1.0 INTRODUCTION:

Over the last few years, the scientific and engineering communities have been witnessing an impressive progress in the field of nanoscience and nanotechnology. 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. Fig. 1.0.1 shows the comparison between the cells and their components according to their size. In this the hydrogen atom shows the size is about 0.1 nanometer, a virus may be about 100 nanometers, a red blood corpuscle approximately 7,000 nanometers in diameter and an average human hair is 10,000 nanometer wide, which gives an idea about how small is nanometer.

Fig. 1.0.1 Relative sizes of cells and their components
1.1 WHAT IS NANOSCIENCE AND NANOTECHNOLOGY?

"Nanoscience" is the study of phenomena exhibited by materials at atomic and molecular level of dimensions ranging from a few nanometers to less than 100 nanometers. In chemistry, this range of sizes has been associated with colloids, micelles, polymer molecules and similar structures such as very large molecules, or aggregates of many molecules. In physics and electrical engineering, nanoscience is most often associated with quantum behavior and the behavior of electrons in nanoscale structures. Biology and biochemistry have also been deeply associated with nanoscience as components of the cell; most interesting structures of biology such as DNA, RNA and sub cellular organelles can be considered as nanostructures [1].

"Nanotechnology" is the implication of science to control matter at the molecular level. At this level, the properties are significantly different from that of the bulk materials. It is also referred to as the term for designing, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale [2]. In other words, nanoscience and nanotechnology is a field that focuses on:

(i) The development of synthetic methods and surface analytical tools for building structures and materials.
(ii) To understand the change in chemical and physical properties due to miniaturization and
(iii) The use of such properties in the development of novel and functional materials and devices [3].

Nanoscience offers an exciting possibility to study a state of matter, which is intermediate between bulk and isolated atoms or molecules as well as the effect of spatial confinement on electron behavior. It also provides an opportunity to explore the problems related to surface or interface because of their interfacial nature [4].
Nano, the Greek word for ‘dwarf’ indicates one billionth of something. In 1974 the word nanotechnology was introduced by Taniguchi [5] Japan. Nanotechnology refers to the technology of rearranging and processing of atoms and molecules to fabricate materials to nano specifications. The matter of nanoscale shows different behavior in its chemical, biological, electrical, magnetic and other properties than its bulk form. This technique is gaining more importance in chemical field because of faster, cheaper and better products could be made available through the synthesis of nanoparticles.

In 1915 Scientist Ostwald entitled his famous book on colloid chemistry, “The world of neglected dimension.” implies a science in its own right. The opinion was correct because physical and chemical properties of colloids depend on their size and shape.

Nanostructured materials have been the subject of intensive research due to their fundamental significance for addressing some basic issues of the quantum size effect by reduction of the number of free electrons as well as their potential applications as advanced materials with intriguing chemical, magnetic, optical, thermal and catalytic properties [6-9]. Nanotechnology is currently employed as a tool to explore the darkest avenues of medical sciences in several ways like imaging [10], sensing [11], targeted drug delivery [12], gene delivery systems [13] and artificial implants [14]. Hence nanosized organic and inorganic particles are finding increasing attention in medical applications [15] due to their amenability to biological fictionalization. The novelty of nanoparticles lies in their unique properties which as a result of their small size differ largely from bulk properties [16]. In view of these special properties many investigations into their potential applications have been carried out such as heterogeneous catalyst [17], nonlinear optical devices [18], gas sensors [19], etc.
1.2 EMERGENCE OF NANOTECHNOLOGY:

The first so-called scientific study of nanoparticles took place in 1831, when Michael Faraday investigated the ruby red colloids of gold and made public that the color was due to the small size of the metal particles. Gold and silver have found their way into glasses for over 2000 years as nanoparticles.

