CHAPTER – V

FACILE SYNTHESIS & CHARACTERIZATION
OF THIOSEMICARBAZIDE CAPPED SILVER &
GOLD NANOPARTICLES AND STUDY OF
THEIR IMPEDANCE MEASUREMENT
Facile Synthesis & Characterization of Thiosemicarbazide Capped Silver & Gold nanoparticles and study of their impedance measurement

SECTION A: INTRODUCTION:

Matter can be placed into broad categories according to size. Macroscopic matter is visible with naked eye. Atoms and (most) molecules are microscopic with dimensions < 1nm. Mesoscopic particles, such as bacteria and cells that have dimensions on the order of micron(s), can be observed with optical microscopes. Falling into the gap between microscopic and mesoscopic is another class of matter, the nanoscopic particles. The size of nanoparticles is compared to that of other “small” particles in Figure 5.1, where the bacterium is huge in comparison.

![Figure 5.1: Size comparison of “small” particles](image)

Nanotechnology deals with processes that take place on nanometer scale viz, 1 to 100 nm. Nanoscale materials possess unique properties. Advances are occurring in synthesis of isolated nanostructures. This opens the possibility for creating a new generation of advanced materials with designed properties, not just by changing the chemical composition of components, but by controlling the size and shape of the components. For example, melting point of nanosized metal particles depends upon the size of particles. The smaller a particle becomes more the proportion of surface atoms increases. As particles decrease in size number of surface atoms becomes equal to or even exceeds the number of inner-core atoms. For a typical bulk material the
surface is negligibly small in comparison to the total volume. Surface atoms are more easily rearranged than those in the centre of the particle, and so the melting process, which depends on destroying order of the crystal lattice, can get started at a lower temperature. The melting point of gold metal is 1064°C. For 11-12 nm gold particles it is about 1000°C, then begins to drop dramatically to 900°C for 5 to 6 nm particles and to 700°C for 2 to 3 nm particles 1.

Nanochemistry is an exponentially growing research field in modern science that involves synthesis and application of nanoparticles of different sizes and shapes2. Nanoparticles are different from their bulk counterparts and exhibit unique properties. A typical well-known example is the fluorescence emission from semiconductor nanocrystals (quantum dots, QDs) which is dependent on particle size and covers entire visible spectrum3. Decreasing the size of a particle results in a larger share of atoms being located on the surface, which can increase the influence of surface effects on the material properties. It has, for example, been shown theoretically and experimentally that decreasing the size of a crystalline metal particle will confine the electron motion. In parallel, the electronic bands of the crystal get gradually quantized, thereby resulting in an increase in the band-gap energy4. As described by El-Sayed, new properties, which are possessed neither by bulk solid nor by the molecules or atoms forming the solid, are expected to be observed under these size transitions. This makes nanochemistry interdisciplinary, integrating different areas of research from material science to biomedicine5.

Terminology

As the field of nanostructured materials has evolved, many terms have been used, including the ones discussed below.

*Nanoparticle:* A nanoparticle (NP) has dimensions in the nanometer range, e.g. between 0.5 and 100 nm.

*Nanocrystal:* Nanocrystal is a solid particle that is a single crystal in the nanometer size range 30 nm.

*Nanostructured or nanoscale materials:* A nanoscale material is any solid material that has a nanometer dimension; such as three dimension (particles); two dimensions (thin films); one dimension (thin wire).
Colloids: Solutions can contain particles ranging in size from 0.1 to 10 nm. In colloids the particle size ranges from about 10 to 100 nm. Colloidal particles may consist of single units or groups of them. A 14-nm nanoparticle of gold, for instance, contains about 50,000 atoms. Components of colloids are assigned general names which are analogous to the solution terms: solute (the dispersed medium) and solvent (the dispersing medium or continuous phase). Colloids may form from any combination of liquid, solid or gas, except for gas and gas. Gases always dissolve in each other to form true solutions. Colloidal dispersions of insoluble materials are called sols. Examples of “sols” are the red colloidal gold and yellow colloidal silver nanoparticles. Common colloids are listed in Table 5.1.

