

Study of Synthesis of Gold Nanoparticles

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Abstract: This research deals with an approach to synthesize gold nanoparticles. Gold nanoparticles have been used widely in Industrial as well as Academic fields which includes biomedical and catalytic applications. Engineering in Nanoscience and Nanotechnology includes synthesis of different nanoparticles which can be useful for general public. So various methods are being developed for synthesizing nanoparticles. Lowering the cost of synthesis with available resources is of primary importance in engineering. We have studied various methods for characterization which can be useful to control various features of formed gold nanoparticles. Our selected procedure is synthesizing Ruby Red Gold Nanoparticles. In this experiment we will use HAuCl₄. And with Tyndall Effect observed while using a laser pointer will prove the synthesis of gold nanoparticles.

1. Introduction

Most nanoparticles produced on an industrial scale are nanoparticles, although they also arise as by-products while manufacturing other materials. Specific synthesis processes are employed to produce various nanoparticles, coatings, dispersions or composites. Defined production and reaction conditions are crucial in obtaining such size dependent particle features. Particle size, chemical composition, crystallinity and shape can be controlled by temperature, pH value, concentration, chemical composition, surface modifications and process control. Two basic strategies are used to produce nanoparticles: “top-down” and “bottom-up”. The term “top-down” here refers to mechanical crushing of source material using milling process. In the “bottom-up” strategy, structures are built up by chemical processes. The selection of respective process depends on chemical composition and the desired features specified for the nanoparticles. The “bottom up” strategy has an advantage of controlling sizes, shapes and size ranges. E.g. precipitation reactions, sol-gel processes, aerosol processes etc. We studied different methods of gold nanoparticles for instance Pseudo-template synthesis based on polyhydrosilanes [1], Synthesis from a highly concentrated precursor solution of Au³⁺ ions and casein proteins from milk[2], Synthesis of casein-stabilized gold nanoparticles[3] and Synthesis of amphiphilic gold nanoparticles [4]. The characterization in above mentioned methods was done using UV-vis Spectrophotometry, Transmission Electron Microscopy, Fourier-Transform Infrared Spectroscopy, Dynamic Light Scattering, Atomic Force Microscopy, Field Emission Microscopy, Scanning Electron Microscopy, X-Ray Diffraction etc. However we selected the most feasible method for gold nanoparticle synthesis. Like most of the experiments we also used HAuCl₄.3H₂O. But the overall cost in manufacturing of gold nanoparticles was much lower and reasonably affordable. In this paper we will approach different methods of gold nanoparticle synthesis and compare the material costs and parameters.

2. Material Required (cost as per Sigma Aldrich & their parameters)

| S. No. | Material | Temperature | Pressure | Environment | Cost |
|----------|--|---|----------|--|------------------------|
| 1 | Polyhydrosilane | | | | |
| (i) | Gold (III) Chloride Trihydrate, HAuCl ₄ .3H ₂ O (99.98%) | MP-527 K | Standard | Room Environment | Rs. 10612 per gram |
| (ii) | PDPHS (poly [diphenylsilane-co-methyl(H)silane]) | 198 K (titration) 323 K (vacuum drying of precipitate) | Standard | Argon Atmosphere (titration) Vacuum | Prepared in laboratory |
| 2 | Precursor Solution | | | | |
| (i) | Na ₂ CO ₃ | MP-851 C (NaOH) | Standard | Room Environment | Rs. 3398 per 500 grams |
| (ii) | NaOH | MP-591 K | Standard | Room Environment | Rs. 3278 for 2L (NaOH) |
| (iii) | TMAB (Trimethylamine borane) | MP-368 K BP-445 K | Standard | Room Environment | Rs. 1271 for 5 grams |

