Chapter Two

Materials and Measurement Techniques

2.1. Introduction to Nanomaterials

One of the most significant developments in recent years has been the creation and exploitation of materials with the structural features in between those of atoms and bulk materials with at least one of the dimensions in the nanometer range [1]. The properties of materials of nanometric dimensions are significantly different from those of atoms as well as of bulk materials. Suitable control of the properties of nanometer-scale structures can lead to a new science as well as a new devices and technologies [1, 2]. The underlying theme of nanotechnology is miniaturization. The importance of nanotechnology was pointed out by Feynman as early as 1959, in his often-cited lecture entitled ‘‘There is plenty of room at the bottom’’ [3, 4]. The challenge is to beat Moore’s law, according to which the size of microelectronic devices shrinks by half every four years [1].

There has been an explosive growth of nanoscience and technology in the last few years, primarily because of the availability of new strategies for the synthesis of nanomaterials and new tools for characterization and manipulation. There are different experimental methods available to synthesize metal/metal oxide and semiconductor nanoparticles and these materials are studied by various experimental techniques to understand physical properties for further improvements. This chapter is devoted to the principles of the experimental methods and characterization techniques. Here, we discuss general synthetic approaches of nanoparticles preparation and various characterization techniques utilized in our work.
2.2. Methods of Nanoparticles Synthesis

The synthesis of nanoparticles is an essential component of nanoscience and nanotechnology. Advances in this field largely depend on the ability to synthesize nanoparticles of various different materials, sizes, and morphologies. It is well recognized that properties of metal nanoparticles depend largely on the size, shape, composition, structure, and crystallinity. Therefore, various approaches have been developed to control these parameters and hence, meet the requirements for various applications. Although, the nanoparticles are synthesized by varieties of methods but all those synthetic routes fall into two main categories known as top-down approach and bottom-up approach [5]. Among these two approaches, bottom-up approach is considered to be the most widely used, more suitable and superior in comparison with the other one. A broad general description on these routes is as follow;

2.2.1. Top Down Approach

Among various top down approaches, high energy ball milling is one of the simplest technique to make nanoparticles of some metals and alloys. Hence, the technique is discussed in brief in this section and is as follows;

High-Energy Ball Milling

The milling of materials is of prime interest in the mineral, ceramic processing, and powder metallurgy industry. Typical objectives of the milling process include particle size reduction, solid-state alloying, mixing or blending and particle shape changing. The process includes violent agitation/shaken of powders with typical particle diameters of about 50 μm with a number of hardened steel or tungsten carbide (WC) coated balls in a sealed container. The most effective ratio for the ball to powder masses is five to ten. High-energy milling forces can be obtained using high frequencies and small amplitudes of vibration. Shaker mills (e.g. SPEX model 8000)
which are preferable for small batches of powder (approximately 10 cm$^3$ is sufficient for research purposes) are highly energetic and reactions can take place one order of magnitude faster than with other types of mill. Since the kinetic energy of the balls is a function of their mass and velocity, dense materials (steel or tungsten carbide) are preferable to ceramic balls. During the continuous severe plastic deformation associated with mechanical attrition, a continuous refinement of the internal structure of the powder particles to nanometer scales occurs which raises the temperature less than or equal to 100 to 200$^\circ$C during the process.

A variety of ball mills have been developed for different purposes including tumbler mills, attrition mills, shaker mills, vibratory mills, planetary mills etc. [6]. The basic process of mechanical attrition is illustrated in figure 2.1.

![Schematic representation of the principle of mechanical milling.](image)

The difficulty with the top-down approach is ensuring all the particles are broken down uniformly to required size and contamination by ball milling tools (Fe) and atmosphere (trace elements of O$_2$, N$_2$, in rare gases) can be a problem. The Fe contamination can be minimized by reducing the milling time and using the purest, most ductile metal powders, a thin coating of milling tools by respective material.
Atmospheric contamination can be minimized or eliminated by sealing the vial with a flexible ‘O’ ring after the powder has been loaded in an inert gas glove box. In spite of this, the approach is widely advantageous in terms of high production rates of nano powders. Several milligrams to few kilograms of nanoparticles can be synthesized in short time of few minutes to hours using ball milling technique.

2.2.2. Bottom Up Approach

(a) Sol-Gel Process

The sol-gel process, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel) [7]. The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel and the sol/gel transition controls the particle size and shape.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors. The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides M(OR) can be described as follows:

\[ \text{MOR} + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{ROH} \text{ (hydrolysis)} \]
\[ \text{MOH} + \text{ROM} \rightarrow \text{M-O-M} + \text{ROH} \text{ (condensation)} \]

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials [8]. The process can be characterized by a series of distinct steps which include; formation of sol, gelation, aging of the gel (syneresis), drying of the gel, dehydration, densification and decomposition of the gels. The typical steps that are involved in sol-gel processing are shown in the schematic diagram in figure 2.2.
The importance of this technique arises due to the possibility of synthesizing non-metallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures as compared to the high temperature process which requires melting of glass or firing ceramics. The major difficulties of the technique are controlling the particles growth, stopping the agglomeration of newly formed particles and ensuring the completeness of the reaction. In addition to these, the production rate of nanoparticles is low but the major advantage is one can get mono sized particles by any bottom-up approach.

