Comparative Study of Gold Nanoparticles Synthesized via Wet Chemical and Green Chemistry approach

Sonal Rattan¹²*, Anjali Leal²³, Mamta Sharma², Suresh Kumar² and J K Goswamy²
¹Centre for Nanoscience and Nanotechnology, Panjab University, Chandigarh,
²Department of Applied Sciences, UIET, Panjab University, Chandigarh
³Department of Physics, Panjab University, Chandigarh

*E-mail id:sonalrattan.zenith@gmail.com

Gold nanoparticles (Au NPs) undergo a huge research exposure owing to their extraordinary properties and potential applications. Herein, we report a comparative study between Au NPs synthesized via wet chemical method (reduction using sodium citrate) and green chemistry (reduction using vigna radiata (green grams)). The prepared Au NPs were characterized by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDS). UV-Visible spectrum of Au nanoparticles showed a peak around 534 nm in both the cases. Zeta Potential (ZP) values were 3.62 mV and -2.80 mV of Au nanoparticles prepared via wet chemical method and green chemistry approach respectively.

Keywords: Gold nanoparticles, X-ray Diffraction, Zeta Potential

1. INTRODUCTION

Over the past few years, metal nanoparticles have gained much interest owing to their unique physical, chemical as well as biological attributes and hence is one of the most active area of nanotechnology research [1,2]. Among noble metal nanoparticles, Au NPs have been extensively studied due to their remarkable properties [3, 4]. Au NPs possess the Surface Plasmon resonance (SPR) property which makes them a suitable nanomaterial for bioimaging [5]. Au NPs also find application as an anti-aging component for protecting skin [6]. A variety of polymer/gold nanoparticle based composites show a high potential as a novel material for high quality paints [7]. Variety of sizes and shapes of Au NPs can be easily prepared, which include nanospheres, nanoshells, nanorods and nanoprisms having numerous applications in diverse fields.

Developing techniques for the controlled production of Au NPs having well-defined size as well as shape is challenging. A variety of methods have been reported for synthesising Au NPs. But these processes are known to produce hazardous by products [8]. Hence, continuous efforts are being made to discover green methods for synthesising Au NPs. Green synthesis is a way for avoiding the unwanted or harmful by products via building reliable, environment friendly and sustainable synthesis processes. Gold colloids were first synthesized by Michael Faraday around 150 years back. He used phosphorous for reducing AuCl₄⁻ ions [9]. Among several chemical methods used to produce Au NPs, one of the most commonly used processes has been the Turkevich method [10], in which trisodium citrate was employed to reduce auric chloride ions to give well dispersed Au NPs. The citrate ion coating on Au NPs helps in homogenous dispersion of the colloid.

Herein, we report a comparison of different characteristics of Au NPs synthesized via wet chemical method using trisodium citrate as the reducing agent and green chemistry approach using green grams (vigna radiata) for reducing the gold chloride trihydrate. Several reports have illustrated that biomolecules such as amino acids,
organic acids, flavonoids and phenols which are present in plants play a crucial role in reducing the metal ions into nanomaterials along with capping the metal NPs, which in turn is the reason behind their long term stability. These biomolecules are helpful in enhancing the usage potential of Au NPs for medical purposes by transmitting their intrinsic medicinal properties [11]. Plant extracts are a preferable choice for synthesising Au NPs owing to their excellent biocompatibility [12]. Adding further to this, plant extracts are easy to handle, readily available in abundance and possess a large variety of metabolites which might assist in reducing metal salts to NPs [13].

2. EXPERIMENTAL

2.1 Preparing Au Nanoparticles

2.1. Wet Chemical Method

A definite wt% of \( \text{HAuCl}_4 \cdot 3\text{H}_2\text{O} \) in deionized water was placed on a hot plate with continuous magnetic stirring. Under boiling condition 5 mL of trisodium citrate dihydrate was added to the solution. Au NPs were quickly formed as citrate reduced Gold (III). Heat was turned off when solution turned deep red in color and the solution was allowed to cool and stored in a refrigerator for future purposes.

2.1. Green Chemistry Method

A solution of green grams (20 g) in 100 mL of deionized water was prepared by heating on a magnetic stirrer at a temperature of 70°C for around 1 hour. This plant extract was then poured in a boiling solution of \( \text{HAuCl}_4 \cdot 3\text{H}_2\text{O} \). Au NPs were formed upon the reduction of Au ions present in gold chloride trihydrate salt.

Both the processes lead to the formation of gold nanoparticles. The schematic is presented in figure1.

