1.1 Introduction to Nanoscience and Nanobiotechnology

In the last decade we assisted to the massive advancement of “nanomaterials” in materials science. Nanotechnology, nanoscience, nanostructure, nanoparticles are now the most widely used words in scientific literature. In other words, Nanotechnology deals with small structures and small-sized materials of dimensions in the range of few nanometers to less than 100 nanometers. The unit of nanometer derives its prefix nano from a Greek word meaning extremely small. One nanometer (10⁻⁹ of a meter) is roughly the length occupied by five silicon or ten hydrogen atoms aligned in a line. In comparison, the hydrogen atom is about 0.1 nm, a virus may be about 100 nm, and a red blood corpuscle approximately 7,000 nm in diameter and an average human hair is 10,000 nm wide. Any object possessing any one dimension between 1-100 nm can be defined as “nanomaterial”. When we deal with nanostructures, the ratio between surface (or interface) and inner atoms becomes significant. This means that the quantistic effect and surface atoms with partial coordination influences strongly the physical and chemical behavior of the nanomaterials with that of the bulk solids. Nanomaterials are very attractive for possible machine, which will be able to travel through the human body and repair damaged tissues or supercomputers which small enough to fit in shirt pocket. However, nanostructure materials have potentials application in many other areas, such as biological detection, controlled drug delivery, low-threshold laser, optical filters, and also sensors, among others[1-2]. Nanobiotechnology is a young and rapidly evolving field of research in nanoscience and it is an interdisciplinary area which complies advances in Science and Engineering. Nanobiotechnology is a field that concerns the utilization of biological system optimized through evolution, such as cells, cellular
components, nucleic acid, and proteins to facilitate functional nanostructured and mesoscopic architecture comprised of organic and inorganic materials [2]. Biofunctionlization of nanoparticles is an important contribution of present day nanobiotechnology. On the other hand, bionanotechnology generally refers to the study of how the goals of nanotechnology can be guided by studying how biological "machines" work and adapting these biological motifs into improving existing nanotechnologies or creating new ones [2].

1.2 Overview on Gold and Silver nanoparticles

1.2.1 Early history of nanoparticles

The solutions of liquid gold have been first mentioned by Egyptian and Chinese authors around 5th century BC. In fact, ancient believed in their metaphysical and healing power. For all the middle ages gold colloids have also been used in medicine believing in their curative properties for various diseases. In 15th century Italian artisans in Gubbio and Deruta were able to prepare brightly colored porcelain, called luster as shown in figure 1.1, containing Silver and Silver-copper alloy nanoparticles. The technique was developed in the ancient world during the 9th century and exploited the reducing obtained heating dried genista upto 600 °C to obtain nanoparticles by reducing metal oxides or metal previously deposed on the ceramic piece from a vinegar solution [3,4].

Metal nanoparticles have been used a long time ago e.g. Damascus steel which used to make sword [5-7]. Even though, nanoparticles have been used a long time ago, but nobody realized that it reached nanoparticles scale. Blade made from Damascus steel produce from about 500 AD in Damascus [8].
Figure 1.1: Luster dated 1525 from the workshop of Maestro Giorgio Andreoli in Gubbio, representing Hercules slays the centaur Nessus (left) and Armorial dish: Supper at the House of Simon the Pharisee (right).

It becomes renowned because the extreme strength, sharpness, resilience and the beauty of their characteristic surface pattern [9-10]. The fascinating legend story it can cut clean through rock and still remain sharp enough to cut through a silk scarf dropped on the blade. Many scientists try to reveal this special properties and encounter multi walled carbon nanotube in steel (MWNTs) [11].

