Experiment 20

SYNTHESIS AND CHARACTERIZATION OF GOLD NANOPARTICLES

Objective

The purpose of this experiment is to prepare gold nanoparticles of different sizes from hydrogen tetrachloroaurate(III) ($HAuCl_4$) that is reduced by sodium citrate ($Na_3C_6H_5O_7$), and to determine the characteristic absorption spectra of the as-prepared solutions.

Lab techniques

- Preparing aqua regia to clean the glassware.
- Setting up reflux system.
- Operating graduated pipet, stirrer/hot plate, and UV-vis spectrophotometer.

Introduction

I. Preparation of gold nanoparticles

Nanomaterials are a kind of novel materials with at least one dimension sized between 1~100 nm (1 nm = 10^{-9} m). In this experiment, gold nanoparticles of different sizes are prepared from reduction of tetrachloroaurate(III) ions ($AuCl_4^-$) by controlling the relative amount of sodium citrate. At high molar ratios of $Na_3C_6H_5O_7/AuCl_4^-$, small-sized gold nanoparticles are prepared, and vice versa. The reaction equation is shown as equation 20-1.

$$HAuCl_4(aq) + \underset{\text{Reducing agent}}{Na_3C_6H_5O_7(aq)} \xrightarrow{\text{Reflux for 10 min.}} \underset{\text{Gold nanoparticles}}{Au(s)} \qquad (20\text{-}1)$$

Strict requirements have to be met in order to prepare gold nanoparticles successfully. All glassware used in the experiment should be soaked in aqua regia to clean the surfaces and then washed thoroughly with DI water to remove any remaining acid. It is also important to continuously stir mixtures of $Na_3C_6H_5O_7$ and $AuCl_4^-$ during the reaction that helps synthesize particles with uniform sizes. In this experiment, we will synthesize gold nanoparticles having diameters of about 15 and 33 nm which show different colors.

II. Characterization of gold nanoparticles

The UV-vis spectrophotometer and transmission electron microscope (TEM) are the most frequently used instruments for characterization of gold nanoparticles (Fig. 20-1~20-3). Gold nanoparticles possess characteristic surface plasmon resonance (SPR) absorption bands, which depend on several parameters, including the shape and size of the particles. The SPR absorption bands of the as-prepared 15- and 33-nm gold nanoparticles are centered at 520 and 528 nm, respectively.