| | | | | | |
|----------|---|-------------------------------|---|--|------------------------|
| (iv) | Urea | MP-135 C | Standard | Room Temperature | Rs. 500 per 50 kg |
| (v) | H ₂ AuCl ₄ .3H ₂ O | MP-527 K | Standard | Room Environment | Rs. 10612 per gram |
| 3 | Casein stabilized Gold Nanoparticles | | | | |
| (i) | Casein | MP-553 K | Standard | Room Environment | Rs. 4545 per 500 grams |
| (ii) | H ₂ AuCl ₄ .3H ₂ O | MP-527 K | Standard | Room Environment | Rs. 10612 per gram |
| (iii) | NaBH ₄ | MP->573 K | Standard | Room Environment | Rs. 5595 per 25 grams |
| 4 | Amphiphilic Gold nanoparticles | | | | |
| (i) | Ethylene Glycol | MP-260 K BP-470 K | Standard | Storage-275 K | Rs. 3571 |
| (ii) | Dodecanethiol | MP-264 K BP-539 K to 556 K | Standard | Room Environment | Rs. 1361 per 100 ml |
| (iii) | H ₂ AuCl ₄ .3H ₂ O | MP-527 K | Standard | Room Environment | Rs. 10612 per gram |
| (iv) | Anhydrous Tetrahydrofuran | MP-165 K BP-338 K | V.P.-114mm Hg (288 K) V.P.-143 mm Hg (293 K) | Storage-Cool and Dry In A Sealed Container | Rs. 1573 per 100 ml |
| (v) | Ethanol | Mp-159 K BP-351 K | V.P.-44.6 mm Hg (293 K) | Storage-Cool Place | Rs. 18616 per 2.5 l |
| 5 | Ruby Red Colloidal Gold Nanoparticles | | | | |
| (i) | H ₂ AuCl ₄ .3H ₂ O | MP-527 K | Standard | Room Environment | Rs. 10612 per gm |
| (ii) | Sodium Citrate | MP>573 K | Standard | Room Environment | Rs. 6104 per kg |

3. Synthesis Techniques

The various techniques purposed for the synthesis of Gold Nanoparticle are as follows:

3.1 Pseudo-template synthesis based on polyhydrosilanes [1]

3.1.1 Poly[diphenylsilane-co-methyl(H)silane](PDPHS) was formed by following method:

A THF solution of Sodium/Potassium alloy complex with 18-crown-6 was titrated against a THF solution of CH₃HSiCl₂/(C₆H₅)₂SiCl₂ (Molecular Ratio=1) at 198 K in argon atmosphere. Then methanol was added and thereafter solvent was evaporated. Then product was extracted with chloroform and washed with water. The yield was of 75% white solid polymer precipitate, which was then fractionated in boiling diethyl ether. At the end it was filtered and then vacuum dried at 223 K for 24h.

3.1.2 Polysilane-Au nanoparticles were formed by following method:

0.1 mol polymer was added to 2.5 ml anhydrous toluene which was then irradiated by microwaves for 30s at 300W. Then 0.01 mmol metal salt was added and it was exposed to natural light and stirred gently for 60min when the colour changed to purple. Solids were then separated by centrifugation technique for 15min at 5000rpm.

3.2 Synthesis from a highly concentrated precursor solution of Au³⁺ ions and casein proteins from milk [2]

A stock solution of 100g L⁻¹ denatured casein (from milk) was prepared in 0.05 M Na₂CO₃ and 6M urea aqueous solution. Au(OH)₄⁻ (aq) was prepared by adding 10 M NaOH to 2 M H₂AuCl₄(aq) where colour changed from yellow to colourless due to ligand exchange from AuCl₄⁻ to Au(OH)₄⁻. The solution was then heated at 353 K when trimethylamine borane (TMAB) was added to reduce Au³⁺ ions. The solution which was colourless turned to dark red due to reduction of Au(OH)₄⁻ ions to gold nanocrystals. Then saturated ammonium sulphate was added to solution and dark red precipitate was formed and separated by centrifuge separation method. Precipitate was then washed with water and completely dried in vacuum. Colloidal gold solution was then redissolved in 1 M 2-aminoethanol (aq).