![Schematic representation of sol-gel process of nanomaterials synthesis.](image)

**Figure 2.2:** Schematic representation of sol-gel process of nanomaterials synthesis.

**(b) Liquid Solid Reactions**

Ultrafine particles are produced by precipitation from a solution, the process being dependent on the presence of the desired nuclei. For example, TiO$_2$ powders have been produced with particle sizes in the range 70-300 nm from titanium tetra
isopropoxide [9]. The ZnS powders were produced by reaction of aqueous zinc salt solutions with thioacetamide (TAA) [10]. Precursor zinc salts were chloride, nitric acid solutions, or zinc salts with no common associated ligands (i.e., acetylacetonate, trifluorocarbonsulfonate and dithiocarbamate). The 0.05 M cation solutions were heated in a thermal bath maintained at 70° or 80 °C in batches of 100 or 250 ml. Acid was added drop wise to bring its pH = 2. The reaction was started by adding the TAA to the zinc salt solution, with the molar ratio of TAA and zinc ions being set to the values either 4 or 8. In intervals, aliquots were collected from the reaction solution.

**c) Gas Condensation Processing (GPC)**

Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys [11]. The technique was pioneered by Gleiter and co-workers and is based on vaporization of a metallic or inorganic material using thermal evaporation sources in an atmospheric pressure of 1-50 mbar He (or inert gases like Ar, Ne, Kr) [12]. A general schematic diagram of GPC technique is given in figure 2.3. Cluster forms in the vicinity of the source by homogenous nucleation (gas phase) and grow by coalescence and incorporation of atoms from the gas phase. The particle size of prepared clusters depends critically on their residence time in the growth regime and can be influenced by the inert gas pressure and on the evaporation rate/vapour pressure of the evaporating material. With increasing gas pressure, vapour pressure and mass of the inert gases; the average particle size of the nanoparticles increases. A rotating cylindrical device cooled with liquid nitrogen was employed for the particle collection: the nanoparticles in the size range from 2-50 nm are extracted from the gas flow by thermophoretic forces and deposited loosely on the surface of the collection device as a powder of low density with no agglomeration [13]. Subsequently, the nanoparticles are removed from the surface of the cylinder by means of a scraper in
the form of a metallic plate. In addition to this cold finger device, several techniques known from aerosol science have now been implemented for the use in gas condensation systems such as corona discharge, etc. These methods allow for the continuous operation of the collection device and are better suited for larger scale synthesis of nanopowders. However, these methods can only be used in a system designed for the gas flow [13].

A major advantage over convectional gas flow is the improved control of the particle sizes. Depending on the flow rate of the He-gas, particle sizes are reduced by 80% and standard deviations by 18% [11-13]. Evaporation can be done from refractory metal crucibles (W, Ta or Mo). If metals with high melting points or metals which react with the crucibles are to be prepared, sputtering or laser or electron beam evaporation has to be used.

Figure 2.3: Schematic representation of typical set-up for gas condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media.
(d) Chemical Vapour Condensation (CVC)

Chemical vapour condensation (CVC) was developed in Germany in 1994. It involves pyrolysis of vapours of metal organic precursors in a reduced pressure atmosphere [14]. Particles of Fe, Fe-Co and their oxides have been produced by CVC method [15, 16]. As shown schematically in figure, the evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapour Condensation (CVC) process. A schematic diagram of CVC reactor is shown in figure 2.4. The original idea of the novel CVC process was to adjust the parameter field during the synthesis in order to suppress film formation and enhance homogeneous nucleation of particles in the gas flow. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed. In a certain range of residence time both particle and film formation can be obtained. By changing the gas flow rate, the residence time of the precursor molecules can be adjusted, the pressure difference between the precursor delivery system, the main chamber and the temperature of the

![Figure 2.4: A schematic of a typical chemical vapour condensation reactor.](image-url)
hot wall reactor results in the prolific production of nanosized particles of metals and ceramics instead of thin films as in CVD processing [13]. In the simplest form, a metal organic precursor is introduced into the hot zone of the reactor using mass flow controller. Technique is used for the synthesis of wider range of ceramics including nitrides and carbides, complex oxides such as BaTiO$_3$ or composite structures. In addition to the formation of single phase nanoparticles by CVC of a single precursor, the reactor allows the synthesis of following nanoparticles:

1) Mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor.

2) Coated nanoparticles, i.e., n-ZrO$_2$ coated with n-Al$_2$O$_3$ or vice versa, by supplying a second precursor at a second stage of the reactor. Because CVC processing is continuous, the production capabilities are much larger than in GPC processing. Quantities in excess of 20 g/hr have been readily produced with a small scale laboratory reactor. The microstructures of nanoparticles as well as the properties of materials obtained by CVC are identical to GPC prepared powders.

(e) Laser Ablation

Laser ablation has been extensively used for the preparation of nanoparticles and particulate films [12]. In this process, a high energy pulsed laser with an intensity flux exceeding $10^7$ W/cm$^3$ is used as the primary excitation source of ablation for generating clusters directly from a solid sample in a wide variety of applications [8]. The resulting plasma causes highly efficient vaporization since with current pulsed lasers one can easily generate temperatures at the target material greater than $10^4$ K. This high temperature vaporizes all known substances so quickly that the rest of the source can operate at room temperature. This process yields typically $10^{14}$ - $10^{15}$ atoms from a surface area of 0.01 cm$^2$ in a $10^{-8}$ s pulse [6]. The local atomic vapour density
can exceed $10^{18} \text{atom/cm}^3$ (equivalent to 100 Torr pressure) in the microseconds following the laser pulse. The hot metal vapour is entrained in a pulsed flow of carrier gas (typically He) and expanded through a nozzle into a vacuum. The cool, high-density helium flowing over the target serves as a buffer gas in which clusters of the target material form, thermalize to near room temperature and then cool to a few K.