![Image](image1.png)

**Figure 1.2.1** The Lycurgus cup dates from the fourth century AD. In reflected light (daylight) the glass appears to be green, but when light is transmitted from the inside of the vessel it is red (by Courtesy of the British Museum)

They have most frequently been employed as colorants, particularly for church windows. Until 1959, nobody had thought of using atoms and molecules for fabricating devices. It was first revisioned by Nobel Laureate Physicist Richard Feynman [20] in his lecture at American Physical Society (1959) predicted that “There is plenty of room at the bottom.” where he speculated on the possibility and potential of nanosized materials and recognized the existence of nanostructure in biological system. Various nanomaterials like nanocrystals, clusters, nanowires, nanotubes, nanoporous solids, 2D array of nanoparticles, surfaces and thin films, 3D structures nanoparticles also exist in clusters called quantum dots, Q particles, coulomb islands etc. The clusters are too large to be treated as molecules and too small to be considered as bulk materials.
The new found ability to see and manipulate molecules has enabled scientists to emulate nature by building materials from simple atomic level constituents instead from top down approach. The primary driving force for miniaturization at that time came from the electronics industry which aimed to develop tools to create smaller electronic devices on silicon chips of 40-70 nm dimensions. The use of this term, “nanotechnology” has been growing to mean a whole range of tiny technologies from material sciences where designing of new materials for wide ranging applications are concerned; to electronics where memories, computers, components and semiconductors are concerned; to biotechnology where diagnostics and new drug delivery systems are concerned [21].

1.3 CONSEQUENCES OF MINIATURIZATION:

Every substance regardless of composition exhibits new properties when the size is reduced to less than 100nm. The electronic structure of a nanocrystal critically depends on its size. For small particles, the electronic energy levels are not continuous as in bulk materials but discrete. This arises primarily due to confinement of electrons within particles of dimension smaller than the bulk electron delocalization length; this process is termed as quantum confinement [22]. Nobel metal and semiconductor nanoparticles are unique examples of this principle. The average electronic energy level spacing of successive quantum levels also known as Kubo gap, (Kubo gap $\delta = \frac{4E_f}{3n}$, where $E_f$ is the Fermi energy of the bulk material and $n$ is total number of valence electrons in the nanocrystal), can be tuned to make a system either metallic and non-metallic. For example, for an individual silver nanoparticle of 3 nm diameter containing approximately $10^3$ silver atoms, the value of $\delta$ would be 5-10 meV. Since the thermal energy at room temperature, $kT \approx 25$meV (k is Boltzmann’s constant), the 3 nm particle would be metallic ($kT>\delta$). However, at low temperatures, the level spacing especially in small particles may become comparable to $kT$, rendering them nonmetallic
Thus the properties such as electrical conductivity and magnetic susceptibility exhibit quantum size effects due to the presence of the Kubo gap in individual nanoparticles.

1.4 QUANTUM SIZE EFFECT:

The physical properties of nanomaterials are attracting increasing interest because they differ significantly from bulk properties as a result of surface or quantum size effect [24]. However, these properties are highly dependent on the size of the particles and not on interactions between their surface, ligands, contaminants or a support. This therefore requires the need to control precisely the size distribution of the particles and their surface state.

If a metal with bulk properties is reduced in size in the valence band, the conduction band decreases respectively to such an extent that electronic properties change dramatically. When a metal particle size is decreased, the typical bulk properties like conductivity and magnetism begin to disappear or in other words a quasi-continuous density of states is replaced by a discrete energy level structure and band gap increases. The average energy level separation is comparable to or larger than the experimental energy.

The situation in a small molecular cluster is simple. Three metal atoms for instance form energetically well defined bonding and antibonding molecular orbitals.