Colloidal gold and silver have been used since ancient Roman times to color glass of intense shades of yellow, red or mauve, depending on the concentration of two metals. A fine example is Glass Lycurgus Cup in British museum dated 4\textsuperscript{th} century AD which has unique color. The famous Glass Lycurgus Cup from the Romans times (4\textsuperscript{th} century AD) contains silver and gold nanoparticles in approximate ratio 7:3 which have size diameter about 70 nm [12-13]. The presence of these metal nanoparticles gives special color display for the glass. When viewed in reflected light, for example in daylight, it appears green. However, when a light is shone into the cup and transmitted through the glass, it appears red. This glass can still be seen in British museum shown in figure 1.2.
The first scientific study of metal nanoparticles is dated back to the seminal work of Michael Faraday around 1850 [14]. Faraday was the first to recognize the red color of the gold colloid was due to minute size of the Au particles and that one could turn the preparation blue by adding salt to the solution. He obtained gold colloids reducing H\text{AuCl}_4 by phosphorus, following a procedure already reported by Paracelsus in 16\textsuperscript{th} century about the preparation of “Aurum Potabile” and based on two phase water/CS\textsubscript{2} reaction. Some of the Michael Faraday's preparations are still preserved today in the Faraday Museum in London [15]. Other synthetic methods for colloidal metal particles have been developed in the early 20\textsuperscript{th} century, both physical or chemical, until the fundamental work of Turkevitch in 1951[16]. He started a systematic study of AuNP synthesis with various methods by using Transmission Electron Microscopy (TEM) analysis to optimize the preparative conditions until obtaining what is commonly known as the Turkevitch method.
There is wide application of nanoparticles in present era due to their unique physical and chemical properties. Hence the era of nanotechnology is started and the pioneer idea of nanotechnology was first highlighted by Nobel laureate Richard P. Feynman, in his famous lecture at the California institute of technology (Caltech), 29th December 1959. Richard Feynman proposed a variety of potential nanomachines, which could be engineered to a higher level of functional efficiency then currently available manufactured devices by exploiting changes in behavior of matter at the nanometer length scale. In 1970’s Norio Taniguchi first defined the term nanotechnology. According to him, Nanotechnology is mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule. And in 1980’s another technologist, K. Eric Drexler promoted technological significance in nanoscale and published a famous book entitled "Nanosystems: Molecular Machinery Manufacturing and Computation".

1.2.2 Nanoparticles and their properties

A nanoparticle is by definition a particle where all the three dimensions are in nanometer scale. Nanoparticles are known to exist in diverse shapes such as spherical, triangular, cubical, pentagonal, rod-shaped, shells, ellipsoidal and so forth. Nanoparticles by themselves and when used as building blocks to construct complex nanostructures such as nanochains, nanowires, nanoclusters and nanoaggregates find use in a wide variety of applications in the fields of electronics, chemistry, biotechnology and medicine, just to mention few: For example, gold nanoparticles are being used to enhance electroluminescence and quantum efficiency in organic light emitting diodes [17];
palladium and platinum nanoparticles are used as efficient catalysts [18]; glucose sensors are developed based on AgNP [19]; and iron oxide NP are used as contrast agents in diagnosing cancer in Magnetic Resonance Imaging (MRI) [20]. Nanoparticles contain small enough a number of constituent atoms or molecules that they differ from the properties inherent in their bulk counterparts. However, they contain a high enough a number of constituent atoms or molecules that they cannot be treated as an isolated group of atoms or molecules (Figure 1.3). Therefore, nanoparticles exhibit electronic, optical, magnetic and chemical properties that are very different from both the bulk and the constituent atoms or molecules. For example, the striking colors of metallic NP solutions (such as Au and Ag) are due to the red shift of the Plasmon band to visible frequencies, unlike that for bulk metals where the Plasmon absorption is in the UV region (Plasmon is a quantum of collective oscillation of free electrons in the metals). This red shift of the Plasmon occurs due to the quantum confinement of electrons in the NP, since the mean free path of electrons is greater than the nanoparticle.
Size [21, 22]. Additionally, the optical properties of nanoparticles depend significantly on their size and shape as well as on the dielectric constant of the surrounding medium. For example, in spherical AuNP, the Plasmon absorption red shifts with increasing diameter of the nanoparticle [23]. Likewise, quantum dots (semiconductor nanoparticles such as CdSe and CdTe) exhibit red shift in their band gap (emission) as their size increases [24, 25]. AgNP of spherical, pentagonal and triangular shape appear blue, green and red respectively under a dark field microscope, suggesting strong correlation between optical property and shape of the nanoparticles [26]. Au nanorods exhibit different optical properties than their spherical counterparts. Au nanorods show two Plasmon resonances, one a transverse Plasmon at 520 nm and the other a longitudinal Plasmon at longer wavelengths. Unlike the transverse Plasmon mode, the wavelength of the longitudinal Plasmon mode increases with increasing aspect ratio of the nanorods [27]. Additionally, AuNPs dispersed in different solvents exhibit Plasmon absorption at different wavelengths suggesting the effect of surrounding media [28]. Nanoparticles have large surface to volume ratio, thus surface related phenomena/properties are drastically affected with slight modification of size, shape and surrounding media of nanoparticles. Therefore, the optical properties of desired nanoparticles depending on application can be tuned by generating the nanoparticles of definite size and shape in preferred media and henceforth, develop new effective nanomaterials and nanodevices. This unique size of nanoparticles facilitates development of nanodevices/nanosensors that can travel into cells to probe proteins (enzymes and receptors) or the DNA inside the cell or outside the cell. Consequently, the first step involved in developing nanodevices/nanosensors is to produce hybrid nanoparticles: nanoparticles labeled with molecules that can investigate
or target the specific cellular entities. Though a plethora of hybrid nanoparticles labeled with peptides and proteins have been produced and investigated for their potential applications in biological field [29-31], gold hybrid nanoparticles specifically have emerged as favorites in biomedical applications owing to their exciting chemical, electronic and optical properties along with their biocompatibility, dimensions and ease of characterization. These properties are discussed in the following section.