**(f) Wet Chemical Synthesis (Colloidal Chemical Synthesis)**

Wet chemical synthesis technique is the one of the most widely used method to prepare metal/metal-oxides/semiconductor nanoparticles among various other synthetic techniques which falls in bottom up approaches. The advantage of using this technique is mainly due to its following properties [7];

1. Simple Technique
2. Inexpensive, less instruments are used as compared to many other physical methods
3. Low temperature synthesis, all nanoparticles can be easily prepared below 350 °C
4. Doping of foreign atoms (ion) possible during synthesis
5. Large quantum yield can be obtained
6. Variety of sizes and shapes can be tuned
7. Nanoparticles are obtained in the form of liquid which can be converted into dry powder after drying
8. Self assembly or patterning is possible

The basic principle of nanoparticles preparation by this technique involves the (bio)chemical reduction of metal/semiconductor/metal oxide salts, photochemical and electrochemical pathways, or sonochemical/ thermal decomposition of metallic compounds in aqueous or organic solvents in the presence of a variety of additives such as surfactants, ligands, polymers, etc which are commonly termed as capping.
agents [17]. The shapes, distribution and sizes of thus nanoparticles strongly depends on the various reaction parameters such as temperature, time, pH, type of capping/reducing agents, solvent medium etc. Therefore by controlling these parameters, one can successfully prepare the desired nanoparticles. Although, nanoparticles prepared by this technique may appear complex one but by understanding the nucleation and growth of particles, one can easily form monodispersed nanoparticles of different shapes and sizes.

Some of the metals, metal oxides and semiconductor nanoparticles synthesized by wet chemical synthesis route are listed below;

(1) Highly stable gold nanoparticles by tri sodium citrate reduction where nanoparticles are stabilized by repulsive Coulomb repulsion. Various other metals such as silver, copper, palladium etc. are synthesized similarly using appropriate precursors, temperature, pH and duration of synthesis.

(2) Sulphide semiconductors like CdS and ZnS and PbS etc. by co-precipitation technique.

(3) TiO$_2$ nanoparticles by ammonium hydroxide reduction.

In addition to these, many other nanoparticles prepared chemically using various capping molecules and different reducing agents can be seen in literature [7, 17-19].

(g) Electrochemical Synthesis

Electric discharge technique is one of the classical colloid preparation methods. The electrochemical method of nanoparticle preparation induces chemical reactions in an electrolyte solution via the use of an applied voltage. This technique has the advantage of being compatible with a wide variety of materials. Metallic nanoparticles have been prepared by electrochemical pathways with and without the use of nanoporous hard templates. Electrochemical deposition is carried out by
coating one face of the membrane with a metal film, which acts as a cathode for electroplating. Appropriate metal ions are then electrochemically reduced and deposited within the pores of the template membranes. The size and morphology of the nanoparticles can be controlled by varying the electrodeposition parameters, such as potential, number of coulombs passed, temperature, deposition time, appropriate surfactants, or soluble polymers, etc., during the deposition process. Finally, the nanoparticles are released from the template by physicochemical means. Recently, Zhu et al. reported triangular plate-shaped gold nanoparticles prepared by electrochemical method [17]. Upon aging, these nano has turned from triangular nanoplates to rhombic nanostructures.

2.2.3. Preparation of Nanoparticles for the Present Study

In the present work, metals, metal oxides, ionic and graphene nanoparticles composites are synthesized using two well established synthetic routes known as wet chemical synthesis and electrochemical synthesis methods. Both the chemical routes of synthesis have advantages of being low cost, easy synthesis, requirement of low cost instruments and greener chemistry. Brief synthesis procedures for all the nanoparticles prepared in our case are given in their respective chapters.

2.3. Characterization Techniques

The prepared nanoparticles in this entire thesis work are characterized by various characterization techniques like optical absorption spectroscopy, fluorescence spectroscopy, FTIR spectroscopy (FTIR), X-ray powder diffraction (XRD), differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and electrical conductivity measurements.
(Keithley source meter, 2636A). A concise discussion on these techniques is provided here.

2.3.1. **Optical Absorption Spectroscopy**

Spectrophotometry is the quantitative technique used for the measurement of transmittance or reflectance of solutions, transparent or opaque solids, or gases. The technique uses photometers that can measure a light beam's intensity as a function of its color (wavelength). It is used in various scientific fields including semiconductors, laser and optical manufacturing industries, printing, forensic examination and in laboratories for the study of chemical substances. Depending on the control or calibration, a spectrophotometer is able to determine the optical spectrum of the substance under investigation.

Currently, UV-Visible absorption instruments come in two configurations: single beam and double beam. In a conventional single-beam spectrophotometer, the blank and the sample are measured consecutively, with an interval of several seconds for a single wavelength measurement and up to several minutes for a full spectrum measurement. The lamp drifts in this case result in significant errors over long time intervals. In order to compensate for these changes in lamp intensity between measurements on blank and sample cuvettes, the dual-beam spectrophotometer was developed. In this configuration, spectrophotometer consists of an additional chopper placed in the optical path, near the light source which switches the light path between a reference optical path and a sample optical path to the detector. The advantage of using chopper is that it rotates with such a speed that the alternate measurements of blank and sample occur several times per second which corrects medium and long-term changes in lamp intensity Compared with single-beam designs, dual-beam instruments contain more optical components that reduce throughput and sensitivity.
Figure 2.5 shows a typical block diagram of UV-absorption spectrometer which consists of a light source, sample holder, a diffraction grating in a monochromator or a prism and a detector. The routinely used radiation sources in spectrophotometer is a Tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm), Xenon arc lamp, (160-2,000 nm) and more recently, light emitting diodes (LED) for the visible wavelengths are also employed. The detector is typically a photomultiplier tube, a photodiode, a charge-coupled device (CCD). Single photodiode detectors and photomultiplier tubes are used with scanning monochromators to filter the light so that single wavelength beam of light reaches the detector at one time. The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength. Fixed monochromators are used with CCDs and photodiode arrays. As both of these devices consist of many detectors grouped into one or two dimensional arrays, they are able to collect light of different wavelengths on different pixels simultaneously.
UV/Vis spectrophotometry is well capable to examine liquid samples, although the absorbance of gases and even of solids can also be measured. In order to measure the optical spectrum, samples are typically placed in cuvettes (transparent cell of rectangular shape with an internal width of 1 cm) which are made of high quality fused silica or quartz glass as these are transparent throughout the UV, visible and near infrared regions.