**Table 5.1: Types of colloids**

<table>
<thead>
<tr>
<th>Disperse Phase</th>
<th>Continuous Phase</th>
<th>Names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>Gas</td>
<td>Aerosols: fog, mist</td>
</tr>
<tr>
<td>Solid</td>
<td>Gas</td>
<td>Aerosols: smoke</td>
</tr>
<tr>
<td>Gas</td>
<td>Liquid</td>
<td>Foams: whipped cream</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Emulsions: mayonnaise, milk</td>
</tr>
<tr>
<td>Solid</td>
<td>Liquid</td>
<td>Sol: colloidal gold</td>
</tr>
<tr>
<td>Liquid</td>
<td>Solid</td>
<td>Gels: jellies</td>
</tr>
</tbody>
</table>

**Preparation of Noble Metal Nanoparticles**

Many techniques, including chemical and physical means, have been developed to prepare metal nanoparticles, such as chemical reduction using a reducing agent,  electrochemical reduction, photochemical reduction, and heat evaporation (including chemical vapor deposition). Nanoparticles can be made by evaporating atoms from the surface of a metal by using a high energy laser & then cooling them into nanoparticles (a physical method). Physical ways usually need a high temperature (over 1000 °C), vacuum and expensive equipments. There are also easy and convenient chemical methods that use dilute aqueous solutions and simple equipment.

A series of reduction techniques using molecular hydrogen, alcohols, or NaBH₄ have been reported for the synthesis of colloidal metal nanoparticles. Since nanoparticles possess a large fraction of their atoms on the external surface, they...
have to be stabilized by capping agents such as polymers\textsuperscript{23}, surfactants\textsuperscript{24}, dendrimers\textsuperscript{25}, and ionic liquids\textsuperscript{26}. Applications in catalysis are clear as these systems offer high surface areas and a high concentration of low-coordinated sites and surface vacancies, which are required for high catalytic performances\textsuperscript{27}. Besides the inherent size–activity relationship, the particle shape also has to be taken into account\textsuperscript{28}. For example, hexagonal Pt(111) surfaces were reported to be about 3–7 times more active for aromatization reactions than cubic Pt(100) surfaces\textsuperscript{29}. Thus, controlling the particle morphology is widely utilized to tune their activity and selectivity\textsuperscript{30}.

Reaction time, temperature, and the concentration of reactants added during particle synthesis allow control over the particle size\textsuperscript{31} as well as particle ripening\textsuperscript{32}. Unprotected nanoparticles are usually unstable and coagulation is unavoidable during the catalytic transformation\textsuperscript{33}. To produce stable nanoparticles and to retain their high activity it is necessary to terminate the particle growth and to stabilize the surface. Protection has been achieved through the addition of capping agents or by immobilization in solid materials with high specific surface areas\textsuperscript{31, 34, 35}. Capping agents used for this purpose are mainly polymers or long-chain alkyl surfactants with polar head groups that bind to the nanoparticle surface through covalent or electrostatic interactions. The stabilization itself is explained by electrostatic or steric effects or by a combination of both.

Alternatively, nanoparticles have been immobilized or grafted onto inorganic supports to improve their stabilization and recycling ability\textsuperscript{31, 36}. Porous materials also allow control over the particle growth according to the pore size and the enhancement of dispersion and concentration of the active sites in the host matrix\textsuperscript{37}. Progress in the discovery of new support materials for heterogenization of homogeneous catalysts has been periodically reviewed\textsuperscript{38}.

Capping agents stabilizes the nanoparticles and prevents them from aggregating. Polymers are good stabilizing agents because they can cover a larger surface area of the nanoparticles. Other organic agents can be used though as long as it can attach itself with the nanoparticles.
Reducing Agents

In general, chemical reduction reactions involve reducing agents that are reacted with a salt of metal according to the following chemical equation:\(^{39}\)

\[
mMe^{n+} + n\text{Red} \rightarrow mM{e^0} + n\text{O}_x
\]

**Table 5.2**: Guidelines for the choice of reducing agents and reaction conditions in the preparation of Au, Ag and Cu nanoparticles\(^{39}\)