1.1.3 Physical and Chemical properties of Gold and Silver nanoparticles

In this panorama AuNP and AgNP are playing a protagonist role. The reason for AuNP and AgNP success lies in a favorable combination of physical-chemical properties and advances in chemical synthesis. The main characteristic of AuNP and AgNP is the Surface Plasmon Absorption (SPA), which has $10^5$ – $10^6$ larger extinction cross sections than ordinary molecular chromophores and is also more intense than that of other metal nanoparticles, due to the weak coupling to interband transition. The frequency of gold and silver SPA can also be turned from visible to near infrared acting on shape, size or nanoparticles assembly. Furthermore AuNP and AgNP have high chemical stability and photostability and especially AuNP are nontoxic for living organisms. Their physicochemical stability, bright color and biocompatibility explain why traces of AuNP and AgNP utilization are dated back to the 5th century B.C.in china and Egypt.

Chemical properties: Au and Ag are known for being generally inert and, especially gold, for not being attacked by O$_2$ to a significant extent. This makes AuNP and AgNP stable in ordinary conditions [32]. Both Au and Ag are reactive with sulphur, in particular bulk silver often undergoes to tanning due to the formation of an Ag$_2$S surface layer. In case of organic thiols, ligation to nanoparticles surface is particularly effective for the
contemporary presence of a σ type bound, in which sulphur is the electron density donor and the metal atom is the acceptor, Plus a π type bound, in which metal electron are partially delocalized in molecular orbitals formed between the filled d orbitals of the metal and the empty d orbitals of sulphur [32]. Other than thiols and disulphides, also alchilamine and phenilphosphine have been successfully used for AuNP and AgNP ligation[3,8].

Solutions of AgNP have applications as bactericidal agents because the Ag+ ions interfere with bacteria metabolism. Since AgNP are exposed to a certain extent of surface oxidation by atmospheric O₂, Ag sols can release Ag+ ions with concentration sufficient to act as bactericides [32].

High surface to bulk atoms ratio and overall chemical inertness confers catalytic activity to AuNP and AgNP. AgNP are suitable for oxidation of organic compounds, CO, NO and degradation of aromatic and chlorine derivatives. AuNP were active in the oxidation of CO and H₂ as well as in the reduction of NO and in a wide range of other typical catalytic reactions [3, 33].