In present work all the measurements were carried out using double beam instrument Analytikjeena specord 200 plus. The absorption spectrum were recorded in the range 190 to 1100 nm with scan speed 20 nm/min and slit width 2 nm for various colloids of our gold nanoparticles, silver nanoparticles, silver loaded graphene oxide, titanium oxide, copper iodide and aluminum oxide to study temporal evolution of the nanoparticles and surface plasmon resonance phenomenon. The obtained absorption curves were further used for appropriate band gap calculation of nanoparticles using Tauc’s equation [20]

2.3.2. Fluorescence Spectroscopy

Fluorescence spectroscopy is a precise, inexpensive and easily mastered quantitative analytical technique that occurs only when a molecule absorbs light photons from the UV-visible light spectrum (200-900 nm) and then rapidly emits characteristic photons as it returns to it’s ground state. In general, all chemical compounds absorb energy at particular wavelength which causes excitation of electrons bound in the molecule between discrete electronic energy states. The condition for a molecule to make an electronic transition is that the absorbed energy must be equivalent to the difference between the initial electronic state and a high-energy state. This value is always constant and is termed as the excitation wavelength which represents characteristic of the molecular structure. If conditions permit, an excited molecule returns back to its
ground state by emitting energy in terms of heat and/or energy quanta such as photons. The emission energy or wavelength of these quanta are also equivalent to the difference between two discrete energy states and are characteristic of the molecular structure. Fluorescence is observed only when emitted photons return to its initial state in less than $10^{-9}$ sec. In this process, the emitted energy is always less than that of excitation energy as some energy within the molecule is lost through heat or vibration, i.e., the emission wavelength is always longer than the excitation wavelength. The difference between the excitation and emission wavelengths is called the Stokes shift. Fluorescent compounds or fluorophors can be identified and quantified on the basis of their excitation and emission properties. A typical Jablonski diagram representing the emission processes is given in figure 2.6.

Figure 2.7 represents a schematic diagram of a typical fluorimeter consisting of a light source, excitation monochromator, sample holder, emission monochromator

![Figure 2.6: Schematic presentation representing Jablonski diagram for emission processes.](image)
and recorder. The light source produces light photons over a broad energy spectrum, typically ranging from 200 to 900 nm. Photons impinge on the excitation monochromator, which selectively transmits light in a narrow range centered about the specified excitation wavelength. The transmitted light passes through adjustable slits that control magnitude and resolution by further limiting the range of transmitted light. The filtered light passes into the sample cell causing fluorescent emission by fluorophors within the sample. Emitted light enters the emission monochromator, which is positioned at a 90° angle from the excitation light path to eliminate background signal and minimize the noise due to stray light. Again, emitted light is transmitted in a narrow range centered about the specified emission wavelength and exits through adjustable slits, finally entering the photomultiplier tube (PMT). The signal is amplified and creates a voltage that is proportional to the measured emitted intensity. Noise in the counting process arises primarily in the PMT. Therefore, spectral resolution and signal to noise is directly related to the selected slit widths.

![Block diagram illustrating working steps of fluorescence spectrophotometer.](image-url)
Since source intensity may vary over time, most research grade fluorimeters are equipped with an additional “reference PMT” which measures a fraction of the source output just before it enters the excitation monochromator and used to ratio the signal from the sample PMT. Not all fluorimeters are configured as described above. Some instruments employ sets of fixed band pass filters rather than variable monochromators. Each filter can transmit only a selected range of wavelengths. Units are usually limited to 5 to 8 filters and are therefore less flexible. Fiber optics are also employed for “surface readers”, to transmit light from the excitation monochrometers to the sample surface and then transport emitted light to the emission monochrometers. This setup has the advantage of speed, but has the disadvantages of increased signal to noise, which increase the probability of quenching.

In the present work, fluorescence study was done on gold nanoparticles using Horiba Scientific Fluoromax-4 Spectrofluorometer.

2.3.3. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a simple thermodynamical technique used to measure thermal properties of materials to establish a connection between temperature and specific physical properties of substances. The technique was first developed by E. S. Watson and M. J. O’Neill in 1962 and it was introduced commercially in 1963 [21]. The first successful adiabatic differential scanning calorimeter was developed by P. L. Privalov and D. R. Monaseldze in 1964, it was used for the analysis of bio-compounds [22]. The technique has advantages over many other analytical techniques such as gas-liquid chromatography, mass and UV-visible spectroscopy which requires the sample either in volatile form or in solution forms, this may destroy the original structure of the matrix containing sample. DSC is the only method in which sample is used in its original form for the analysis and
provides direct determination of the enthalpy associated with the process of interest as a function of temperature. This helps in the determination of various properties of material including specific heat, glass transition, phase changes, melting point, crystallization and product stability of organic, inorganic and polymeric materials. The technique is frequently used in chemistry, biochemistry, cell biology, biotechnology, pharmacology and recently, in nanoscience to measure thermodynamic properties of the biomolecules and nano-sized materials.