<table>
<thead>
<tr>
<th>Metal Species</th>
<th>E(^0)/V</th>
<th>Reducing agent</th>
<th>Conditions</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(^{3+})</td>
<td>≥ +0.7</td>
<td>Alcohol, polyols</td>
<td>≥ 70°C</td>
<td>Slow</td>
</tr>
<tr>
<td>Ag(^+)</td>
<td>≥ +0.7</td>
<td>Aldehydes, Sugars, Hydrazine, (H_3PO_2), NaBH(_4), Boranes Citrate</td>
<td>&lt; 50°C Ambient</td>
<td>Moderate Fast</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>&lt; 0.7 And ≥ 0</td>
<td>Polyols, Aldehydes, Sugars, Hydrazine, hydrogen NaBH(_4)</td>
<td>&gt;120°C 70-100°C &lt;70°C Ambient</td>
<td>Slow Slow Moderate Fast</td>
</tr>
</tbody>
</table>

**Table 5.2** gives a list of reagents most commonly used in the reduction of gold, silver, and copper salts along with the appropriate conditions. Brief description of chemical methods to prepare gold, silver and copper nanoparticles are described.

**Synthesis of Gold Nanoparticles**

Synthesis of gold nanoparticles by reducing agents such as sodium borohydride\(^{40}\), ascorbic acid in presence of cetyltrimethylammonium bromide (CTAB)\(^{41}\), sugars (glucose, fructose and sucrose)\(^{42}\) have been reported. One common method to synthesize gold nanoparticles is reduction of hydrochloroauric acid, HAuCl\(_4\) with sodium citrate, \(C_6H_5O_7\)Na\(_3\). Spherical gold NPs are surrounded by a
layer of AuCl$_2^-$ ions providing a negative charge to the NPs preventing aggregation by electrostatic repulsion $^{43}$.

**Synthesis of Silver Nanoparticles**

Many chemical reduction methods have been used to synthesize silver nanoparticles from silver salts $^{44-53}$. The reactions described here use silver nitrate as the starting material. Chemical reduction methods that have been used to synthesize silver NPs from silver nitrate vary in the choice of reducing agent, the relative quantities and concentrations of reagents, temperature, mixing rate, and duration of reaction. The diameters of resulting particles depend upon conditions. Greenish-yellow ($\lambda$ max 420 nm) colloidal silver with particle sizes from 40 - 60 nm has been reported from reduction with sodium citrate at boiling$^{54}$. Silver colloids described as brownish or yellow-green, with absorption maxima at 400 nm and particle size of about 10 nm, result from reduction with ice-cold sodium borohydride followed by boiling for one hour$^{55}$. A method using both sodium citrate and sodium borohydride at boiling gives a greenish colloid absorbing at 438 nm with particle size 60 - 80 nm$^{56}$. Clear yellow or greenish-yellow colloidal silver can be obtained depending upon the duration of the reaction with ice cold sodium borohydride $^{57}$.

**Mechanism of Particle Formation**

Metal atoms produced by reduction in solutions are essentially insoluble, leading to clusters called embryos through slow aggregation:

\[ xMe^0 \leftrightarrow (Me^0)^{em} \]

The existence of very small metal clusters containing a number of atoms correspond to the “magic numbers”, are more stable. The intermediate-sized embryos either dissociate or grow to become stable. Introduction of new metal atoms into the system enable the embryos to reach a critical size and separate from the solution as solid particles, called the nuclei $(Me^0)^{nucl}$

\[ (Me^0)^{em} + yMe^0 \rightarrow (Me^0)^{x+y}\nucl \]

The nuclei grow to primary nanosize particles through further addition of metal atoms:
At this stage, either the diffusion of atoms onto primary particles continue (diffusion mechanism, eqn \((A)\)) or nanosize primary particles aggregate to form the final metal particles (aggregation mechanism, eqn \((B)\)).

\[
(\text{Me}_n^0)_{\text{nuc}} + m\text{Me}_p^0 \rightarrow (\text{Me}^0_{n+m})_{pp}
\]

\[
(\text{Me}_p^0)_{pp} + n\text{Me}_p^0 \rightarrow (\text{Me}_p^0)_p \quad (A)
\]

\[
m(\text{Me}_p^0)_{pp} \rightarrow (\text{Me}_p^0)_p \quad (B)
\]

It is most likely for both growth and aggregation mechanisms to happen simultaneously in the same system. The density and the shape of the final particles depend on which mechanism prevails in the system\(^{39}\). Growth mechanism will favor the formation of high density regular shaped metal crystals. Metal particles produced via aggregation will be mostly spherical and with a lower density.

