Chapter 3
Synthesis and Structural Properties of Gold Nanoparticles (Au-NPs) by the Chemical Reduction Method using Sodium Borohydride

This chapter deals with chemical synthesis of gold nanoparticles (Au-NPs) and their characterization as well as analysis of structural, microstructural and optical properties.
3.1. Introduction

Lately, nanoparticles (NPs) are beginning to replace conventional materials in science and engineering due to their larger surface-to-volume ratio and the large amount of atoms at their grain boundaries [1]. They have become important materials in the development of many unique devices that are used for various pharmaceutical, biological, and biomedical purposes [2,3]. The size of NPs primarily accounts for their exceptional functionality [4]. The metallic nanoparticles are the most common NPs used in research and several fields due to their enhanced physical and chemical properties [5]. These particles are used for many purposes, which include optoelectronics, medical diagnosis, catalysis, as well as chemical and biosensing. The most important metallic NPs are the gold nanoparticles, which are extensively used in the field of biomedicine and biotechnology due to their high electron conductivity and large surface area, as well as their inertness and stability [6]. The Au-NPs are biocompatible and non-cytotoxic with excellent electronic, optical and magnetic properties [7]. They are employed in many fields/functions such as medicine, pharmacology, biosensor, and drug delivery [8–12]. The Au-NPs can be amassed in the tumor cells, and can help the microscopic analysis of cancer cells and chemotherapy due to their optical scattering ability. Au-NPs have possessed unique physicochemical properties due to their shape, size and chemical interaction ability [13]. In the past few years, Au-NPs attracted a lot of attention due to the availability of small-sized NPs which possess a larger surface-to-volume ratio than the bulk materials and hence suitable for catalytic use. Recently, there have been an increase in the use of Au-NPs for catalytic purposes [14]. Gold compounds have proven to be an effective catalyst in the catalytic synthesis of organic substances [15]. Gold has been known to be an unreactive metal for a long time but its ability to act as a mild Lewis acid was recently discovered. Gold can activate unsaturated functional groups, such as alkenes and alkynes, to create carbon-carbon, and carbon-heteroatom bonds under very mild conditions due to this property [16]. Gold can also efficiently activate sp, sp², and sp³ carbon–hydrogen bonds. This discovery of gold as viable catalyst may represent a major breakthrough in organic chemistry. Hence, techniques that are used in the synthesis of Au-NPs with regulated shape, size and composition are of paramount importance. More studies are currently being carried out to identify the relationship between the morphological properties of nanomaterials and their optical,
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electrical and magnetic properties [17–23]. However, they produce very dissimilar results. Au-NPs can be produced by various techniques such as chemical, physical, thermal and biological methods. It should be noted that several factors, which include temperature, pH, concentration of reducing agent and synthesis time, also have effects on the synthesis of Au-NPs [20,24,25]. Sodium citrate and borohydride have been the most common reducing agents in the synthesis of Au-NPs for a long time. In the current article, the chemical technique has been used to synthesize Au-NPs by using sodium borohydride as a stabilizing agent [26,27]. The use of sodium borohydride produced a high concentration of NPs that probably occur because NaBH₄ increases the overall ionic strength [28–31]. The characterization of the Au-NPs was carried out using different instruments.

3.2. Synthesis of Gold Nanoparticles Using Sodium Borohydride

Au-NPs were chemically synthesized using sodium borohydride (NaBH₄) as a stabilizing agent. 0.5 mM of gold chloride was placed in a conical flask containing 100 double distilled water and the resulting solution was stirred for 1 hr at 80 ºC [32]. Thereafter, 38.8 mM of (NaBH₄) was dissolved in 30 ml ice double distilled water and this was added in drops to the solution of gold chloride, which was then stirred for 30 min. and after that the solution turned red, indicating the formation of Au-NPs. The equation for the chemical reaction is given below.

\[ \text{H}_2\text{AuCl}_4 + \text{NaBH}_4 \rightarrow \text{Au} + \text{BH}_3 + \text{HCl} + \text{NaCl}_3 \]  (3.1)