Physical properties: Since solid to liquid transition begins at interfaces, a well-known feature of nanometric particles is the lower melting temperature with respect to the bulk. For instance gold undergoes a decrease in melting temperature of about 400 °C going from 20 nm to 5 nm particles and about 50 °C going from bulk to 20 nm particles [34]. Thermal conductivity is enhanced for small particles due to higher surface to volume ratio. While phonons energy become higher for very small particles and Raman spectroscopy can be used to measure cluster Size [3].
AuNP and AgNP exhibit strong absorption of electromagnetic waves in the visible range due to Surface Plasmon Resonance (SPR). SPR is caused due to collective oscillations of the conduction electrons of nanoparticles upon irradiation with visible light. The SPR is highly influenced by shape and size of the nanoparticles. Recently, the absorption spectra of individual AgNP were correlated with their size and shape determined by Transmission Electron Microscopy (TEM) [32]. The results indicate that spherical and roughly spherical nanoparticles absorb in the blue region of the spectrum, while decahedral nanoparticles and particles with triangular cross-sections absorb in the green and red part of the spectrum, respectively. The width and position of the SPR not only depends on the particle size as suggested earlier, but also on the chemical properties of the nanocrystalline surface, referred to as chemical interface damping [33]. Quantum size effects also enhance the deviation of conductivity from the usual ohmic behavior in metal nanoparticles [34, 35]. A comparative description of physical and chemical properties of Gold and Silver are discussed in Table 1.1.
Table 1.1. Physical and chemical properties of Bulk, Au and Ag nanoparticles

<table>
<thead>
<tr>
<th>Bulk properties</th>
<th>Silver</th>
<th>Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic Configuration</td>
<td>[Kr] 4d^{10} 5s^{1}</td>
<td>[Xe] 5d^{10} 6s^{1}</td>
</tr>
<tr>
<td>Atomic Number- Weight</td>
<td>47-107.87 u.a.</td>
<td>79-196.97 u.a.</td>
</tr>
<tr>
<td>Lattice</td>
<td>f.c.c.</td>
<td>f.c.c.</td>
</tr>
<tr>
<td>Density</td>
<td>10.50 g cm^{-3}</td>
<td>19.28 g cm^{-3}</td>
</tr>
<tr>
<td>Electronic density</td>
<td>5.86 $10^{28}$ m^{-3}</td>
<td>5.90 $10^{28}$ m^{-3}</td>
</tr>
<tr>
<td>Fermi Energy</td>
<td>5.48 eV</td>
<td>5.51 eV</td>
</tr>
<tr>
<td>Ionization Energy</td>
<td>7.57 eV</td>
<td>9.22 eV</td>
</tr>
<tr>
<td>Electric Resistivity</td>
<td>1.61 $10^{-6}$ Ω cm</td>
<td>2.20 $10^{-6}$ Ω cm</td>
</tr>
<tr>
<td>Melting Temperature</td>
<td>1235 K</td>
<td>1338K</td>
</tr>
<tr>
<td>Boiling Temperature</td>
<td>2435 K</td>
<td>3243K</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>4.29 W cm^{-1}K^{-1}</td>
<td>3.17W cm^{-1}K^{-1}</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>23.350 j mol^{-1}K^{-1}</td>
<td>25.418 j mol^{-1}K^{-1}</td>
</tr>
<tr>
<td>(25°C)</td>
<td></td>
<td>(25°C)</td>
</tr>
<tr>
<td>Standard Potential</td>
<td>+ 0.80 V</td>
<td>+ 1.69 V</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>1.9</td>
<td>2.4</td>
</tr>
</tbody>
</table>

