# Experiment 16

# 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 surface plasmon resonance (SPR) absorption spectra of the as-prepared solutions.[1,2]

## 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. Nanomaterials

Nanomaterials are a kind of novel materials with at least one dimension sized between 1~100 nm (1 nm = $10^{-9}$ m). Due to the reduction in size, weight, and volume, as well as the change in curvature and the increase in surface area, many properties of the substance, such as optical properties, magnetism, electricity, thermal conductivity, *etc.*, have changed and their applicability has increased.[3] Taking gold as an example, gold nuggets have a golden metallic luster, but when the size is reduced to the nanometer scale, they appear red due to the surface plasmon resonance effect. Also due to their obvious optical, chemical, and catalytic properties, gold nanoparticles have been successfully utilized in biomedical testing.

Surface plasmon resonance means that when nanoparticles are irradiated with electromagnetic radiation under appropriate conditions, the free electrons on their surface can be excited to oscillate collectively, and their quanta are called surface plasmons, or surface plasmon polaritons. In this process, electromagnetic radiation of a specific frequency interacts with surface plasmons and is absorbed or scattered. Since this oscillation is limited to the surface, its resonance conditions are susceptible to changes in the shape of the surface and its surrounding environment. For example, the resonance frequency of gold nanoparticles is related to their shapes and particle sizes. This phenomenon is also called particle plasmon resonance.[4]

## II. Preparation of gold nanoparticles

In this experiment, gold nanoparticles of different sizes are prepared from the reduction of tetrachloroaurate(III) ions ($AuCl_4^-$) by controlling the concentration of sodium citrate. At high molar ratios of $Na_3C_6H_5O_7$ / $AuCl_4^-$, small-sized gold nanoparticles are produced, and vice versa. The reaction is shown as equation 16-1.

$$\underset{}{HAuCl_4(aq)} + \underset{\text{Reducing agent}}{Na_3C_6H_5O_7(aq)} \xrightarrow{\text{Reflux for 10 min.}} \underset{\text{Gold nanoparticles}}{Au(s)} + CO_2(g) + \cdots \qquad (16\text{-}1)$$

Strict requirements must be met to prepare gold nanoparticles successfully. All glassware used in the experiment should be rinsed with aqua regia to clean the surfaces and then washed thoroughly with DI water to remove any residual acid. When the tetrachloroauric(III) acid solution is heated to boiling, sodium citrate is added to react with it. 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.

## III. Spectroscopic analysis of gold nanoparticles

The UV-vis spectrophotometer and transmission electron microscope (TEM) are the most frequently used instruments for the characterization of gold nanoparticles (Fig. 16-1~16-2). Gold nanoparticles possess characteristic SPR absorption bands, which depend on several parameters including the shapes and sizes of the particles. The SPR absorption bands of the as-prepared 13- and 24-nm gold nanoparticles have the maximum absorbance at 520 and 525 nm, respectively.

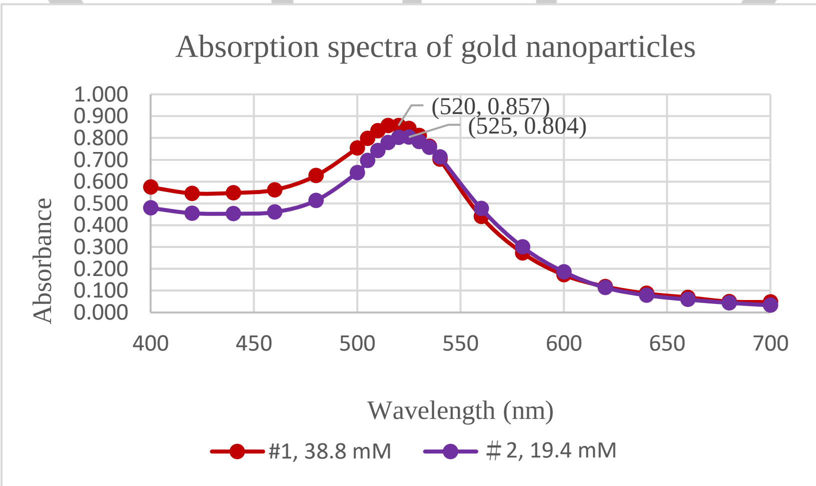


Figure 16-1 Absorption spectra of synthesized gold nanoparticles

(A) (B)

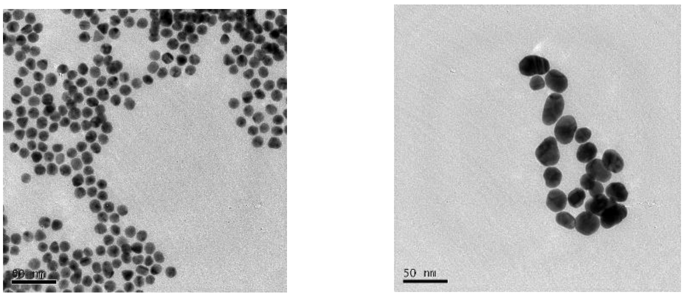

Figure 16-2 TEM images of synthesized gold nanoparticles

(A) Product of 1.0 mL of 38.8 m*M* $Na_3C_6H_5O_7$ and 8 mL of 1 m*M* $HAuCl_4$

(B) Product of 1.0 mL of 19.4 m*M* $Na_3C_6H_5O_7$ and 8 mL of 1 m*M* $HAuCl_4$

### IV. Characteristics of gold nanoparticle colloids

The gold nanoparticles synthesized in this experiment are a type of colloid. The solute particle size of the colloid is between 1~1000 nm. They can suspend uniformly in the solvent and have the Tyndall effect that can scatter light. If the colloidal solution is added with an electrolyte or heated and stirred, the solute particles will coagulate and settle, destroying the properties of the colloid.