DSC is based on a simple principle of physical/phase transformation of a material as a function of regulated temperature. During a change in temperature, DSC measures a heat content, which is radiated or absorbed excessively by the sample on the basis of a temperature difference between the sample and a reference material, the later is inert in the temperature range. Based on the mechanism of operation, DSC can be classified into two types: heat-flux DSC and power-compensated DSC [23]. The difference between the two lies in their arrangement of keeping sample and reference pans within the instrument. In a heat flux DSC, the sample material enclosed in a pan and an empty reference pan both are placed in same thermoelectric disk surrounded by a furnace whereas in case of power-compensated DSC, pans are kept in separate furnaces which are heated by separate heaters. In both the cases, furnaces are heated at a linear heating rate in order to maintain the constant temperature of the sample and reference, and the heat is transferred to the sample and reference pan through the thermoelectric disk. However, owing to the heat capacity (Cp) of the sample, there would be a temperature difference between the sample and reference pans, which is measured by area thermocouples and the consequent heat flow is determined by the thermal equivalent of Ohm’s law: \( q = \frac{\Delta T}{R} \), where \( q \) is “sample heat flow”, \( \Delta T \) is ‘temperature difference between sample and reference’ and \( R \) is ‘resistance of
thermoelectric disk’. In a power-compensated DSC, the sample and reference pans are placed in separate furnaces heated by separate heaters. The sample and reference are maintained at the same temperature and the difference in thermal power required to maintain them at the same temperature is measured and plotted as a function of temperature or time. In our case, these measurements were done using power-compensated TA instruments model DSC Q 20.

2.3.4. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a simple analytical technique used to determine material’s thermal stability and its fraction of volatile components by measuring the weight change as a function of temperature or time in a controlled atmosphere. The measurement is normally carried out in air or in an inert atmosphere such as Helium, or Argon, or in a lean oxygen atmosphere (1 to 5% O$_2$ in N$_2$ or He) to slow down oxidation. The weight loss of the material results from different processes such as water desorption, or from chemical reactions is recorded that release gases with the change in temperature. In contrast, some materials can gain weight by reacting with the surrounding atmosphere in the test environment. The technique is commonly employed in research and testing to determine characteristics of materials such as a general material, polymers, degradation temperatures, absorbed moisture content, the level of inorganic and organic components, decomposition points of explosives and solvent residues.

A number of thermogravimetric methods, such as, thermogravimetry, thermovolumetry and differential thermal analysis (DTA) are being employed on an increasingly large scale in the investigation of chemical reactions in the liquid as well as solid states at elevated temperatures. Thermogravimetric Analysis (TGA) is finding increasing utility in investigations of the pyrolysis and combustion behavior of
materials. A continuous measurement of change in either of the physical properties such as weight, volume, heat capacity etc. is involved in these techniques.

TGA instruments can be divided into two general types; vertical and horizontal balance. Vertical balance instruments have a specimen pan hanging from the balance (TA Instruments, etc) or located above the balance on a sample stem (Netzsch). It is necessary to calibrate these instruments in order to compensate for buoyancy effects due to the variation in the density of the purge gas with temperature as well as the type of gas. Vertical balance instruments generally do not have reference pan and are incapable of true DTA or DSC measurements (Netzsch being an exception) [24]. Horizontal balance instruments (TA, Perkin Elmer, etc.) normally have two pans (sample and reference) and can perform DTA and DSC measurements. They are considered free from buoyancy effects but require calibration to compensate for differential thermal expansion of balance arms. One common instrument for general purpose use is, the TA Instruments Model SDT Q600. A general schematic diagram of thermal gravimetric analytical instrument is given in figure 2.8. A sample size of 2-4 mg is sufficient to produce good data, heating rates as high as 100 °C/min and as low as 1 °C/min can be used for analysis.