3.3 Synthesis of casein-stabilized gold nanoparticles [3]

0.2ml 1% HAuCl_4 solution was taken and 10ml casein (aq) was added to it. Solution was then stirred for 30min and then 1.2ml ice cold 0.01 M NaBH_4 was added. After more 30min a very small amount of HCl or NaOH was added in order to keep pH constant. After 24h gold nanoparticle solution was refrigerated at 277K.

3.4 Synthesis of amphiphilic gold nanoparticles [4]

49.4 L⁻⁶ (0.107 mmol) of 1-mercaptoundec-11-yl-hexa(ethylene glycol) or EG-6 was added to 9.9 L⁻⁶ (0.041 mmol) of dodecanethiol or C-12 (EG-6:C12=72:28). The solution was vigorously stirred. Then 0.196 mmol of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 10ml freshly distilled anhydrous tetrahydrofuran (THF) was added. Then solution was stirred for 20min at room temperature. Thereafter 1 M solution of lithium triethylborohydride was added. A slight colour change to dark red-brown was observed. Solution was then stirred for 3h. Then 10ml ethanol (99.8%) was added and THF was evaporated in rotary evaporator. To precipitate nanoparticles 150ml of hexane was added. Then mixture was kept overnight at 255 K. The black precipitate was formed and filtered using 0.2 μm PTFE membrane. The precipitate was then washed several times with hexane until colour turns purple. Then it was dried in oven at 333 K. Nanoparticles were then dispersed in Milli-Q water and purified via dialysis against Milli-Q water using regenerated cellulose by dialysis membrane for 45h. It was then dried in rotary evaporator and then in an oven at 333 K until the colour of purified particles changed to black.

3.5 Synthesis of Ruby Red colloidal gold nanoparticles

20 ml of very dilute (0.001 M) solution of HAuCl_4 (pale yellow colour, Sigma Aldrich) was taken in a beaker. Then we added 180 ml of distilled water at room temperature into the same beaker in order to decrease the molarity to 0.00001 M. Then beaker was put in an oven and heated to 355 K. At around 359 K 2ml of Sodium Citrate solution was added into the beaker. Then we stirred the solution occasionally and gently until the colour of the solution in the beaker turned deep purple. However the heating was done until the solution turned ruby red in colour. At this stage of solution turning into ruby red, gold nanoparticles were formed in the beaker.

4. Characterization

Following characterization methods were employed for Experiment 3.1, 3.2, 3.3 and 3.4:

- 4.1 UV-Vis Spectrophotometry
- 4.2 Transmission Electron Microscopy
- 4.3 Atomic Force Microscopy
- 4.4 Field Emission Microscopy
- 4.5 Scanning Electron Microscopy
- 4.6 X-Ray Diffraction
- 4.7 Selected Area Electron Diffraction
- 4.8 Dynamic Light Scattering
- 4.9 Fourier-Transform Infrared Spectroscopy

In Experiment 3.5 laser light was used for testing based on the characteristic that colloidal particles does not dissolve in solution but get dispersed and therefore scatter light. The laser pointer passed through the colloidal solution when observed in a dark room. The path of the laser light (Tyndall Effect) was observed due to scattering of light by gold nanoparticles. This proved presence of gold nanoparticles in the solution.

5. Conclusion & Discussions

Form the study of various methods of synthesis of gold nanoparticles, the most feasible and efficient method is as follows.

1. Psuedo-template synthesis of gold nanoparticles based on polyhydrosilanes
 2. Dense aqueous colloidal gold nanoparticles prepared from highly concentrated precursor solution
 3. Preparation of casein stabilized gold nanoparticles for catalytic applications
 4. Amphiphilic gold nanoparticles: Synthesis, characterization and adsorption to PEGylated polymer surfaces
- Different methods of characterization of gold nanoparticles were also explored which includes spectrophotometry, atomic force microscopy, field emission microscopy, direct light scattering, Fourier Transform Infrared Spectroscopy, X-Ray Diffraction etc. among others as per the requirement.

The selected method of synthesis of colloidal gold nanoparticles from $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ showed positive results after Laser Light Scattering (Tyndall Effect).

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