, resulting in the porous walls.

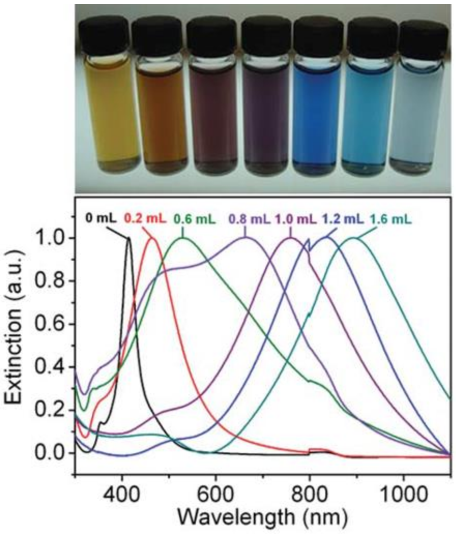

***Figure* 5**. *Upper panel: vials containing aqueous suspension of Au-Ag nanoparticles prepared by titrating Ag nanoparticles with different volumes of $HAuCl_4$ solution. Lower panel: the corresponding extinction spectra of the aqueous suspension (Reproduced from reference 3).*

During this replacement process, the extinction spectra change with the morphological evolution (Fig. 5). The extinction efficiency factor of each nanostructure can be quantified based on the extinction spectra using Beer-Lambert Law (eqn. 5) using UV-vis spectrometer.

$$A = \varepsilon c l \tag{5}$$

where A is the measured absorbance of wavelength maximum of the LSPR; ε is the molar extinction efficiency factor at this wavelength ($N_A Q_{ext}$ with N_A is the Avocado constant); c is the molar concentration of the sample; and l is the path length of the beam travelling through the sample. At a fixed path length usually determined by the cuvette that is used, the absorbance is proportional to the molar concentration of the nanoparticles. By plotting the absorbance as a function of nanoparticle molar concentration, the slope gives the molar extinction efficiency factor (slope = εl) and the extinction efficiency factor of individual nanoparticle can be derived. The accuracy of the experimental data highly depends on uniformity of the sample and accurate concentration measurement. In this module, we will learn the synthesis of the metal nanoparticles and study their optical properties.

Materials, Supplies and Instrumentation

Chemicals:

- Silver nitrate ($AgNO_3$)
- Trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$)
- Poly(vinylpyrrolidone), M.W. 55000 (PVP)
- Tetrachlororauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$)
- Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$)
- 18 MΩ water

Supplies:

- A balance with resolution of 1 mg
- A 100 mL and a 50 mL 3-neck round bottom flasks
- Magnetic stir bars
- A condenser and glass stoppers
- A magnetic stir plate and heating mantle
- A centrifuge and appropriate centrifuge tubes
- A bath sonicator
- A timer

- UV-Vis acrylic cuvettes
- Pasteur pipettes and bulbs
- Calibrated micropipette and appropriate tips
- Laser Pointer

Instrumentation:

- UV-Vis spectrophotometer
- Transmission electron microscope (TEM)

Experimental Procedures

Solution Preparation:

- 50 mM PVP (5.6 mg/mL), 5 mL
- 112 mM sodium citrate (33.4 mg/mL), 5 mL
- 12 mM KCl (0.89 mg/mL), 5 mL
- 115.0 mM $AgNO_3$ (19.6 mg/mL), 3 mL
- 1 mM $HAuCl_4$ (0.39 mg/mL), 10 mL
- 100 mM $CuSO_4$ (25 mg/mL), 5 mL

Solutions will be prepared in advance by instructors.

Synthesis of Silver Nanoparticles:

Add 19 mL H_2O to 100 mL flask with a stir bar. Add 0.4 mL of 115.0 mM $AgNO_3$. Place on a heating mantle with a condenser for approximately 10 min and bring to a boil. When the solution begins to boil, quickly add 1 mL of PVP and 0.25 mL of 12 mM KCl solutions and stopper the flask. Wait 2 min for the solution to reequilibriate then quickly add 1 mL of 112 mM citrate solution. Start a timer and record any changes in color you observe. After approximately 1 min the solution should be light yellow indicating the nucleation. In about 5 min, the reaction should then change to a green hue and become turbid (opaque). Once the reaction becomes turbid, allow it to remain on heat for an additional 10 min. Then carefully remove from heat and cool in air. Allow the solution to cool for at least 10 min.

For purification, evenly distribute the nanoparticle suspension into two 15 mL centrifuge tubes. Make sure the tubes have the same weight, then centrifuge at 6500 rpm for 15 min. The centrifuge will cause the nanoparticles to sediment at the bottom of the tube while the various reactants remain in the supernatant. Remove from the centrifuge and extract all the supernatant with a Pasteur pipette (being careful not to disturb the pellet at the bottom). If the pellet is disturbed the sample can easily be centrifuged an additional time. Next add 5 mL H_2O to each tube, sonicate to redisperse, and centrifuge for an additional 20 min at 6500 rpm. Remove the supernatant, add 1.1 mL of H_2O to each tube, and briefly sonicate to redisperse particle. Then combine both samples into one of the centrifuge tubes for further use.