Such analysis relies on a high degree of precision in three measurements, namely weight, temperature and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required. To determine composition and purity one must take the mass of the substance in the mixture by using thermal gravimetric analysis.
2.3.5. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared (FTIR) spectroscopy is non-destructive widely used analytical tool used for determining qualitative and quantitative features of IR-active molecules in organic or inorganic materials precisely [25, 26]. The technique is applicable for all the three phases of a matter including solids, liquids and gases which provide unique spectrum corresponding to each sample under examination. Every IR spectrum represents the fingerprint of the corresponding molecule which cannot be matched with any other spectrum. It is this feature which makes IR spectroscopy useful for (1) identification of unknown materials, (2) determination of quality of sample and (3) determination of amount of components in the mixture. Moreover, the technique has advantage in terms of its sensitivity, speed and operating conditions. The infrared spectrum broadly classified into three main regions of electromagnetic spectrum: the far infrared (<400 cm\(^{-1}\)), the mid-infrared (4000–400 cm\(^{-1}\)) and the near-infrared (13000–4000 cm\(^{-1}\)).
It is the only analytical method which provides both ambient temperature operation and the ability to directly monitor vibration of the functional groups which characterize molecular structure and govern the course of chemical reactions. Many infrared applications employ the mid-infrared region which includes the frequencies corresponding to fundamental vibrations of virtually all the functional groups of organic molecules. The mid-infrared spectrum (4000–400 cm\(^{-1}\)) can be approximately divided into four regions and the nature of a group frequency may generally be determined by the region in which it is located. The regions are generalized as follows: the X–H stretching region (4000–2500 cm\(^{-1}\)), the triple-bond region (2500–2000 cm\(^{-1}\)), the double-bond region (2000–1500 cm\(^{-1}\)) and the fingerprint region (1500–600 cm\(^{-1}\)). The fundamental vibrations in the 4000–2500 cm\(^{-1}\) region are generally due to O–H, C–H and N–H stretching. O–H stretching produces a broad band that occurs in the range 3700–3600 cm\(^{-1}\). N–H stretching is usually observed between 3400 and 3300 cm\(^{-1}\). C–H stretching bands from aliphatic compounds occur in the range 3000–2850 cm\(^{-1}\). If the C–H bond is adjacent to a double bond or aromatic ring, the C–H stretching wave number increases and absorbs between 3100 and 3000 cm\(^{-1}\). Triple-bond stretching absorptions fall in the 2500–2000 cm\(^{-1}\) region because of the high force constants of the bonds. C≡C bonds absorb between 2300 and 2050 cm\(^{-1}\), while the nitrile group (C≡N) occurs between 2300 and 2200 cm\(^{-1}\). These groups may be distinguished since C≡C stretching is normally very weak, while C≡N stretching is of medium intensity. These are the most common absorptions in this region. Thus, each band in an infrared spectrum can be assigned to a particular deformation of the molecule, the movement of a group of atoms, or the bending or stretching of a particular bond. This is possible for many bands, particularly stretching vibrations of multiple bonds that are ‘well behaved’. However, many vibrations are
not so well behaved and may vary by hundreds of wave numbers, even for similar molecules. This applies to the bending and skeletal vibrations, which absorb in the 1500–650 cm\(^{-1}\) region, for which small steric or electronic effects in the molecule lead to large shifts. A spectrum of a molecule may have more than hundred absorption bands, but there is no need to assign the vast majority. Each IR spectrum can be regarded as a ‘fingerprint’ of the molecule under study.

The spectrum can be recorded using FTIR spectrometer whose basic components are shown schematically in figure 2.9. The radiation emerging from the source (Globar or Nernst) is passed through an interferometer to the sample before reaching a detector (deuterium tryglycine sulfate (DTGS)). Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to digital form by an analog-to-digital converter and transferred to the computer for Fourier-transformation. The most common interferometer used in FTIR spectrometry is a Michelson interferometer, which consists of two perpendicularly plane mirrors, one of which can travel in a direction perpendicular to the plane. A semi-reflecting film, the *beamsplitter*, bisects the planes of these two mirrors. The beam splitter material has to be chosen according to the region to be examined. Materials such as germanium or iron oxide are coated on an ‘infrared-transparent’ substrate such as potassium bromide or caesium iodide to produce beamsplitters for the mid- or near-infrared regions. Thin organic films such as poly (ethylene terephthalate) are used in the far-infrared region. If a collimated beam of monochromatic radiation of wavelength \(\lambda\) (cm) is passed into an ideal beam splitter, 50% of the incident radiation will be reflected to one of the mirrors while 50% will be transmitted to the other mirror. The two beams are reflected from these mirrors, returning to the beam splitter where they recombine and interfere.
In the present study, FTIR spectrum is recorded for AuNPs, graphene-AgNPs composites, using Nicolet 5700 FT-IR spectrometer in transmission mode with KBr window, the spectral range 400-4000 cm\(^{-1}\) and linear velocity 0.632 cm/s. All the spectra were recorded in their powder form with wavelength precision of 0.01 cm\(^{-1}\).

Figure 2.9: Block diagram illustrating working steps of measuring FTIR spectrum.

2.3.6. X-ray Powder Diffraction (XRD)

X-ray diffraction (XRD) is one of the most important non contact and non-destructive techniques to analyze all kind of matters- ranging from fluids to powder and crystals. From research to production and engineering, XRD is an indispensible method for structural materials characterization and quality control which make use of Debye-Scherrer method. The technique provides a unique diffraction pattern corresponding to each crystalline substance including nanomaterials which helps to study detailed structural properties such as lattice parameter, strain, grain size, phase composition, preferred orientation (Laue), order-disorder transformation and thermal expansion. XRD technique is quite effective only for those nanomaterials which are having grain size ranging from 2 nm to 100 nm [7]. The principle of XRD is based on a very
simple phenomenon of diffraction whereby monochromatic X-ray beam is elastically scattered by electrons of atoms. It is this scattered X-ray beam which provides useful information about atomic arrangement. At advanced level even a diffracted beam can also be computed only when Bragg’s law or Laue equation is satisfied by such scattering. These diffracted waves from different atomic planes can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore provide us the information regarding the distribution of atoms in a material.