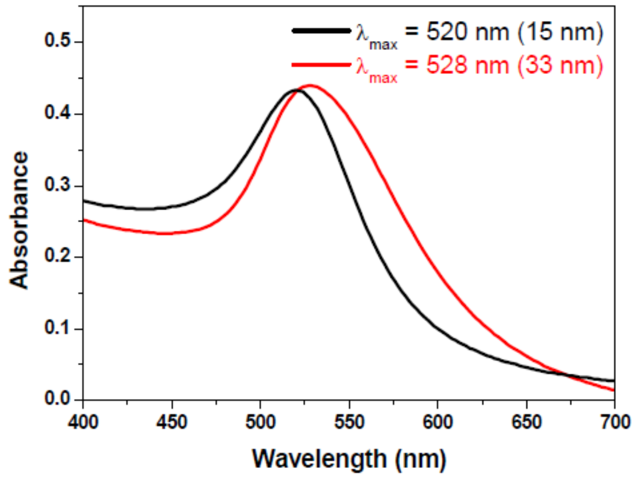

Figure 20-1 Absorption spectra of synthesized gold nanoparticles

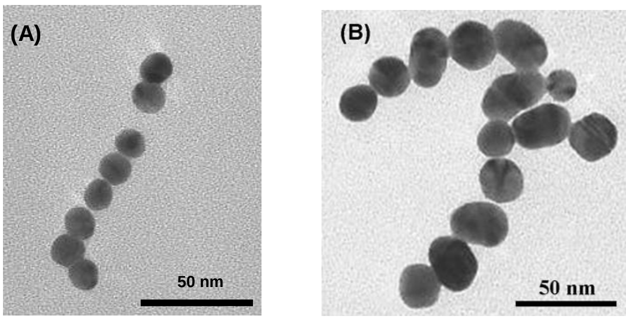

Figure 20-2 TEM images of synthesized gold nanoparticles

(A) Product of 1.8 mL of 38.8 mM $Na_3C_6H_5O_7$ and 15 mL of 1 mM $HAuCl_4$

(B) Product of 1.0 mL of 38.8 mM $Na_3C_6H_5O_7$ and 15 mL of 1 mM $HAuCl_4$

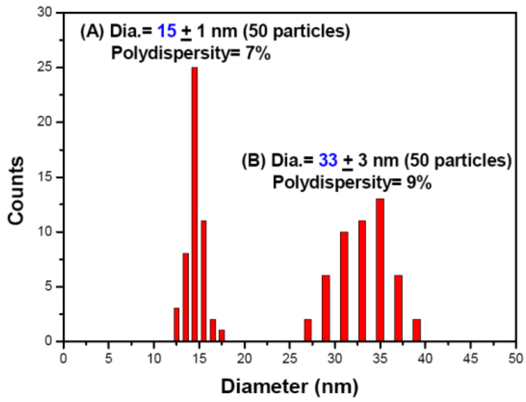

Figure 20-3　Analysis of diameters of synthesized gold nanoparticles

Apparatus

Round bottom flask (50 mL), condenser, rubber tube (2), funnel, dropper, sample bottle (7 mL), stirrer/hot plate, magnetic stirring bar, sand bath, small and large extension clamp, spectrophotometer (SP-830 Plus/SH-U830(S)), cuvettes (2), latex gloves, and timer.

Shared: transfer pipet (15 mL), graduated pipet (2 mL), pipet filler, linen cotton gloves, and laser pointer.

Chemicals

Concentrated hydrochloric acid, 12 M HCl(aq)

Concentrated nitric acid, 15 M HNO_3

1 mM Hydrogen tetrachloroaurate(III) trihydrate, $HAuCl_4 \cdot 3H_2O$

38.8 mM Sodium citrate, $Na_3C_6H_5O_7$

1 M Sodium chloride, NaCl

Procedure

I. Cleaning the apparatus

1. Mix 5 mL of concentrated nitric acid with 15 mL of concentrated hydrochloric acid in a beaker to prepare 20 mL of aqua regia. Clean all glassware (round bottom flask, condenser, cuvettes, and sample bottle) as well as the magnetic stirring bar by aqua regia. **Wash off the acid with large amount of DI water, otherwise it may affect the synthesis.** Drip-dry the washed apparatus.

   Caution: Aqua regia is strongly corrosive and has an irritating, pungent smell. Wear latex gloves while using aqua regia and use it in the fume hood.

   Note: All glassware should be washed with aqua regia (HNO_3/HCl = 1/3(v/v)). The prepared aqua regia can be used repeatedly and recycled in the indicated waste bottle after use.

II. Preparation of gold nanoparticles with the smaller diameter (ca. 15 nm)

2. Measure 15 mL of 1 mM $HAuCl_4$ solution with a transfer pipet into a 50 mL round bottom flask. Add a magnetic stirring bar.
3. Set up the reflux system in the sand bath container as shown in Fig. 20-4. Adjust the reflux system at the center of hot plate that the stir bar shall be stirring strongly and continuously.

   Note 1: Sand bath is used to help heating the system homogeneously. It is not necessary to add too much sand in the container.

   Note 2: Wet the rubber tubes with water before connecting to the condenser and connect it firmly. Run the cooling water from bottom to top and adjust the water flow.
4. Heat the solution with stirring until it boils.

   Note: Do not start heating until the lab instructor check your setup.
5. Use a 2 mL graduated pipet to measure 1.8 mL of 38.8 mM $Na_3C_6H_5O_7$ solution, and add it to the vigorously boiling Au(III) solution through the top of the condenser.