The final size depends on the super saturation, the fraction of metal atoms involved in the nucleation step relative to the total amount of metal in the system, and on the degree of aggregation\(^{39}\). High super saturation of metal atoms will generate a large number of nuclei and consume a major fraction of metals in the system. In this situation if the aggregation mechanism is prevented, further increase in size will occur by incorporation of remaining metallic species in solution and the final particles will remain in nanosize range. In order to produce larger particles (in sub-micrometer and micrometer range), a small number of nuclei should be created, consuming only a small fraction of metal atoms, which next grow by integration of the remaining metal in solution. This condition can be achieved by slow reactions, slow addition of metal species into system\(^{58,59}\) or added seeds\(^{60,61}\).

### Applications of Silver and Gold Nanoparticles

Compared with organic dyes the absorption of light by gold and silver nanoparticles is 5–6 orders in magnitude higher. This implies that a metal NP is over 1 million fold more likely than comparable dye to absorb light, such as near-Infrared (NIR) light and convert it into thermal energy. As a result, these nanoparticles have recently been used in thermal therapy and optical imaging of tumours\(^{62,63}\).

Silver and gold nanostructures have been studied as important colorimetric sensors due to their high extinction coefficient. The sensitivity of surface plasmon
peaks to environmental changes can lead to optical detection of binding materials on the silver surface. The sensitivity of such an optical sensor is strongly dependent on size, shape, structure of the nanoparticles, and the surrounding medium. For example when the refractive index of surrounding medium changes, the intensity and position of the surface plasmon peak changes. An increase in the refractive index often causes the surface plasmon peak to shift to longer wavelength. The red shift of surface plasmon peak can also be caused by the aggregation of the particles and has been used for detection of glucose and protein\textsuperscript{63-66}. One example is use of boronic acid-capped silver NPs for detection and monitoring of blood sugar. The interactions of boronic acid-capped silver NPs and glucose resulted in aggregation of the nanoparticles and were accompanied by a shift in the plasmon peak of silver NPs from 397 nm to 640 nm\textsuperscript{67}.

The ability of gold and silver nanostructures to enhance local electric fields has led to their applications as surface enhanced Raman scattering (SERS). The enhancement factor can be as much as $10^{14}$-$10^{15}$, which enables the detection of individual molecules absorbed on metal particles \textsuperscript{68,69,63}. The maximum signal amplification in SER spectroscopy ($10^{15}$) can be achieved with silver particles of about 50 nm \textsuperscript{69}.

Silver has been known for antibacterial activity since ancient Greece times. Currently, the investigation of this phenomenon has gained more attention due to the increase of bacterial resistance to antibiotics, caused by their overuse. Silver nanoparticles can be used in medicine to reduce infections in burn treatment, to prevent bacteria colonization on dental materials, stainless steel materials, to eliminate microorganisms on textile fabrics, or they can be used for water treatment \textsuperscript{70,71,72}.

Antimicrobial activity of colloid silver particles is influenced by dimensions of the particles. The extremely small size nanoparticles results in the particles having a large surface area relative to their volume. This allows them to easily interact with other particles and increases their antibacterial efficiency. In heterogeneous catalysis, it is well known that the increasing proportion of surface atoms with decreasing particle size makes small metal particles highly reactive. Silver has been utilized as an oxidation catalyst especially for production of ethylene oxide from ethylene \textsuperscript{73}.
SECTION B: PRESENT WORK

In the present work, we report the formation, morphology and study of “ac-impedance” of Thiosemicarbazide -capped silver and gold nanoparticles. This method utilizes a simple chemical reduction of metal iodide employing sodiumborohydride. The advantage of this method is ease of preparation, convenience in use and especially, the obtained nanoparticles are uniform in their shapes and sizes. Time-dependent UV-vis spectroscopy and Scanning electron microscopy (SEM) are employed to monitor the formation process of metal nanoparticles. Specifically, we observed changes in the shapes of these nanoparticles (during the formation of the nanoparticles). This may be helpful in understanding the growth of nanoparticles and creates a new dimension in controlling the shapes of nanoparticles.

Reagents and Instruments:

All the reagents used were of AR grade. Thiosemicarbazide was purchased from Aldrich. Silver nitrate was obtained from National Refinery Pvt Ltd, ChloroAuricacid was purchased from FINAR Chemicals Pvt Ltd and a 0.1 M aqueous solution was used as stock solution. Sodium borohydroxide was obtained from Merck, India. Organic-free water was used throughout the experiment.