Except for single crystalline nanoparticles, the randomly oriented crystals in nanoparticles cause broadening of the diffraction peaks. This has been attributed to the absence of total constructive and destructive interferences of X-rays in a finite-sized lattice [27]. The effect becomes more pronounced when the crystallite sizes are of the order of a few nanometers. Moreover, inhomogeneous lattice strains and structural faults also lead to broadening of peaks in diffraction patterns. Detailed analytical procedures for XRD patterns for polycrystalline and amorphous materials have been discussed by Klug and Alexander [28]. The simplest and most widely used method for estimating the crystallite size is from the full width at half maximum (FWHM) of a diffraction peak using the Scherrer equation, which is given by

$$ D = \frac{k \lambda}{\beta \cos \theta} $$

(2.1)

where $D$ is the crystallite size, $\lambda$ is the wavelength of the X-ray used, $\beta$ is the FWHM, $\theta$ is the diffraction angle and $k$ is Scherrer constant [27-29]. The major assumptions are that the sample is free from residual strain and has a narrow grain size distribution.
X-ray patterns can be recorded by different methods, these are powder method, single crystal method and Laue method. Among these methods, powder method is perhaps the most widely used X-ray diffraction technique for characterizing materials. A simple schematic diagram of X-ray diffractometer is given in figure 2.10. As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied. The technique is also used widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials). The term “powder” really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d spacings in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. For example, the diffraction lines of graphite would be different from diamond even though they both are made of carbon atoms. This phase identification is important because the material properties are highly dependent on structure.
In the present study, X-ray diffraction patterns were recorded using Philips X’pert powder diffractometer using CuKα X-ray source having wavelength 1.54056 Å. The patterns were recorded both in powder form as well as in film form coated on glass slide.

2.3.7. Scanning and Transmission Electron Microscopies (SEM and TEM)

Electron microscopy is an analytical technique used to know information regarding morphology, crystalline structure and orientation of material making up a sample. The technique uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimen. This signal after interacting with solid provides a 2-D image of material, data are collected over a selected area of surface of sample. Area ranging from 1 to 5 microns in width can be imaged in scanning mode whereas magnification ranging from 10x to approx 500,000x with special resolution of 1 nm to 100 nm can be achieved. The highest received resolution using conventional SEM < 30 kV in 2009 is 0.4 nm [30]. Microscopic images are formed when an accelerated beam of electrons with an effective wavelength of 0.1 nm, carrying significant amount of kinetic energy (2 to 200 keV) is incident on the surface of the solid, this energy is dissipated as a variety of signal produced by electron-ion (sample) interactions. These signals include secondary electrons, backscattered electrons and diffracted backscattered electrons that are used for elemental analysis. The various possible interactions of high energy electron beam with sample are shown systematically in figure 2.11. Among these various possible interactions, backscattered radiation provides important information in case of SEM analysis.

Figure 2.12 represents schematic ray diagram of scanning electron microscope and transmission electron microscope. The major component of electron microscope include: vacuum system, electron beam generation system (electron Gun), electron
Figure 2.11: The various possible interactions of high energy electron beam with sample.

beam manipulation system (electromagnetic lenses), beam specimen interaction system, detector, signal processing system and display and recording system.

The environment within the column is an extremely important part of the electron microscope. Without sufficient vacuum in the SEM, the electron beam cannot be generated nor controlled. The vacuum of the SEM needs to be below $10^{-4}$ torr to operate, although most microscopes operate at $10^{-6}$ torr or greater vacuum. The higher the vacuum (the lower the pressure), the better the microscope will function. The electron gun is the beam generation system of an electron microscope. The electron gun is composed of three components; (1) a filament made of tungsten wire, lanthanum hydroxide crystal, or cerium hydroxide, (2) a grid cap that controls the flow of electrons and (3) a positive charged anode plate that attracts and accelerate the electrons down to the column to specimen. Depending upon the type of sample and
Figure 2.12: Schematic diagram of Scanning electron microscope (SEM) and transmission electron microscope (TEM) representing all its components.
resolution needed, SEM can be operated at different voltages. This usually ranges from 0.1 to 40 kV. Higher the voltage, better the resolution. The electron beam generated in this system further travel down to the column of electron beam manipulation consisting of electromagnetic lens known as condenser lenses. These lenses reduce the size of beam’s cross over spot. Signal detection begins when electron beam coming from manipulation system interact with specimen. The various possible interactions are shown in figure 2.11. The majority of work done on SEM is for topographical information which is mainly provided by secondary electrons that are produced by interaction of beam with the specimen. The manipulation of this signal begins with the amplifier in the detector and ends with the image on the viewing screen. The signal in SEM is converted to an image viewed on a cathode ray tube. The brightness, contrast, resolution, magnification, depth of the field, noise and composition determine the quality of a micrograph is taken care by display and recording system [31].

Since, the electrons in scanning electron microscopy penetrate into the sample within a small depth, so that it is suitable for surface topology, for every kind of samples (metals, ceramics, glass, dust, hair, teeth, bones, minerals, wood, paper, plastics, polymers, etc). It can also be used for chemical composition of the sample’s surface since the brightness of the image formed by backscattered electrons is increasing with the atomic number of the elements. It means that the regions of the sample consisting of light elements (low atomic numbers) appear dark on the screen and heavy elements appear bright. The main constraints of SEM are; (1) limited information about resolution and crystallography, (2) samples must be conductive and (3) materials with atomic number smaller than the carbon cannot be detected. These all constraints can be resolved by transmission electron microscopy.
Transmission Electron Microscopy (TEM) is a technique where an electron beam interacts and passes through a specimen. The electrons are emitted by a source are focused and magnified by a system of magnetic lenses. The geometry of TEM is similar to SEM seen in figure 2.12. The electron beam is confined by the two condenser lenses which also control the brightness of the beam, passes the condenser aperture and “hits” the sample surface. The electrons that are elastically scattered consist the transmitted beams, which pass through the objective lens. The objective lens forms the image display and the following apertures, the objective and selected area aperture are used to choose the elastically scattered electrons that will form the image of the sample. Finally the beam goes to the magnifying system that is consisted of three lenses, the first and second intermediate lenses which control the magnification of the image and the projector lens. The formed image is shown either on a fluorescent screen or on monitor or both and is printed on a photographic film. The best resolution obtained in this case to 1.7 Å (point to point) and 1.4 Å line to line with maximum possible magnification of 15,00,500x and an operating voltage of 300 kV.