   Note: When sodium citrate is added to the Au(III) solution, the mixture should keep well mixing by magnetic stirring.
6. Observe and record the color changes at the beginning of the reaction. Continue stirring and boiling for 10 min. The color of the solution will turn into wine-red, indicating the formation of gold nanoparticles having a smaller diameter.
7. Turn off the heat and remove the hot sand bath, but keep stirring while the solution cools to room temperature.

   Caution: Wear linen cotton gloves while removing the hot sand bath heating system.
8. Continue the characterization procedures in parts IV and V.

III. Preparation of gold nanoparticles with the larger diameter (ca. 33 nm).

9. Use a clean round bottom flask. Repeat steps 2~7 to prepare gold nanoparticles with larger sizes, but use 1.0 mL instead of 1.8 mL of 38.8 mM sodium citrate solution. The color of the solution will turn into purple-red, indicating the formation of gold nanoparticles having a larger diameter.

   Note: Each group is assigned to prepare gold nanoparticles with one size.

IV. Visible light absorption spectra of gold nanoparticles

10. Turn on the spectrophotometer (SP-830 Plus/SH-U830(S)) to warm it up at least 15~20 min.
11. Transfer 1 mL of the gold nanoparticle solutions into a test tube and add 3~4 mL of DI water to dilute the sample.

12. Fill one cuvette with 1/2 height of diluted sample solution; fill another cuvette with DI water as the blank solution.
13. Zero set the spectrophotometer:
    Press “A/T/C” key setting Mode to “A” (Absorbance); then set the analytical wavelength to 400 nm. Press “BLANK” key to zero set.
14. Blank adjust the spectrophotometer:
    Wipe the cuvette containing blank solution with lens cloth. Place the cuvette in cuvette holder and align in same direction to control the path of the light. Close lid and press “BLANK” key to blank adjust.
15. Absorbance measurement:
    Wipe the cuvette containing sample solution with lens cloth and place in cuvette holder. Close lid; read and record the “Absorbance”.
16. Repeat the analysis at various wavelengths, increasing the analyzing wavelength at 20 nm intervals from 400 to 700 nm. Change the wavelength at 5 nm intervals between 510~540 nm.
    Note: Blank adjust the spectrophotometer with the blank solution each time when the wavelength is changed.

V. Tyndall effect

17. Place 2 mL of 1 M NaCl in another test tube. Pass the red light beam from the laser pointer through the NaCl and gold nanoparticle solutions. Observe and compare the scattering of light by solutions, which illustrates the Tyndall effect.
18. Add NaCl solution to the gold nanoparticle solution in the test tube drop by drop; observe and record the color changes.
19. Fill portions of gold nanoparticles solution into a sample bottle and take home as a souvenir by choice. Dispose the residue into gold nanoparticles recycling bottle.

References

1. Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735.
2. She, J. L., Chang, Y. D., Chang, H. T., and Chen, J. T. *Chemistry (The Chinese Chem. Soc., Taipei)*, **2004**, *62*, 563.

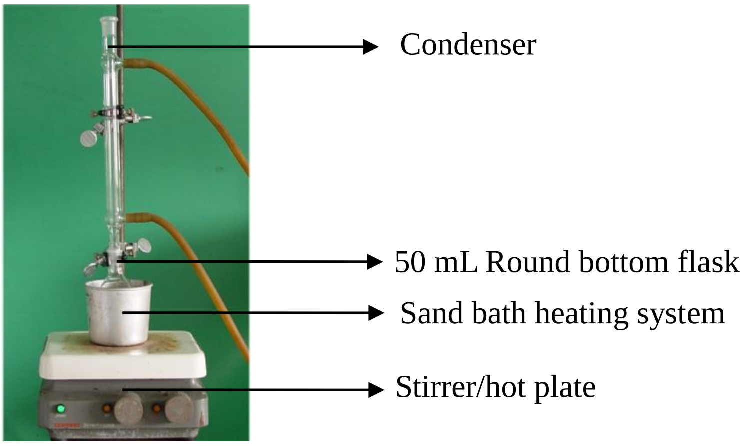

Figure 20-4 Reflux system for synthesis of gold nanoparticles