The quantum size effect arises due to the dramatic reduction in a number of electrons [25]. This occurs most drastically in low band gap materials where the effective mass of electrons is small. This phenomenon is observed when a colloidal particle becomes comparable to de Broglie wavelength of charge carrier.
Recently Volokotin [26] et. al. clarified that quantum size strongly affects the thermodynamics of the metal nanoparticles. It has been found from the spectral studies that the binding energies of metal nanoparticles consisting of fewer atoms than 1000 vary periodically due to quantum size effect. The phenomenon was first reported by Knight [27] et. al. in an experiment, involving sodium nanoparticles. This shows discontinuous existence of nanoparticles having certain stable structures.

Different methods of organizing quantum dot super lattices of metals and semiconductors have received significant interest in recent times. The tailoring of particles sizes and the inter particle separation can in principle cause unique magnetic, optical and electronic behavior [28-32]. For example, several nanocluster assemblies organized in different length scales have been found to be promising due to their potential application in diverse areas such as opto-electronic devices, single electron transistors and chemical sensors [31-36].
Recently much attention has been paid to the synthesis and characterization of bimetallic nanoparticles due to their catalytic, electronic, optical, structural and thermal properties [37-42] and subsequent technological applications as catalyst, sensors, nanoelectronic devices [43-48] and biosensors [49]. The properties and applicability of nanoparticles not only depend upon their size and length but also on the combination of component metals (composition) and their fine structure as either an alloy or core shell structures. Bimetallic nanoparticles with well defined alloy structures of noble metals like Pt-Ru, Pt-Mo, Au-Ag, provide practical examples for the influence of metals, compositions and their structure on their catalytic properties [50-54].

Thus the properties of traditional materials change at nano level due to the quantum effect and the behavior of surfaces start to dominate the behavior of bulk materials. The optical, electrical, mechanical, magnetic and chemical properties can be systematically manipulated by adjusting the size, composition and shape of the nanoscale materials. Nanomaterials have tremendous potential applications in catalysis [55], photocatalysis [56], optoelectronics [57], single-electron transistors, light emitters [58], nonlinear optical devices [59], magnetic resonance imaging enhancement [60], cell labelling [61], cell tracking [62], in vivo imaging [63] and DNA detection [64]. The wide range of applications shown by nanomaterials is mainly due to (i) large surface area and (ii) small size. Electron transport manifested in phenomena like Coloumb blockade [65] as well as the catalytic and thermodynamic properties of structures can be tailored when one can rationally design materials on this length scale. Therefore, analytical tools and synthetic methods allow one to control composition and design on this nanometer range and will undoubtedly yield important advances in almost all fields of science.
1.5 PROPERTIES OF METAL AND METAL OXIDE NANOPARTICLES:

Nanoparticles are defined very generally as objects whose three spatial dimensions are confined to less than 100nm, intermediately between the molecular state and the bulk state. These objects show chemical and physical properties different from those of the bulk materials. It has even been suggested that they are a new state of matter.

The physical and chemical properties of metal nanoparticles depend upon several factors such as (i) large surface atom, (ii) large surface energy, (iii) spatial confinement (iv) particle size, structure, organization of the particles and their dispersity. Numerous studies [66-70] on size and shape dependent properties have been carried out in the last two decades. The size dependent physical and chemical properties have been reviewed extensively by many scientists [71-73]. The few properties of nanomaterials are discussed in the following:

a) Optical Property:

The modified electronic configuration of a confined crystal has great effects on the optical transitions between different energy levels. Furthermore, the scattering of light from tiny particles is affected by the modified electron cloud which influences the dielectric function of the material [74]. Metal nanoparticles [75] which are of particular interest in this work, are optically active in the visible range of the spectrum. For last few decades, metallic nanoparticles have fascinated researchers due to their colorful colloidal solutions. Mie was the first to explain the red color of gold nanoparticles in 1908 by solving Maxwell’s equation for an electromagnetic light wave interacting with small metallic spheres. The color exhibited by metallic nanoparticles is due to the coherent excitation of all the “free” electrons within the conduction band leading to an in-phase oscillation and is known as ‘Surface Plasmon Resonance’. A colloidal solution of noble–metal nanoclusters has an intense color. When the crystal size becomes
smaller than the wavelength of the visible light, nanoparticles partially transmit the light which results in changes of the color of the dispersion. The reason for this modification is the presence of a strong optical absorption in the visible region arising from the surface plasmon excitation in response to the external electromagnetic field. As nanocluster size decreases, there is a dramatic increase in the surface plasmon resonance band width, accompanied by a shift in the resonance position (generally a red-shift). As an example, gold particles of 30-500nm in size changes their color from blue to red. For the smaller Au nanoparticles, there is broad surface plasma absorption between the green and yellow wavelengths allowing only red light to be transmitted. This is one reason for the typical red color of stained glasses containing a dispersion of gold nanoparticles [76-79].