3.3. Characterization of Au-NPs

The Au-NPs were characterized using different techniques. The UV-Visible Absorption Spectrophotometer (Perkin Elmer Lambda-35) and Photoluminescence Emission Spectrophotometer were used to analyse the optical properties of Au-NPs within the range of 450-600 nm. At room temperature, Fourier transformed infrared spectroscopy were reported on a spectrophotometer. The Au-NPs were dried for 4 hours at a temperature of 60º C and combined with KBr to produce a circular disk fit for Fourier transformed infrared (FTIR) measurements. FTIR indicated the presence of numerous bonding vibrational frequencies. The crystalline nature and structure of Au-NPs were analysed by X-ray diffraction (Rigaku Miniflex) with radiations of Cu-Kα (λ=1.5406 Å). This was carried out using a current of 15 mA and voltage of 30 kV in the range of 20, which was varied from 25º to 85º. The composition and
microstructure of the Au-NPs were analysed using energy dispersive X-ray spectroscopy (EDX) and the SEM (JEOL, Japan). The images of Au-NPs gathered from the transmission electron microscope (TEM; JEOL, JEM-2100) were used to analyse the surface structure of the NPs.

3.4. Results and Discussion

3.4.1. X-Ray Diffraction

The XRD analysis was used to study the crystalline structure of the Au-NPs synthesized using sodium borohydride (NaBH₄). The XRD pattern shows that the Au-NPs were produced by the reduction of gold ion (Au³⁺) to metallic gold (Au⁰) [33], as shown in Fig 3.1. Powder X software was used to index the XRD patterns. Samples were produced by drop-casting of gold sol on the surface of a glass. The XRD plot of the produced sample was found by Bragg reflections at diffraction angle, 2θ, as of 38º, 44º, 64º and 77º, which correspond to (111), (200), (220) and (311) Miller indices respectively. These are the Bragg’s reflections of FCC structure of crystalline metallic gold. The intensity of the (111) diffractions had greater intensity than the (200), (220) and (311) diffractions peaks. The XRD pattern indicated that the Au-NPs have crystalline structure [34]. The diffraction peaks obtained is akin to that of the standard metallic gold (JCPDS-card no.04-0784) [35].

![Fig. 3.1: XRD Pattern of Au-NPs](image-url)
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The crystallite size of the prepared sample was found to be 21 nm by using the Debye-Scherrer equation [36,37].

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(3.2)

Where, \( D \) is the average crystallite size, \( k \) is constant = 0.9, \( \lambda \) is the wavelength of X-ray radiation (Cu K\(\alpha\)=1.5406 Å), \( \beta \) is the full width at half-maximum (FWHM), \( \theta \) is the Bragg angle 2\(\theta\).

3.4.2. Scanning Electron Microscopy (SEM) and EDX analysis

The SEM machine was utilized to analyse the surface morphology of Au-NPs. Thin layers of the Au-NPs sample were prepared on a copper grid coated with carbon by putting a very small quantity of the sample on the grid, which was then dried under a mercury lamp for 15 minutes. Different sizes of the spherical and cubic shaped Au-NPs were observed [38] and are shown in Fig.3.2(a). Some of the nanoparticles in this SEM image are large in size due to the accumulation of small nanoparticles. The metallic gold was confirmed by EDX analysis and shown in Fig.3.2 (b). The elemental composition of the synthesized particles was analysed through EDX, which were observed to include ions of chlorine (Cl), sodium (Na), silicon (Si), oxygen (O) and gold (Au) and are shown in Fig.3.2 (b). Presence of Si signal was due to the fact that samples were prepared on the glass (SiO\(_2\)) substrates [39].
Fig. 3.2: (a) SEM images of Au-NPs

Fig. 3.2: (b) EDX images of Au-NPs
3.4.3. Transmission Electron Microscopy

TEM analysis was carried out on suspended centrifuged particles obtained from the synthesis of Au-NPs. Samples of Au-NPs used for the analysis were prepared by placing a drop of suspended centrifuged particles on Formvar-coated copper grids, which were then dried. TEM was used to analyse the size and morphology of the Au-NPs as shown below in Fig.3.3. The image from the analysis shows that the Au-NPs are smooth, hexagon spherical and nanorods in shapes and have a uniform particle size, which varies between 20 nm to 25 nm with an average particle size of 22 nm obtained using ImageJ software [40][41]. The particle size obtained from TEM analysis is comparable to the average crystallite size as calculated by Debye–Scherrer’s formula from the XRD pattern. Homogeneous nanoparticles with definite shapes are important in chemical sensing and production of optical, electronic and medical devices because the shape and size of Au-NPs determine their optical properties [42].