## Apparatus

Round bottom flask (25 mL), condenser, rubber tube (2), dropper, sample vial (7 mL), stir bar, stirrer/hot plate, stainless steel cup (2), small and large three-prong clamps, spectrophotometer (SP-830 Plus/SH-U830(S)), cuvette (2), NBR gloves, timer, beaker (100 mL), and test tube (2).

Shared: transfer pipet (5, 15 mL), graduated pipet (2, 10 mL), funnel, pipet filler, sea sand, lens cloth, cotton gloves, and laser pointer.

## Chemicals

Concentrated hydrochloric acid, 12 *M* HCl

Concentrated nitric acid, 15 *M* $HNO_3$

1 m*M* Hydrogen tetrachloroaurate(III), $HAuCl_4 \cdot 3\,H_2O$

38.8 and 19.4 m*M* Sodium citrate, $Na_3C_6H_5O_7 \cdot 2H_2O$

1 *M* Sodium chloride, NaCl

## Procedure

| Procedure | Illustration |
| --- | --- |
| I. Preparation of gold nanoparticles | |

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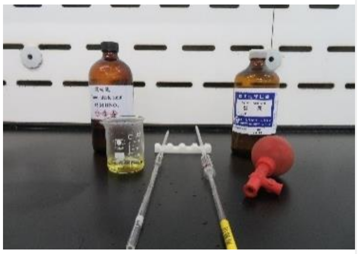
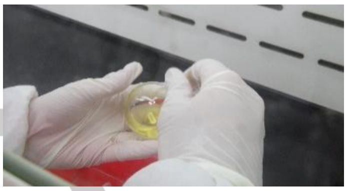
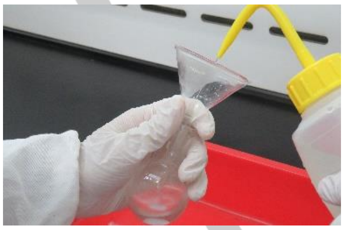
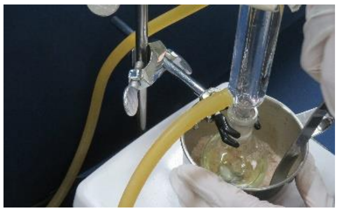
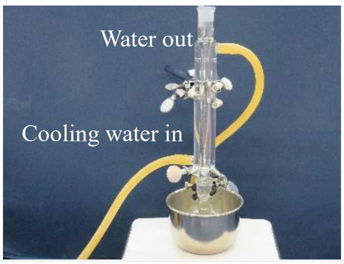
|---|---|---|
| 1 | Mix 5 mL of conc. $HNO_3$ with 15 mL of conc. HCl in a beaker to prepare 20 mL of aqua regia.<br><br>Caution: Aqua regia is strongly corrosive and has an irritating, pungent smell. Wear NBR gloves and operate in a fume hood. |  |
| 2. | (1) In the fume hood, clean the stir bar and all glassware (round bottom flask, condenser, 2 cuvettes, and sample vial) by aqua regia.<br>(2) Rinse the glassware with DI water once in the fume hood; then take them back to your bench.<br>(3) Keep washing off the acid with plenty of DI water 4~5 times. Drip-dry the washed apparatus.<br><br>Note: The aqua regia can be used repeatedly and recycled in the waste bottle after use. | <br> |
| 3. | (1) Measure 8.0 mL of 1 m*M* $HAuCl_4$ with a 10 mL graduated pipet into a 25 mL round bottom flask. Add a stir bar.<br>(2) Place a steel cup at the center of the stirrer/hot plate, set up the reflux system according to Fig. 16-3, and check the stir bar shall be stirring steadily and continuously.<br>(3) Add an appropriate amount of sea sand at about the same height as the solution surface into the steel cup to serve as a sand bath heating system.<br>(4) Proceed with subsequent heating only after inspection by the instructor.<br><br>Note 1: Connect the ground glass joint tightly.<br>Note 2: Wet the rubber tubes with water before connecting to the condenser. Run the cooling water from bottom to top and adjust the water flow. Keep the rubber tubes and power cable away from the stirrer/hot plate. | <br><br><br><br> |