Unique optical property of nanomaterials may also be due to quantum size effect which arises primarily because of confinement of electrons within particles of dimension smaller than the bulk electron delocalization length. This effect is more pronounced for semiconductor nanoparticle, where the band gap increases with a decreasing size. The same quantum size effect is also shown by metal nanoparticles when the particle size is >2nm.

b) Magnetic Property:

Magnetic properties of nanostructured materials are distinctly different from that of bulk materials. Ferromagnetic particles become unstable when the particle size reduces below a certain size as the increase in surface energy provides a sufficient energy for domains to spontaneously switch polarization directions and become paramagnetic. But this transformed paramagnetism behaves differently from the conventional paramagnetism and thus is referred to as superparamagnetism [80]. In other words, ferromagnetism of bulk materials disappears and gets transferred to superparamagnetism in the nanoscale due to the high surface energy.
The magnetic properties of nanoparticles [81] are different from those of bulk materials for sizes in the range of a few interatomic distances to about one micrometer. The magnetic properties of 3d-metal clusters (like Fe and Co) differ significantly from the bulk [82] and depend strongly on the particle size, the material they are embedded in and their coverage. Early experiments at the beginning of the 1990s on small magnetic clusters in the gas phase [83-86] have shown that the total magnetic moment depends on the size of the cluster; in particular it is a function of the number of atoms. Both orbital and spin moments on the surface of tiny magnetic nanoparticles are strongly enhanced. The spin moment then decreases to the bulk value as the size of the particle exceeds a few nanometers [87]. This is a consequence of the fact that a high number of atoms with lower coordination number sit on the surface and therefore exhibit uncompensated distributions of magnetic moments (spins). This effect is very strong only for tiny clusters of less than 1000 atoms but in some cases it is present for larger particles also [82]. Interesting applications of small magnetic particles are in stable colloidal suspensions known as ferrofluids. Other systems like an array of FePt particles on a substrate are interesting candidates for high-density magnetic storage media [88].

c) Mechanical Properties:

The mechanical properties of nanomaterials increase with the decrease in size. Most of the studies have been focused on the mechanical properties of one dimensional structure such as nanowire. The enhanced mechanical strength of nanowires or nanorods is ascribed to the high internal perfection of the nanowires. Generally, imperfections such as dislocations, micro-twins, impurities, etc. In crystals are highly energetic and should be eliminated from the perfect crystal structures. The smaller the cross-section of nanowires, the less is the probability of finding in it any imperfections as nanoscale dimension makes the elimination of such imperfections possible. The
clusters interact fully with one another, yet the effect of cluster size is still important. Clusters of metals and ceramics in the size range of 5 - 25 nm have been consolidated to form ultrafine grained polycrystals that have mechanical properties remarkably different from and frequently better than those of their conventional coarse grained counterparts [89].