2.3.8. Energy Dispersive Spectrometer (EDS)

One of the instruments most commonly used in conjunction with the SEM is the Energy Dispersive X-ray Spectrometer (EDS or EDX). It is an analytical technique makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis [32]. The technique is sometimes also referred as energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA). Combining the EDS system with the SEM allows the identification at microstructural level of compositional gradients at grain boundaries, second phases, impurities, inclusions and small amounts of material etc.
In the scanning mode, the SEM/EDS unit can be used to produce maps of element location, concentration and distribution. The general schematic diagram of EDS is given in figure 2.13. The X-ray spectrometer converts an X-ray photon into an electrical pulse with specific characteristics of amplitude and width. After analysis of the electrical pulses, the output is a histogram of the X-ray energy received by the detector, with individual “peaks”, the heights of which are proportional to the amount of a particular element in the specimen being analyzed.

The locations of the peaks are directly related to the particular X-ray “fingerprint” of the elements present. Consequently, the presence of a peak, its height and several other factors, allow the analyst to identify elements within a sample. With the use of appropriate standards and software, quantitative analysis of all elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for “light” elements (Z < 10). Since the sensitivity (ability to detect the presence of an element above background noise) of the EDS is very poor...
for low atomic weight elements, elements lighter than carbon cannot be detected. Further, resolution limits of the X-ray energy levels may affect the positive identification of certain elements (i.e., molybdenum and sulfur) due to overlapping energy slots. Quantitative analysis is usually limited to flat, polished specimens. Unusual geometries, such as fracture surfaces, individual particles and films on substrates may be analyzed, but with considerably greater uncertainty.

2.3.9. X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical and electronic state of the elements that exists within the material [33]. XPS was developed by Heinrich Rudolf Hertz in 1887 but could not explain its basic working principle, which was later explained in 1905 by Albert Einstein. After this, K. Siegbahn and his research group developed several significant improvements in the equipment and in 1954 they recorded first high-energy-resolution XPS spectrum of cleaved sodium chloride [33, 34]. In 1969, Siegbahn and a small group of engineers at Hewlett-Packard developed the first commercial monochromatic XPS instrument for which he was awarded with a Nobel Prize in Physics in 1981 [35]. The technique is based on the principle of photoelectric effect. The spectrum is obtained by irradiating the material with a monochromatic beam of X-ray while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 layers (depth between 10 – 100 Å) of the material. This ejection of electron provides the useful information about the material under investigation. The electron binding energy of each of the emitted electrons can be determined by using Ernest Rutherford equation:

\[ E_{Binding} = E_{Photon} - (E_{Kinetic} + \phi) \]  

\[ ... (2.2) \]
Where $E_{\text{Binding}}$ is the binding energy (BE) of the electron, $E_{\text{Photon}}$ is the energy of the X-rays being used, $E_{\text{Kinetic}}$ is the kinetic energy of the electron as measured by the instrument and $\phi$ is the work function dependent on both the spectrometer and the material. A ray diagram representing X-ray photoelectron spectroscopy principle is shown in figure 2.14.

Figure 2.14: A ray diagram representing XPS principle.

Figure 2.15 shows a simple schematic diagram of X-ray photoelectron spectrometer. It consists of X-ray source, sample and an electron energy analyzer. In common practice AlK$_\alpha$ (1486.6 eV) or MgK$_\alpha$ (1253.6 eV) radiations are used to irradiate the sample whereas Concentric Hemispherical Analyzer (CHA) is used to analyze the energy of photoelectron ejected from the sample. Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exists in or on the surface of the material under examination. These characteristic spectral peaks correspond to the electron
configuration of the electron within the atoms. The number of detected electrons in each of the characteristic peaks is directly related to the amount of element within the XPS sample. XPS detects only those electrons which reach the detector but as the detectors in XPS instruments are typically one meter away from the material irradiated with X-rays, photoelectrons can undergo inelastic collisions, recombination, excitation etc. [35]. In order to overcome these difficulties, XPS detectors must be operated under ultra high vacuum conditions.

In principle, XPS detects all the elements except H or He because of small cross section of H due to small size whereas, He is incapable to form solid compounds and its 1s orbital has tiny cross section for photoemission. XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, papers, wood, plant parts, teeth, bones, biomaterials, viscous oils, glues and many others [34]. A few specially designed XPS instruments can also analyze volatile liquids, or materials at pressures of roughly 1 torr, but these are relatively few of these types.

Figure 2.15: Block Diagram of X-ray photoelectron spectrometer.
2.3.10. Electrical Conductivity Measurements

The charge transport properties of fabricated memory devices were studied using our home built two probe set up, as shown in figure 2.16. The setup consists of a base plate made up of copper and two connected electrode terminals with tungsten tips having diameter 0.05 mm. These two electrodes serve as cathode and anode which are further connected to BNC connectors and are extended to Keithley source meter 2636 A for current-voltage measurements. All the electrical measurements were recorded in cyclic voltage sweep mode in an order sequence of zero to positive, positive to zero, zero to negative and negative to zero with a scan step voltage of 0.04 V, stable wait between two reading of 50 m sec and after every reading, a wait of 20 m sec. The reproducibility is checked at more than 10 different places for all the prepared devices.

Figure 2.16: A simple diagram illustrating homemade two electrode conductivity setup for room temperature charge transport (I-V) measurements. 1. tungsten electrodes, 2. contacts to outer electrodes, 3. acrylic base of setup, 4. sample and 5. aluminum contacts.
References