The UV-visible spectra were recorded on a Schimadzu UV-vis spectrophotometer, and the solutions were taken in a 1 cm well-stoppered quartz cuvette. Fourier transform infrared (FTIR) spectral characteristics of the samples were collected on a Schimadzu FTIR spectrometer using KBr pellets. The FTIR spectrum was recorded over 45 scans of each sample, and the background spectrum was automatically subtracted. The formation of single-phase compound was checked by X-ray diffraction (XRD) technique. The XRD pattern was taken with X-ray diffractometer (XPERT-PRO) at room temperature, using CuKα radiation λ=1.5406 A˚ over a wide range of Bragg angles (30° ≤ 2θ ≤ 85°). SEM micrograph of capped Ag-NP & Au-Np was obtained on a NOVA-230 with an operating voltage of 10 KV. For TEM analysis, the specimen was suspended in distilled water, dispersed ultrasonically to separate individual particles, and one or two drops of suspension deposited onto holey-carbon coated copper grids and dried under Infrared lamp.
Novocontrol Apha A Impedance Analyzer was used to determine ac impedance analysis of Ag & Au nanoparticles at room temperature.

**Synthesis of Thiosemicarbazide capped Silver nanoparticles employing NaBH₄ at room temperature:**

A total of 2.5 mL of 10⁻² M AgNO₃ was added to 75 mL of triply distilled organic-free water. A total of 5 mL of 10⁻² M thiosemicarbazide (dissolved in hot water) was added as stabilizer to the above solution with stirring. After 10 min of mixing, 2.5 mL of 10⁻² M potassium iodide (KI) was dropped into the solution slowly, yielding a green yellow AgI colloid. A total of 20 mg of NaBH₄ was added to AgI colloidal solution, and the reaction mixture was continually stirred for about 20 min. The silver colloid was finally obtained. During the whole reaction, colour of the colloidal solution changed from green-yellow to nut-brown at beginning, then to brown, and finally to black.

\[
\text{AgNO}_3 + \text{KI} \rightarrow \text{AgI}
\]

Schematic representation of capped silver nanoparticles

**Synthesis of Thiosemicarbazide capped Gold nanoparticles employing NaBH₄ at room temperature:**

A total of 2.5 mL of 10⁻² M ChloroAuric acid was added to 75 mL of triply distilled organic-free water. A total of 5 mL of 10⁻² M thiosemicarbazide (dissolved in hot water) was added as stabilizer to the above solution with stirring. After 10 min of mixing, 2.5 mL of 10⁻² M potassium iodide (KI) was dropped into the solution slowly, yielding a green yellow AuI colloid. A total of 20 mg of NaBH₄ was added to the AuI colloidal solution, and the reaction mixture was continually stirred for about 20 min. The silver colloid was finally obtained. During the whole reaction, the colour of the colloidal solution changed from yellow to dark red at beginning, then to brown, and finally to black.
Results & Discussions:

*Evolution and Characterization of Silver & Gold Nanoparticles:*

UV-visible spectroscopy is one of the most widely used techniques for structural characterization of silver nanoparticles. The surface Plasmon resonance (SPR) band is broad indicating poly-dispersed nanoparticles. The optical absorption spectra of metal nanoparticles are dominated by surface Plasmon resonances (SPR), which shift to longer wavelengths with increasing particle size. The position and shape of plasmon absorption of metal nanoclusters are strongly dependent on the particle size, dielectric medium, and surface-adsorbed species.

In this present work, the aggregates of silver / gold nano particles have been synthesized by using silver nitrate / chloroauric acid and thiosemicarbazide as capping agent. The nanoparticle formation was initially identified by the absorption spectra. They were presented in Fig 5.2 & Fig 5.3.

After addition of precursor salt solution to potassium iodide solution, colour of the solution changes from colourless to light yellow (for AgNO₃ solution) and golden yellow to lemon yellow (for HAuCl₄ solution) indicates the nucleation of metal particle at the infancy. The spectra were recorded in distilled water system.

From UV data, the surface plasmon absorption of silver nanoparticles have shorter wavelength band in visible region at 432 nm and for the gold nanoparticles the band appeared at 535 nm indicates the polydisperssion of metal nanoparticles.