1.3 Synthesis of metallic nanoparticles

Nanoparticles are being viewed as fundamental building blocks of nanotechnology. They are the starting point for preparing many nanostructured materials and devices. Their synthesis is an important component of rapidly growing research efforts in nanoscale Science and Engineering. The nanoparticles of a wide range of materials can be prepared by a number of methods.
Generally, the manufacturing techniques fall under two categories: ‘bottom-up’ and ‘top-down’ approach. The bottom-up approach refers to the build-up of a material from the bottom, i.e. atom-by-atom, molecule-by-molecule or cluster-by-cluster. The colloidal dispersion is a good example of bottom up approach in the synthesis of nanoparticles. Nanolithography and nanomanipulation techniques are also a bottom-up approach. Top-down approach involves starting with a block bulk material and designing or milling it down to desire shape. This technique is similar to the approach used by the semiconductor industry in forming devices, utilizing pattern formation (such as electron beam lithography). Both approaches play very important roles in modern industry and most likely in nanotechnology as well. There are advantages and disadvantages in both approaches. The main challenge for top-down approach is the creation of increasingly small structure with sufficient accuracy whereas in bottom-up approach, the main challenge is to make structure large enough and of sufficient quality to be of useful as materials[36]. Bottom-up approach promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition, and better short and long range ordering. This is because the bottom-up approach is driven mainly by the reduction of Gibbs free energy, so that nanostructures and materials such produced are in a state closer to a thermodynamic equilibrium state. On the contrary, top-down approach most likely introduces internal stress, in addition to surface defects.

Many colloidal nanoparticles synthesis have been known [37-39], but recent worked is dedicated to nanoparticles syntheses specifically for the construction of devices and nanostructures. These particles may consist of a particular material, be of a particular size, or have specialized surface functionality. It has even become possible to have some
degree of control over the nanoparticles shape [40, 41]. Stability of nanoparticles is also become one of the point. And synthesis sometimes also involves the use of a stabilizing agent, which associates with the surface of the particle, provides charge or solubility properties to keep the nanoparticles suspended, and thereby prevents their aggregation. And another very important method for metal nanoparticles synthesis is “green synthesis” i.e. use of biological entities to produce nanoparticles and the advantage is its ecofriendly behavior and biocompatibility hence a great deal of interest has been focused on ecofriendly benign nanomaterials in the few past years. The growing interest by nature’s effectiveness and the selectivity of the biological systems much efforts has been developed for synthesize inorganic nanoparticles with different shape and size. Microorganisms, including viruses, bacteria, and fungi and plants has been used for synthesis of gold and silver nanoparticles and our research groups has published good publication on biosynthesis of metal nanoparticles [42-43]. Another interesting area of research is the interaction between inorganic nanoparticles and biological structures which is most exciting area of research and the crux of my research work [44-45].

1.4 Physicochemical characterization of nanomaterials

The nanomaterials can be characterized using various techniques, which provide important information for the understanding of different physicochemical features of materials. Some of the most extensively used techniques for characterization of Nanomaterial’s are as follows:

(a) X-ray diffraction (XRD),

(b) Scanning electron microscopy (SEM),

(c) Transmission electron microscopy (TEM).
(d) Atomic force microscopy (AFM)

(e) Optical Spectroscopy

(i) Ultraviolet-visible (UV-Vis) spectroscopy,

(ii) Fluorescence spectroscopy,

(iii) Fourier transform infrared (FTIR) spectroscopy,

(f) Thermal Analysis (TA)

(a) X-Ray Diffraction

X-ray diffraction is a very important technique that has long been used to determine the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, defects, etc. [46]. The X-ray diffraction patterns are obtained by measurement of the angles at which an X-ray beam is diffracted by the crystalline phases in the specimen. Bragg’s equation relates the distance between two (h, k, l) planes (d) and the angle of diffraction (2θ) as: \( n\lambda = 2dsin\theta \), where, \( \lambda \) = wavelength of X-rays, \( n \) = an integer known as the order of reflection (h, k and l represent Miller indices of the respective planes) [47]. From the diffraction patterns, the uniqueness of nanocrystal structure, phase purity, degree of crystallinity and unit cell parameters of the nanocrystalline materials can be determined. X-ray diffraction technique is nondestructive and does not require elaborate sample preparation, which partly explains the wide use of XRD methods in material characterization.