**d) Thermal Properties:**

As compared to the study of other well known properties of the nanomaterials, this study has seen slower progress. This is partially due to the difficulties of experimentally measuring and controlling the thermal transport in nanoscale dimensions. Atomic Force Microscope (AFM) has been introduced to measure the thermal transport of nanostructures with nanometer scale having a high special resolution providing for a promising way to probe the thermal properties with nanostructures. Recent advances in experiments have showed that certain nanomaterials have extraordinary thermal properties as compared to their macroscopic counterparts. This is attributed due to several factors such as the small size, the special shape; the large interfaces modified the thermal properties of the nanomaterials rendering them to quite different behavior. As the dimension goes down to nanoscales, the size of the nanomaterial is comparable to the wavelength and the mean free path of the photons. Due to the photon confinement and quantization of photon transport, the phototransfer within the materials will be changed significantly resulting in modified thermal properties. For e.g. nanowires [91] from silicon have a much smaller thermal conductivity as compared to bulk silicon. Carbon nanotubes [92] have extreme high thermal conductivity in axial direction leaving high anisotropy in the heat transports in the materials. Metal and semiconductor nanoparticles are found to have significantly lower melting point or phase transition temperature as compared to their bulk counterparts. The lowering of the melting points is observed when the particle size is >100 nm and is attributed
to increase in surface energy with a reduction of size. The decrease in the phase transition temperature can be ascribed to the changes in the ratio of surface energy to volume energy as a function of size.

e) Melting Point:
According to theoretical approach the Van der Waals forces i.e. cohesive forces between the atoms and molecules affect the melting point of the substance. When clustering of molecules or atoms takes place then depending upon the size of the cluster the melting point varies. In general it is found that atomization energy per atom for spherical cluster increases irregularly on going from 1 to 500 atoms. Since the solid to liquid transitions begin 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 the melting temperature [93] of about 400°C going from 20 nm to 5 nm particles and of about 50 °C from bulk to 20 nm particles. Melting temperature Tm depends on the particle size ‘d’ as,

\[ Tm = A + \frac{B}{d} \]

General rule for physical properties dependent upon surface to volume ratio that can be described by using the size equations structure as in the above equation.

f) Colour:
The colour of the metal nanoparticles in suspended state changes with the size. As the size decreases band gap increases and thus the position of the fluorescence band is shifted to the shorter wave length [94]. Since ancient time gold was used to stain glass with beautiful colours such as red, purple and burgundy [95]. Gold nanospheres have a characteristic red colour, while silver nanospheres are yellow. The colour is due to the collective oscillation of the electrons in the conduction band, known as surface plasmon oscillation. The oscillation frequency for silver and gold is usually in the visible region.
g) Specific Surface Area:

Nanoparticles present a higher surface to volume ratio with decreasing size of the nanoparticles. Specific surface area is relevant for catalytic reactivity, electrical, optical and thermal properties, although stabilization of the surface area, nanoparticles topology (roughness) and interface with support material are also relevant aspects. When a metal particle decreases in size to become a nanoparticle or a nanocrystal a greater proportion of atoms are found at the surface [96]. The metallic nanoclusters are built up by hexagonal (HCP) or cubic (CCP) close packed atoms (nuclearities). As this is the case in most bulk metals, where a central atom is surrounded by 1, 2, 3... closed packed cells.

Table 1.5.g.1 Schematic illustration of metal nanocrystals, in closed-shell configurations with their magic numbers of atoms and the relation between the total number of atoms and the % of surface atoms

<table>
<thead>
<tr>
<th>Full Shell Clusters</th>
<th>Total Numbers of Atoms</th>
<th>Surface Atoms (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 shell</td>
<td>11</td>
<td>92</td>
</tr>
<tr>
<td>2 shells</td>
<td>55</td>
<td>76</td>
</tr>
<tr>
<td>3 shells</td>
<td>147</td>
<td>63</td>
</tr>
<tr>
<td>4 shells</td>
<td>309</td>
<td>52</td>
</tr>
<tr>
<td>5 shells</td>
<td>561</td>
<td>45</td>
</tr>
<tr>
<td>7 shells</td>
<td>1451</td>
<td>35</td>
</tr>
</tbody>
</table>
h) Chemical Properties:

Gold nanoparticles are resistant to strong oxidizing agents and strong acids however “aqua regia” or solutions containing I⁻ or CN⁻ can immediately dissolve them. Both Au and Ag are reactive with sulphur, in particular bulk silver often undergoes tanning due to the formation of an Ag₂S surface layer. In case of organic thiols, ligation to nanoparticle surface is particularly effective for the contemporary presence of sigma type bond in which sulphur is the electron density donor and the metal atom is the acceptor, plus a π type bond in which metal electrons are partially delocalised in molecular orbitals formed between the filled d orbitals of the metal and the empty d orbitals of sulphur [97].

Solutions of Ag nanoparticles have applications as bactericidal agents because the Ag⁺ ions interfere with bacterial metabolism. Since Ag nanoparticles are exposed to a certain extent surface oxidation by atmospheric O₂, silver sols can release Ag⁺ ions with concentration sufficient to act as bactericides [97].
The significance of nanoscale quantum confinement of the electrons provides visualization of the shift in the characteristics of the material depending upon the size of nanoparticles. The electrons are not as free to move thus creating new samples for applications hold a promise.

In a metal, electrons are highly delocalized over a large space (i.e. least confined). As the separation between the valence and conduction bands vanishes it renders the metal its conducting properties [98], whereas when the separation between the valences and conduction band becomes comparable to or larger than KT, the metal becomes semiconductor. When this confinement further increases the energy separation, the metal becomes insulator. In noble metals the decrease in size below the electron mean free path gives rise to intensive absorbance in the near UV visible region.

i) Electronic Properties:

It was found that for, 2D super lattices consisting of large (5 nm) Au nanoparticles, the electronic behavior was dominated by the coulomb block effect at low temperature, while the current-voltage response was ohmic at room temperature [99]. TiO$_2$ nanoparticles exhibited a blue coloration due to stored electrons within the particles when subjected to UV. A partial disappearance [100] of the blue color was seen upon contact with Au nanoparticles as electrons were transferred from TiO$_2$ to Au nanoparticles. TiO$_2$ films cast on conducting glass plates were modified, by adsorbing Au nanoparticles (5 nm diameter) from toluene solution and selective formation of Au islands and larger particles on the TiO$_2$ surface was observed [101]. The effect of spin-orbit scattering on discrete energy levels in Au nanoparticles and other nanoparticles showed level-to-level fluctuations of the effective g-factor from zeeman splitting and the statistics were found to be well characterized by random matrix predictions [102]. Energy transfer from a surface bound area near to the gold core was observed upon photo irradiation [103].
In semiconductor the nanoscale becomes important due to the quantum confinement of the electrons [104]. As the particles size decreased below the Bohr radius of the semiconductor material used, the electron becomes more confined in the particle [104]. This leads to an increase in the band gap energy. Furthermore the valence and conduction bands break into quantized energy levels. The study by Bawendi [105], of the CdSe spherical nanoparticles of various sizes illustrates the macroscopic realization of quantized energy levels.

j) **Electrochemical Properties:**

Electrochemical properties of metal nanoparticles are strongly size dependent. In fact cluster made by few hundred or tens of atoms have been used to investigate the transition from the metal like capacitive charging to the redox like charging. Upto 15 charging peaks were observed by differential pulse voltametry in case of Au (I).