**Fig 5.2:** UV-Visible Spectral studies of thiosemicarbazide capped silver nanoparticles
Particle size measurements using SEM, XRD & TEM studies:

The SEM (Scanning Electron Microscopy) images for silver & gold nanoparticles were presented in Fig 5.4 & Fig 5.5 respectively. Form these figures it was observed that the formed nanoparticles are crystalline in nature with certain degree of porocity. The schererr rings which are characteristic of FCC for silver and gold nanoparticles were clearly observed. From this the structures seen in SEM images reveals that synthesized nanoparticles are nanocrystalline in nature.

It was observed that silver nanoparticles were scattered over the surface and no aggregation noticed but gold nanoparticles are aggregated over the surface.
Fig 5.4: SEM image of Thiosemicarbazide capped AgNP

Fig 5.5: SEM image of Thiosemicarbazide capped AuNP

XRD Studies:

Fig 5.6 shows the XRD pattern of powder silver nano particles. The presence of peaks at 2θ values 38.1, 44.09, 64.36 corresponds to (1 1 1), (2 0 0), and (2 2 0) planes of silver respectively. Thus the XRD spectrum confirmed the crystalline structure of silver nanoparticles. The other peaks are organic impurities. All the peaks in XRD pattern can be readily indexed to face-centered cubic structure of silver as per available literature. The average size of the gold nanoparticles was calculated from XRD data according to the line width of the maximum intensity reflection peak by using the Scherrer equation. It is well known that with diminishing crystallite size the measured XRD pattern exhibits broadening, and very often overlapping reflections. The broadening of the reflections is inversely proportional to the
crystallite size (i.e. size of coherently diffracting domains). The relation is known as Scherrer’s equation where “\( \gamma \)” is the diffraction angle of a particular reflection. The total diffracted intensity for a given Bragg reflection from a crystallite is the sum of independently diffracted intensities by each of the unit-cell columns making-up the crystallite. It means that the calculated size distribution is infact a distribution of diffraction column lengths in a given crystallographic direction perpendicular to the diffraction planes and not of crystallite (coherently diffracting domains) sizes. Theoretical considerations show that the interference function of a polycrystalline or nano crystalline solid is identical to that of an arrangement of isolated particles with the same size or size distribution as those of the polycrystalline or nano crystalline solid\(^{74,75}\). Thus the values of Scherrer’s formula are solely an estimate of a volume-weighted average column length. This explains the difference between experimental and theoretical values, and the values from the Scherrer’s formula is termed “apparent crystallite size”\(^ {76}\).

Scherrer’s Formula

\[
B = \frac{k\lambda}{s \cos \theta}
\]

Where;
- \( s \) is the crystallite size,
- \( \lambda \) is the wavelength of the X-ray radiation (\( \text{CuK}_\alpha = 0.15406 \text{ nm} \)),
- \( k \) is a constant taken as 0.94,
- \( \theta \) is the diffraction angle and
- \( B \) is the line width at half maximum height.

From the obtained spectrum the size of the silver nano particle is calculated as 15 ±2 nm.

Similarly XRD spectrum of thiosemicarbazide capped gold nanoparticles was depicted in Fig 5.7 and the presence of peaks at \( 2\theta \) values 38.31, 44.60, 64.74, 77.72, 81.92 corresponds to \((1\ 1\ 1),\ (2\ 0\ 0),\ (2\ 2\ 0),\ (3\ 1\ 1)\) planes of gold respectively. Thus the XRD spectrum confirmed the crystalline structure of gold nanoparticles, which are consistent with the fcc structure of the gold. The average size of the gold nanoparticles was calculated from the XRD data according to the line width of the maximum intensity reflection peak by using the Scherrer equation and it is 20±2 nm.
TEM Studies:

Silver & Gold nanoparticles are further examined using transmission electron microscopy (TEM). The TEM images of synthesized silver and gold nanoparticles were recorded and presented in Fig 5.8 & Fig 5.9 respectively. The average size of silver and gold nanoparticles was observed as 15±2 nm & 20±2 nm respectively which were in agreement with Scherers equation.
FT-IR spectral studies:

The IR spectra of the free thiosemicarbazide and the particles capped by dithizone are given in Fig 5.10, 5.11 & 5.12. The reason for the intensity difference between the spectra is believed to be the thiolate molecules on the nano particle forming a relatively closely packed thiol layer and molecular motion being constrained. Thus, this steric constraining effect on the transverse mode (rocking mode, wagging mode, etc.) is stronger than that on the longitudinal mode (stretching mode, etc). Therefore, the change of the peak intensity of the longitudinal modes is smaller than that of the transverse mode. The C–S stretching mode is due to the
position of the C=S bond nearest to the surface of the silver particle, and a chemical bond can form between S and Ag & Au atoms.