X-ray diffraction broadening analysis has been widely used to determine the crystal size of nanoscale materials. The average size of the nanoparticles can be estimated using the Debye–Scherrer equation: \( D = k\lambda / \beta \cos\theta \), equation (1) where \( D \) = thickness of
the nanocrystal, \( k \) is a constant, \( \lambda = \) wavelength of X-rays, \( \beta = \) width at half maxima of (111) reflection at Bragg’s angle \( 2\theta \) [48].

**(b) Scanning Electron Microscopy**

Scanning Electron Microscopy (SEM) is one of the most widely used techniques for characterization of nanomaterials and nanostructures. The resolution of the SEM approaches a few nanometers, and the instruments can operate at magnifications that are easily adjusted from \(~10\) to over \(300,000\). This technique provides not only topographical information like optical microscopes do, but also information of chemical composition near the surface. A scanning electron microscope can generate an electron beam scanning back and forth over a solid sample. The interaction between the beam and the sample produces different types of signals providing detailed information about the surface structure and morphology of the sample. When an electron from the beam encounters a nucleus in the sample, the resultant coulombic attraction leads to a deflection in the electron's path, known as Rutherford elastic scattering. A fraction of these electrons will be completely backscattered, reemerging from the incident surface of the sample. Since
the scattering angle depends on the atomic number of the nucleus, the primary electrons arriving at a given detector position can be used to produce images containing topological and compositional information [49]. The high-energy incident electrons can also interact with the loosely bound conduction band electrons in the sample. However, the amount of energy given to these secondary electrons as a result of the interactions is small, and so they have a very limited range in the sample. Hence, only those secondary electrons that are produced within a very short distance from the surface are able to escape from the sample. As a result, high-resolution topographical images can be obtained in this detection mode [50].

(c) Transmission Electron Microscopy

Transmission electron microscopy (TEM) is typically used for high resolution imaging of thin films of a solid sample for nanostructural and compositional analysis. The technique involves: (i) irradiation of a very thin sample by a high-energy electron beam, which is diffracted by the lattices of a crystalline or semicrystalline material and propagated along different directions, (ii) imaging and angular distribution analysis of the
forward-scattered electrons (unlike SEM where backscattered electrons are detected), and (iii) energy analysis of the emitted X-rays [51]. The topographic information obtained by TEM in the vicinity of atomic resolution can be utilized for structural characterization and identification of various phases of nanomaterials, viz., hexagonal, cubic or lamellar [52]. One shortcoming of TEM is that the electron scattering information in a TEM image originates from a three-dimensional sample, but is projected onto a two-dimensional detector. Therefore, structural information along the electron beam direction is superimposed at the image plane. Selected area diffraction (SAD) offers a unique advantage to determine the crystal structure of individual nanomaterials, such as nanocrystals and nanorods, and the crystal structures of different parts of the sample. In SAD, the condenser lens is defocused to produce parallel illumination at the specimen and a selected-area aperture is used to limit the diffracting volume. SAD patterns are often used to determine the Bravais lattices and lattice parameters of crystalline materials by the same procedure used in XRD [53].

In addition to the capability of structural characterization and chemical analyses, TEM has been also explored for the other applications in nanotechnology. Examples include the determination of melting points of nanocrystals, in which, an electron beam is used to heat up the nanocrystals and the melting points are determined by the disappearance of electron diffraction [54]. Another example is the measurement of mechanical and electrical properties of individual nanowires and nanotubes [55].
(d) Atomic Force Microscopy (AFM)

The AFM consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke’s law. Depending on the situation, forces that are measured in AFM include mechanical contact force, Van der waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (Magnetic Force Microscopy), solvation forces etc. Typically, the deflection is measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. By monitoring the motion of the probe as it is scanned across the surface, a three dimensional image of the surface is constructed.
(e) Optical Spectroscopy

Optical spectroscopy has been widely used for the characterization of nanomaterials and the techniques can be generally categorized into two groups: absorption (UV-Vis) and emission (fluorescence) and vibrational (infrared) spectroscopy. The former determines the electronic structures of atoms, ions, molecules or crystals through exciting electrons from the ground to excited states (absorption) and relaxing from the excited to ground states (emission). The vibrational technique involves the interactions of photons with species in a sample that results in energy transfer to or from the sample via vibrational excitation or de-excitation. The vibrational frequencies provide the information of chemical bonds in the detecting samples.