![Fig. 3.3: TEM images and particle size of Au-NPs](image)

3.4.4. FTIR Spectrophotometer

The FTIR data were recorded of Au-NPs with the help of (Perkin-Elmer Lambda-35) in the range (400–4000) cm\(^{-1}\) and shown in Fig.3.4. This spectral region is essential because numerous stretch modes involving the bonding of hydrogen atom with carbon and oxygen atoms are also clearly obtained in this region. FTIR spectra of Au-NPs were recorded at room temperature and were used to analyse the functional and vibrational groups that exist in the particles. The strong band observed at 3447 cm\(^{-1}\) is
due to the O-H bonds, which denote the presence of aromatic alcoholic and phenolic compounds [43]. The absorption peak at 2940 cm\(^{-1}\) may be responsible for the C-H stretching vibrations of the alkanes. Also, the presence of C-C stretching aromatic ring and amide I may be responsible for the narrow peak obtained at 1640 and 1383 cm\(^{-1}\). The stretching group of C-O is observed at 1035 cm\(^{-1}\) [44]. The weak peak at 834 and 590 cm\(^{-1}\) may be due to stretching of alkyl halide groups [45]. Thus, the reduction and stabilization of Au-NPs were attributed to the alcoholic, carboxylic and phenolic compounds [43].

![Fig. 3.4: FTIR Spectra of Au-NPs](image)

**3.4.5. UV-Visible Spectroscopy**

UV-visible absorption spectroscopy is the main method of ascertaining the optical properties of metallic nanoparticles because the absorption bands give the exact diameter and aspect ratio of the nanoparticles. The solution of colloidal gold nanoparticles has a characteristic red color. The surface electron cloud in NPs can move and absorb the electromagnetic radiation of a specific energy. The optical properties of the Au-NPs were investigated using UV-visible spectroscopy (Perkin Elmer-Lambda 35. Spectrophotometer) in the range of 350-800 nm, are given in Fig.3.5. and the absorption peak was observed at 521 nm [46].
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3.4.6. Photoluminescence Spectroscopy (PL)

The ability of Au-nPs to absorb incident energy is indicated by photoluminescence spectra (PL). Photoluminescence spectrum is an important means of studying energy levels, and defects in NPs, which can be used to determine the optical and electronic properties of the nanoparticles [47]. PL spectra of the Au-nPs at room temperature are shown in Fig.3.6. The optical properties of Au-nPs were due to electrons in 5d (valence) and 6sp (conduction) orbitals. The valence s and d electrons of the component atoms must be collectively considered as six bands, consisting of five bands called the d bands that are quite flat and situated a few eV below the Fermi level, and a conduction or sp band [48]. A laser beam was used to excite the Photoluminescence Au-nPs at 405 nm, and emission spectra was seen at 519 nm. PL emission between 500-590 nm range is attributed to electronic transitions between the sp band just below the Fermi level and the first d-band (d1) in the vicinity of the point L in the Brillouin zone [49].
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3.5. Conclusions

In this study, Au-NPs were successfully synthesized using the method of chemical reduction. The structure of Au-NPs was analyzed using the XRD data. Crystalline size of the particles was determined as 21 nm using Debye Scherrer’s equation. Different sizes of cubic and spherical Au-NPs were confirmed by SEM. The presence of Au, Cl, Na, Si and O ions were confirmed using the EDX. Surface morphology and particle sizes were analyzed with the TEM technique, which gave an average particle size of 22 nm. The optical properties of Au-NPs were ascertained by UV-visible spectroscopy and photoluminescence spectra. The absorption and emission peaks were observed at 521 nm and 519 nm respectively. Lastly, the FTIR spectra were used to determine the functional groups responsible for the formation of gold nanoparticles.
REFERENCES:


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