Synthesis of Hollow Gold-Silver Nanoparticles:

Add 10 mL H_2O to the 50 mL flask. Place on a heating mantle with magnetic stirring and allow to heat for 10 minutes, so that it starts to boil. Next add 1.0 mL of PVP solution and 1.0 mL of the silver nanoparticle suspension. Wait 2 min for the solution to equilibrate. Begin adding 1 mM $HAuCl_4$ dropwise to the reaction flask. Add the $HAuCl_4$ solution no faster than 0.5 mL/min (~20 drops/min). Groups will be using different amounts of Au^{3+} solution, so that the hollow particles can be tuned to different wavelengths. Instructors will provide specific quantities of Au to be added for each group. It will likely take 2 and 6 mL to reach the desired wavelength (e.g., 650 nm); however this value may be anywhere from 1-3 mL depending on the particle size and concentration of the silver nanoparticles being used. Make note of any observed color during this process.

Acquisition of UV-Vis Spectra:

Add 1.9 mL H_2O to a cuvette and acquire a blank spectrum. To this add 0.1 mL of remaining Ag solution to yield a 20× dilution. If needed, dilute the solution further to achieve a clean spectrum. Record the wavelength of maximum absorbance and the value of this absorbance. If this spectrum has a maximum value greater than one, then dilute the sample so that the maximum is ~1 a.u. In a separate cuvette, directly add 2 mL of the Au-Ag reaction solution. Record its maximum wavelength and similarly dilute the sample to a maximum absorbance at ~1 a.u.

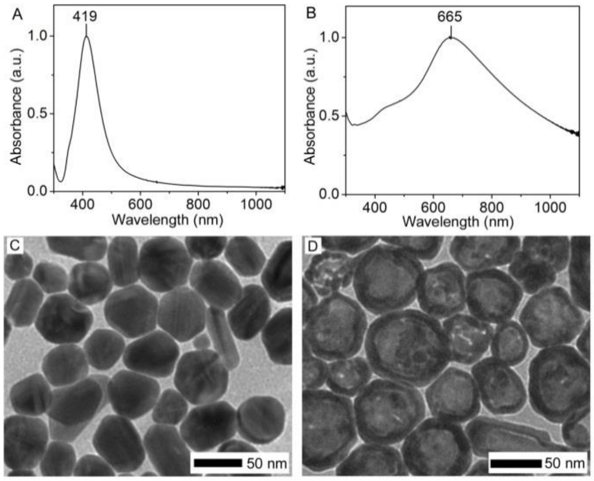

***Figure 6**. UV-Vis spectra of the nanoparticle suspension: (A) Ag nanoparticles; and (B) hollow Au-Ag nanoparticles. TEM images the (C) Ag nanoparticles; and (D) hollow Au-Ag nanoparticles.*

Investigation of Absorption and Scattering

Acquire a standard red laser pointer and the samples, in cuvettes, used for the prior UV-Vis study. In clean cuvettes, prepare 2 mL of H_2O and 2 mL of 100 mM $CuSO_4$. Shine the beam downward through each sample. *Record any pertinent observations particularly relating to the shape and intensity of the beam.* The beam can be more easily visualized in a darkened room, to minimize ambient light.

TEM imaging:

The TEM samples are prepared by putting a drop of the nanoparticle suspension on the TEM grid and allowing it to dry at room temperature. The TEM image will be recorded on the Jeol 1400. The TEM images will be obtained with the assistance of the TA. Identify the size and shape of the nanoparticles. Specifically, measure the diameter of a statistically significant sample of nanoparticles.

Post Experiment Cleaning:

Clean all glassware following use. Condensers and stoppers need to be thoroughly rinsed with deionized water. Rinse flasks into the liquid waste then thoroughly scrub with soap and water in the sink. Be careful not to scratch the glass. Used centrifuge tubes, pipette tips, and cuvettes should be discarded in solid waste, and all unusable glassware should be disposed of in glass waste. All glassware will be acid-washed under the supervision of the instructors.

Lab Report:
Lab reports will contain the sections described below, and are expected to be written as though it were to be published in a scientific journal. The content described in each section is expected to be present in the report, but additional information is expected.

Abstract – Briefly describe the purposes and broad methodology of the experiment. Include a summary of the major results from YOUR experiments.

Introduction – The background of the experiments is outlined. Specifically, the origin and nature of the optical properties should be considered with regard to the experiments performed and the synthetic methods utilized should be thoroughly explained.

Experimental Methods – All experimental procedures are briefly described in such a manner that the reader could repeat the experiment. Important information includes (but is not limited to) equipment used, quantities of solutions, reagents, reaction times, and dilutions should all be included. Methods are expected to describe the procedure followed by the author of the report.

Results and Discussion – All results should be presented, described, and the implications of these data discussed. Include a sample calculation for all unique calculations. Clearly labeled figures should be included which show the relevant data, and any significant observations during the reaction of deviations from protocol should be discussed.

Additionally, the following discussion questions should be integrated into the text:

1. Mie theory calculations were performed on Ag nanospheres of varying diameters resulting in the relationship
   $$D = \sqrt{(24.01 + (\lambda_{max} - 385) * 100)} + 4.9 \qquad (5)$$
   where D is the sphere diameter and λ_{max} is the LSPR maximum.[17] Use this equation to calculate the diameter based on the UV-Vis spectrum and the LSPR maximum based on TEM measurements for the AgNPs that were synthesized. Remark on the origin of any discrepancies.
2. Briefly compare your results for hAuNP synthesis to those of other groups. What trends are observed as the quantity of Au increases.
3. Provide a rationalization as to why the LSPR redshifts as (A) AgNP diameter increases and (B) hAuNP wall thickness decreases. Consider what happens to the photon energy as the wavelength increases.

References – Full citations for references utilized to write the report should be included. A good reference section will include the lab handout, possibly a textbook, and a handful of peer-reviewed papers to support arguments made and background information utilized. In text citations should use a superscript number corresponding to the full citation in the reference section. Look through this handout for examples.

References

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