(i) UV-Vis Spectroscopy

It deals with the study of electronic transitions between orbitals or bands of atoms, ions or molecules in gaseous, liquid and solid state [56]. The metallic nanoparticles are known to exhibit different characteristic colors. Mie was the first to explain the origin of this color theoretically in 1908 by solving Maxwell’s equation for the absorption and scattering of electromagnetic radiation by small metallic particles [57]. This absorption of electromagnetic radiation by metallic nanoparticles originates from the coherent oscillation of the valence band electrons induced by an interaction with the electromagnetic field [58]. These resonances are known as surface Plasmon, which occur only in the case of nanoparticles and not in the case of bulk metallic particles [59]. Hence, UV-Vis can be utilized to study the unique optical properties of nanoparticles [60].
(ii) Fluorescence Spectroscopy

In this technique, light of some wavelength is directed onto a specimen, prompting the transition of electron from the ground to excited state, which then undergoes a non-radiative internal relaxation and the excited electron moves to a more stable excited level. After a characteristic lifetime in the excited state, the electron returns to the ground state by emitting the characteristic wavelength in the form of light. This emitted energy can be used to provide qualitative and sometime quantitative information about chemical composition, structure, impurities, kinetic process and energy transfer.

(iii) Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy deals with the vibration of chemical bonds in a molecule at various frequencies depending on the elements and types of bonds. After absorbing electromagnetic radiation, the frequency of vibration of a bond increases leading to transition between ground state and several excited states. These absorption frequencies represent excitations of vibrations of the chemical bonds and thus are specific to the type of bond and the group of atoms involved in the vibration. The energy corresponding to these frequencies correspond to the infrared region (4000–400 cm\(^{-1}\)) of the electromagnetic spectrum. The term Fourier transform (FT) refers to a recent development in the manner in which the data are collected and converted from an interference pattern to an infrared absorption spectrum that is like a molecular "fingerprint"[61]. The FTIR measurement can be utilized to study the presence of protein molecule in the solution, as the FTIR spectra in the 1400–1700 cm\(^{-1}\) region provides information about the presence of –CO- and –NH- groups [62]. Attenuated total reflection (ATR) is a sampling technique used in conjunction with infrared spectroscopy.
which enables samples to be examined directly in the solid or liquid state without further preparation. ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the sample. The penetration depth into the sample is typically between 0.5 and 2 micrometres, with the exact value being determined by the wavelength of light, the angle of incidence and the indices of refraction for the ATR crystal and the medium being probed. The number of reflections may be varied by varying the angle of incidence. The beam is then collected by a detector as it exits the crystal. Most modern infrared spectrometers can be converted to characterize samples via ATR by mounting the ATR accessory in the spectrometer's sample compartment. The accessibility of ATR-FTIR has led to substantial use by the scientific community.

(f) **Thermal Analysis (TA)**

Thermal analysis (TA) comprises a group of techniques in which a physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme. In differential thermal analysis, the temperature difference that develops between a sample and an inert reference material is measured, when both are subjected to identical heat–treatments. Both thermogravimetry and evolved–gas analysis are techniques which rely on samples which decompose at elevated temperatures. The former monitors changes in the mass of the specimen on heating, whereas the latter is based on the gases evolved on heating the sample. Electrical
conductivity measurements can be related to changes in the defect density of materials or to study phase transitions.