The FTIR spectrum of the nanocrystals provides additional information about the local molecular environment of thiosemicarbazide. The FTIR spectrum of thiosemicarbazide capped Ag nanoparticle is represented in Fig. 5.11. From the spectrum of free thiosemicarbazide, it can be noticed that the amino group appeared at 3374 cm\(^{-1}\) and -C=S stretchings appeared at 1626, 1527 cm\(^{-1}\) respectively. The band appeared at 800 cm\(^{-1}\) is assigned to C=S stretching mode. Generally, the vibrational spectrum of Ag-NPs capped with thiosemicarbazide molecule is similar to the spectrum of thiosemicarbazide indicating that, the organic molecules have indeed become a part of the nanoparticles.

FT-IR analysis of thiosemicarbazide capped silver nanoparticles was presented in Fig 5.12. From the figure it is clearly observed that the decrease in the intensities of -NH & -C=S stretchings were clearly observed. This indicates that the formation of gold nanoparticles capped by thiosemicarbazide.

![Fig 5.10 IR Spectrum of thiosemicarbazide](image-url)
Fig 5.11 IR spectrum of Thiosemicarbazide capped silver nanoparticles

Fig 5.12 IR spectrum of Thiosemicarbazide capped gold nanoparticles
IMPEDANCE measurement of thiosemicarbazide capped silver and gold nanoparticles:

Impedance (symbol \( Z \)) is a measure of overall opposition of a circuit to current, in other words: how much the circuit impedes the flow of current. It is like resistance, but it also takes into account the effects of capacitance and inductance. Impedance is measured in ohms, [symbol: \( \Omega \)].

Impedance is more complex than resistance because effects of capacitance and inductance vary with the frequency of current passing through the circuit and this means **impedance varies with frequency**! The effect of resistance is constant regardless of frequency.

\[
\text{Impedance, } Z = \frac{V}{I}
\]

\[
\text{Resistance, } R = \frac{V}{I}
\]

- \( V \) = voltage in volts (V)
- \( I \) = current in amps (A)
- \( Z \) = impedance in ohms (\( \Omega \))
- \( R \) = resistance in ohms (\( \Omega \))

Electrochemical impedance spectroscopy (EIS) has long been employed for studying electrochemical systems, including those involved in corrosion, electrodeposition, batteries and fuel cells. For impedance measurements, a small sinusoidal AC voltage probe (typically 2-10 mV) is applied, and current response is determined. The in-phase current response determines the real (resistive) component of impedance, while the out-of-phase current response determines the imaginary (capacitive) component. The AC probe voltage should be small enough so that system response is linear, allowing simple equivalent circuit analysis. Impedance methods are quite powerful, in that they are capable of characterizing physicochemical processes of widely differing time constants, sampling electron transfer at high frequency and mass transfer at low frequency. Impedance results are commonly fitted to equivalent circuits of resistors and capacitors, such as the
Randles circuit shown in Fig 5.13\textsuperscript{3}, which is often used to interpret simple electrochemical systems. This equivalent circuit yields the Nyquist plot shown in Fig 5.14, which provides visual insight into the system dynamics. In Figs 5.10 and 5.11, $R_{ct}$ is charge-transfer resistance, which is inversely proportional to the rate of electron transfer; $C_d$ is double-layer capacitance; $R_s$ is the solution-phase resistance; and, $Z_w$ is Warburg impedance, which arises from mass-transfer limitations. If an analyte affects one or more of these equivalent circuit parameters and these parameters are not affected by interfering species, then impedance methods can be used for analyte detection. $R_s$ arises primarily from the electrolyte resistance and is analytically useful mainly in conductivity sensors. The Warburg impedance, which can be used to measure effective diffusion coefficients, is seldom useful for analytical applications.