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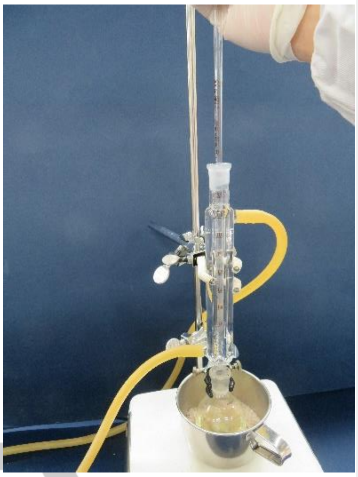
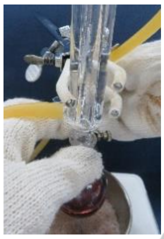
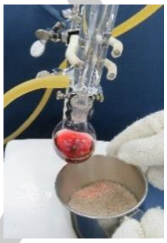
| 4. | (1) Stir and heat the solution until it boils.<br>(2) For the odd-numbered groups, use a 2 mL graduated pipet to measure 1.0 mL of 38.8 m*M* sodium citrate. For the even-numbered groups, measure 1.0 mL of 19.4 m*M* sodium citrate. Add it quickly from the top of the condenser and observe and record the change in color of the solution.<br><br>Note: When adding sodium citrate solution, stir the Au(III) solution continuously to mix the reactants thoroughly. |  |
| 5. | After the reaction mixture boils, keep uniform stirring of the solution, but turn the heating to “low” or turn it off. Use the remaining heat of the sand bath to keep the solution boiling for 10 min. |  |
| 6. | Remove the hot sand bath, and let the solution cool to room temperature with continuous stirring.<br><br>Caution: Wear cotton gloves to remove the hot sand bath system, and place the sand bath on the bench where it is not easily touched. The stirrer/hot plate is still at a high temperature, so be careful of burns.<br>Note: You can use another steel cup to fill with water, wipe the bottom of the cup, and place it on the stirrer/hot plate to absorb heat to accelerate cooling. |    |

## II. Visible light absorption spectra of gold nanoparticles

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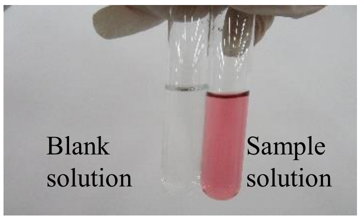
|---|---|---|
| 7. | (1) Use a clean test tube to fill about 2 mL of gold nanoparticle solution and 8 mL of DI water, and mix evenly.<br>(2) Fill one cuvette with the diluted sample solution to about 1/3 the height; fill another cuvette with DI water to the same height as the blank solution. |   |

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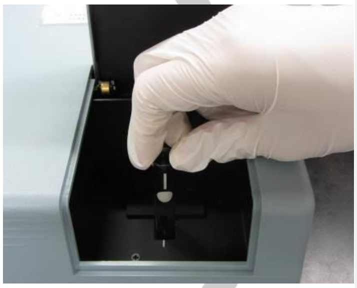
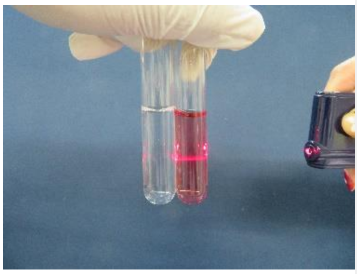
| 8. | (1) Turn on the spectrophotometer to warm it up for 15 min.<br>(2) Press the mode setting button “A/T/C” to “A” (Absorbance); then set the analytical wavelength to 400 nm. Press the “BLANK” button to zero set.<br>(3) Wipe the cuvette containing the blank solution with a lens cloth. Place the cuvette in the cuvette holder and align its white mark to the mark on the holder to fix the light path. Close the lid and press the “BLANK” button for blank adjustment. The reading should be “0.000”.<br>(4) Wipe the cuvette containing the sample solution and place it in the cuvette holder. Read and record the absorbance.<br>(5) Repeat the analysis at various wavelengths, increasing the analyzing wavelength at 20 nm intervals from 400 to 700 nm. Blank adjust the spectrophotometer with the blank solution each time when the wavelength is changed.<br>(6) Change the wavelength at 5 nm intervals between 500 and 540 nm. |     |
| 9 | Compare the colors of gold nanoparticle solutions prepared with two concentrations of sodium citrate. |  |
| III. Colloidal properties | | |
| 10. | Take 2~3 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. |  |

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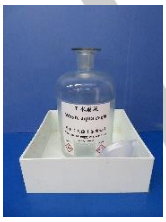
| 11. | Add 1 *M* NaCl to the gold nanoparticle solution in the test tube drop by drop; observe and record the color changes. |  |
| 12. | Fill portions of gold nanoparticle solution into a sample vial and take them home as a souvenir by choice. |  |
| 13. | Dispose of the gold nanoparticle solution and aqua regia into indicated recycling bottles, respectively. |   |


Figure 16-3  Reflux system for synthesis of gold nanoparticles

## 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.
3. Wang, C. R. C. *Science Development*, **2002**, *354*, 48。
4. Chen, C. D.; Chang, P.; Wang, C. R. C. *Chemistry* (The Chinese Chem. Soc., Taipei), **2003**, *61*, 161.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