### 1.5 Applications of nanomaterials

Nanotechnology offers an extremely broad range of potential applications from electronics, optical communications and biological systems to new smart materials. The wide range of applications shown by nanostructures and nanomaterials are due to (i) the unusual physical properties exhibited by nanosized materials, e.g. AuNP used as an inorganic dye for coloration of glass, (ii) the large surface area, such as AuNP supported on metal oxide are used as low temperature catalyst and Application of Nanomaterial’s nanoparticles for various sensors, and (iii) small size. For many applications, new materials and new properties are introduced. For example, various organic molecules are incorporated into electronic devices [63]. Some of the applications of nanostructures and nanomaterials are highlighted in the following:

#### 1.5.1 Molecular electronic and nanoelectronics

The last few years have been witnessing a tremendous progress in the molecular electronic and nanoelectronics [64]. For example, AuNP function as a carrier by attaching various functional organic molecules or biocomponents [65]. AuNP can also be used as a mediator to connect different functionalities together in the construction of nanoscale electronics for the applications of sensors and detectors [66].

#### 1.5.2 Nanorobots

Promising applications of nanotechnology in medical science also referred to as nanomedicine, have fascinated a lot. One of the attractive applications of nanomedicine is
the creation of nanoscale devices for improved therapy and diagnostics. Such nanoscale devices are known as nanorobot [67]. These nanorobots have the potential to serve as vehicles for delivery of therapeutic agents and detectors against early disease and perhaps may repair metabolic or genetic defects.

1.5.3 Biological applications

It has been well known that living cells are the best examples of machines that operate at the nano level and perform a number of jobs ranging from generation of energy to extraction of targeted materials at very high efficiency. The ribosome, histones and chromatin, the Golgi apparatus, the interior structure of mitochondrion, the photosynthetic reaction center, and the fabulous ATPases that power the cell are all nanostructures, which work quite efficiently [68]. Ancient Indian medicinal system, Ayurveda has been using gold in different formulations for curing acute diseases such as rheumatoid Arthritis [69]. With present day understanding of nanoscience, one can unambiguously get enlightened that these formulations contained gold nanoparticles. Thus, the fusion of ancient wisdom and present understanding of nanoscience can imparts more light on future development of medical sciences.

The area of research in the field of nanotechnology is as diverse as physics, chemistry, materials science, microbiology, biochemistry and also molecular biology. The interface of nanotechnology in combination with biotechnology and biomedical engineering is emerging by the use of nanoscale structures in diagnosis, gene sequencing, and drug delivery. Nanotechnology holds promise for enabling us to learn more about the detailed operation of individual cells and neurons, which could help us to re-engineer living systems [70]. One of the important biological applications of colloidal nanocrystals
is molecular recognition [71] certain biological molecules can recognize and bind to other molecules with extremely high selectivity and specificity. For molecular recognition application, antibodies and oligonucleotides are widely used as receptors. If, for example, a virus enters an organism, antibodies will recognize the virus as a hostile intruder, or antigen, and bind to it in such a way that the virus can be destroyed by other parts of the immune system [71]. Antibodies and oligonucleotides are typically attached to the surface of nanocrystals via (i) thiol-gold bonds to gold nanoparticles [72] (ii) covalents linkage to silanized nanocrystals with bifunctional crosslinker molecules [73] and (iii) a biotin-avidin linkage, where avidin is adsorbed on the particle surface [74]. Nanocrystals thus conjugated or attached to a receptor molecules can be directed to bind to positions where ligand molecules are present, which ‘fit’ the molecular recognition of the receptor[75]. This facilitates a set of applications including molecular labeling [76, 77]. For example, the change in color of AuNP from ruby-red to blue due to aggregation has been exploited for the development of very sensitive colorimetric methods of DNA analysis [78]. Other potential biological applications of nanomaterials include the use of colloidal semiconductor nanocrystals as fluorescent probes to label cells & chemical libraries and the use of nanostructured materials as artificial bones [79].

The primary goal of this research was to synthesize new types of metal nanoparticles, evaluate their fundamental optical properties, and develop biological applications and offer advantages in terms of sensitivity, selectivity, and multiplexing capabilities. Nanoparticles are particularly important because of their chemical stability and fascinating optical properties that can be tailored through control over particle size, shape.
References


   (b) Birks, L. S., Friedman, H., *J. Appl. Phys.*., 17, 1946, 687.


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