In the present work, EIS experiments were performed in the frequency range between 1 MHz and 100 MHz with ac voltage amplitude of 10 mV on Novocontrol Apha A Impedance Analyzer at room temperature. Initially the powdered materials
were made into pellets by using the hydraulic pressure machine. The diameters of the silver and gold pellets are 10 mm & 6mm respectively. The thicknesses of silver & gold pellets are found by using venire callipers as 0.61mm & 0.32 mm respectively.

The ac impedance techniques have been widely used to study the dielectric behaviour of polycrystalline ceramics, crystalline, as well as amorphous materials. Fig. 5.15 shows the variation of real part of impedance ($Z'$) with varied frequency at room temperature. It is observed that the magnitude of $Z'$ decreases on increasing the frequency.

Fig.5.16 & Fig 5.17 shows Nyquist plots of impedance in at different temperatures in the frequency range (1-100MHz). At room temperature there is a linear response in $Z''$. This trend indicates the insulating behaviour in the sample. A single arc found in the samples that starts from origin. Hence there is no series resistance that can be attached to the circuit. The resistance of grain (Rg) is directly obtained from the intercept on the $Z'$ axis. The capacitance ($C_g$) due to these effects can be calculated using the relation $f_{max} = 1/(2\pi f) = 1/(2\pi RC)$. Slopes of these plots give grain conduction.

![Graph](image.png)

**Fig 5.15** Frequency dependency of $Z'$ on log-log scale
Fig 5.1: Nyquest plot for thiosemicarbazide capped silver nanoparticles at RT

Diameter of the pellet \((d) = 10\) mm
Radius of the pellet \((r) = 5\) mm \(= 5 \times 10^{-3}\) m
Thickness of the pellet \((t) = 0.61\) mm \(= 0.61 \times 10^{-3}\) m
Area \((A) = \pi r^2 = 3.14 \times 25 \times 10^{-6} m^2\)
Charge transfer Resistance \((R_{ct}) = 2.4 \times 10^7 \Omega\)

\[
\text{Resistance} = \frac{R \times A}{l} = \frac{2.4 \times 10^7 \times 78.57 \times 10^{-6}}{0.61 \times 10^{-3}}
\]

\[
= \frac{2.4 \times 10^7 \times 78.57 \times 10^4}{0.61}
\]

\[
= 309.127 \times 10^4
\]

\[
= 3.09127 \times 10^6 \Omega - m
\]

\[
\text{Conductivity} = \frac{1}{\rho} = \frac{1}{3.09127} \times 10^{-5} \text{mho} - m^{-1}
\]

\[
\text{Conductivity} = 0.32349 \times 10^{-5} \text{mho} - m^{-1}
\]
Fig 5.17: nyquest plot for thiosemicarbazide capped gold nanoparticle at RT

Diameter of pellet \( d \) = 6 mm = 6x10^{-3} m
Radius of pellet \( r \) = 3 mm = 3x10^{-3} m
Thickness of pellet \( t \) = 0.32 mm = 0.32x10^{-3} m
Area of pellet \( A \) = \( \pi r^2 = 3.14 \times 9 \times 10^{-6} \) m\(^2\) = 28.285 \times 10^{-6} m\(^2\)

\[ R = 4.07 \times 10^7 \Omega \]

\[
\rho = \frac{RA}{l} = \frac{4.07 \times 10^7 \times 28.285 \times 10^{-6}}{0.32 \times 10^{-3}}
\]
\[
= \frac{4.07 \times 10^7 \times 28.285 \times 10^4}{0.32}
\]
\[
= 359.749 \times 10^4
\]
\[
= 3.59749 \times 10^6 \Omega - m
\]

\[
\sigma = \frac{1}{\rho} = \frac{1}{3.59749} \times 10^{-6} \text{mho} - m^{-1}
\]
\[
\sigma = 0.27797 \times 10^{-6} \text{mho} - m^{-1}
\]
Conclusion:

In summary, synthesis of thiosemicarbazide capped nanoparticles was achieved by chemical reduction method and the particles were duly characterized by advanced spectral techniques viz UV-Visible, FTIR, XRD, SEM, TEM. The average size of silver and gold nanoparticles was observed as 15 & 19 nm respectively. In addition, we performed electrical ac impedance experiment to study the conductive nature of the materials. The results obtained demonstrate that conductivity is through grains and synthesized materials exhibits semiconductor in nature. Further work is required to study the semiconductor property.
REFERENCES