![Figure 1. Synthesis of Gold Nanoparticles](image-url)
3. RESULTS AND DISCUSSION

Au NPs were prepared by wet chemical method using trisodium citrate dihydrate as a reducing agent and green chemistry approach using green grams acting as reducing agent. The x-ray diffraction pattern of Au NPs as shown in figure 2 gives reflection peaks at 38.10°, 44.13°, 64.43°, and 77.32° corresponding to (111), (200), (220), and (311) miller indices, respectively [14]. The observed XRD pattern was in a good correlation with the standard pattern from the JCPDS data card 04-0784 and confirmed the formation of Au NPs.

Figure 2. X-ray diffraction pattern of Gold Nanoparticles synthesised via (a) Wet Chemical Method (b) Green Chemistry Approach

FESEM images (figure 3(a) and 3(b)) clearly indicate the successful preparation of Au NPs using chemical and green chemistry methods. It was observed that the nanoparticles were almost spherical in shape and some of them had formed aggregations. The aggregation is more pronounced in green chemistry method. In wet chemical method aggregation is less due to capping of Au NPs.

Figure 3. FESEM images of Gold Nanoparticles synthesised via (a) Wet Chemical Method (b) Green Chemistry Approach
Figure 4 displays the energy dispersive x-ray spectroscopy results of Au NPs synthesised (a) via wet chemical method and (b) via green chemistry approach. The elemental analysis showed fine peaks for gold, carbon and oxygen, supporting the electron microscopy results. Aluminium peak was visible in the spectrum shown in figure 4(a) because aluminium was taken as the substrate. The concentration of Au NPs was lesser in the wet chemical method since citrate ions have capped the Au NPs which could not happen in green chemistry method.

Figure 4. EDS analysis of Gold nanoparticles synthesized via (a) Wet Chemical Method (b) Green Chemistry Approach

UV-Visible spectrum for the synthesized Au NPs is shown in figure 5. A peak noticeable in both the spectra around 534 nm corresponds to the surface plasmon resonance property of Au NPs. The absorption band is broader in Au NPs synthesized via green chemistry approach due to increased aggregation of Au NPs. Most of the reports mentioning green synthesis using plant extracts usually exhibit a broad and weak surface plasmon resonance peak of the Au NPs [15, 16]. In this case, the strong SPR peak occurred owing to the high productivity of Au NPs during the synthesis. The position of the SPR absorbance bands relies on the size of the Au NPs [17].

Figure 5. Normalised UV-Visible spectra of Au NPs via (a) Wet chemical method (b) Green Chemistry Approach

Figure 6. FTIR spectra of Au NPs synthesised via (a) Wet chemical method (b) Green Chemistry Approach
Figure 6 shows the FTIR spectra for Au NPs synthesised (a) via wet chemical method and (b) via green chemistry approach. The characteristic peaks located at 1395 cm\(^{-1}\) and 1586 cm\(^{-1}\) in the spectrum in 6(a) were attributed to the symmetric and anti-symmetric bond stretching of COO\(^-\). This data confirmed the interactions between citrate ions and gold chloride trihydrate. FTIR analysis was done to examine the presence of various functional groups present in the plant extract. A broader peak occurred at 3400 cm\(^{-1}\) because of the O-H bonds present in the aromatic/ alcoholic/ phenolic compounds [18]. Smaller peaks observed at 1550 cm\(^{-1}\), 1410 cm\(^{-1}\) and 1371 cm\(^{-1}\) ascertained the existence of aromatic C-O, N-H and C-H bond stretching as shown in figure 6(a) [19]. The absorption peak at ~1500 cm\(^{-1}\) as shown in figure 6(b) is characteristic of amide band. Two peaks occurring at 3400 cm\(^{-1}\) and 1634 cm\(^{-1}\) highlight O-H and C=O bonds which reduce gold (III) ions to gold atoms.

![Figure 6. FTIR Spectra](image)

**Figure 7.** Zeta Potential of synthesized Au NPs via (a) Wet Chemical Method (b) Green Chemistry Approach

Zeta Potential values indicate towards the surface charge and stability of the Au NPs. Figure 7(a) shows the zeta potential value of 3.62 mV for Au nanoparticles synthesised via wet chemical method and 7(b) shows the ZP value of -2.80 mV for Au nanoparticles prepared via green chemistry approach. It confirmed the formation of negative charges on the surface of Au NPs. The low values of ZP are possibly because of the agglomeration of Au NPs.

4. CONCLUSION

The present work was carried out to compare the Au NPs prepared via wet chemical (using trisodium citrate dihydrate as a reducing agent and green chemistry method (using green gram extract as reducing agent). The
particle size observed in green chemistry was smaller than that of wet chemical method but the aggregation was more pronounced. Along with the particle size being larger in wet chemical method, the dispersion was also good due to ionic capping on their surface generated during synthesis process. Different characterisation techniques such as UV-Visible spectroscopy, Field Emission Scanning Electron Microscopy and Zeta Potential ascertained the preparation of gold nanoparticles.

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