The electrochemistry of ligand stabilized Au nanoparticles shows the formation of core charge. Moreover, the quantized capacitance charging of Au nanoparticles, self assembled monolayers on electrode surfaces could be rectified by certain hydrophobic electrolyte ions in aqueous solution. Magneto-electrochemistry of Au nanoparticles with quantized capacitance charging shows the influence of magnetic field on the electrochemistry of Au nanoparticles and in particular, the effect of electron parity upon their charging states [106]. Double layer capacitance was obtained in aqueous media by differential pulse voltametry [107]. Altogether, electrochemistry [108-112] has been used in several ways to fabricate and deposit Au nanoparticles.
### 1.6 TYPES OF NANOPARTICLES:

**i) Metallic Nanoparticles:**

There is particular interest in this class of nanomaterials [113,75]. Noble metal nanoparticles are found in stained glasses of some church building of the middle ages and even as coating material on cups of the late roman empire. Metallic nanoparticles have very interesting properties in catalysis and some are potential candidates for hydrogen storage and others are used in industrial processes involving gas treatments. They also have unusual optical properties as some of them are employed in the recording and media industry because of their magnetic properties. Also, due to their particular confined electronic configuration they can also be used as conducting elements in building of nano-devices (e.g. single-electron tunnel diodes). The most extensively studied nanoparticles today are those made from noble metal in particular Au, Pt, Ag, Cu and Pd. Copper nanoparticles have been studied intensely in the last few years because they are very easy to synthesize using a wide range of techniques [114-120]. The most common method is the wet chemical reaction involving reduction of metallic salts [121]. Copper nanoparticles have interesting optical properties [121,122] and catalytic activity at room temperature and therefore have found applications in biomedicine, optical imaging, and in catalysis of car exhaust [123]. Platinum and palladium nanoparticles are also much investigated because of their catalytic activity. Pt nanoparticles can be produced, typically, by wet chemical reaction and photocatalytic reduction methods [124]. Platinum is an excellent hydrogen absorber and its nanoparticles are currently used as a membrane to purify hydrogen in some fuel processor applications. Palladium-coated nanoparticles are also used as catalysts in many industrial reactions for carbon bond formation [125]. Silver nanoparticles can also be produced by reduction of metal salts in aqueous solution [126]. They can find applications in antimicrobial activity for the improvement of water purification in
some filtering system [127]. Nickel nanoparticles are also interesting systems finding applications in magnetic recording and catalysis [128,129].

ii) Intermetallic Nanoparticles:
Intermetallic compounds are made of two or more metals or of a metal and a nonmetal. Aluminides and silicides of transition metals such as iron, nickel, titanium, and cobalt are a few examples. Intermetallic bulk materials are used for a variety of high-temperature structural applications. Moreover, they offer properties useful in many applications; their low density, good electrical and heat conductivity and in some cases they are magnetic. Since nanoparticles have a large specific surface area, they actively react with oxygen even at room temperature. The formation of oxide shells around intermetallic nanoparticles might protect them against further oxidation at ambient temperature. Generally metallic nanoparticles oxidize easily with increasing temperature and this prevents their application at higher temperatures. Intermetallic compounds, such as iron and nickel, aluminides and silicides exhibit good oxidation resistance which is extremely important for their practical utilization. An example is [130] Fe$_3$Al nanoparticles covered by an alumina (Al oxide or Al$_2$O$_3$) layer. The excellent oxidation and corrosion resistance of intermetallic phases is attributed to the formation of a continuous, fully adherent oxide layer on the surface when exposed to air or oxygen atmosphere at temperatures as high as 1000°C or even higher. Intermetallic compounds of stoichiometric composition generally assume an ordered crystal structure. Owing to the relation between atomic order in the crystal and magnetization, many intermetallics are ferromagnetic at room temperature and present a very strong magnetic anisotropy. In contrast, transition metals and their alloys generally have low magnetic anisotropy therefore different types of nanoparticles made of intermetallic compounds (as e.g. FePt [131-133]) are being investigated as they can be used in industrial
applications such as ultra-high-density magnetic storage systems. It is possible to achieve high density of low-weight single-domain magnetic nanoparticles regularly arranged on a substrate and high response to magnetic stimulation. Other intermetallics like Ti aluminides [134] are used for aerospace and automotive applications. Fe aluminides are employed as magnetic inkbar coding [135,136]. Silicide nanoparticles are also very interesting from the point of view of the production and the applications. These nanoparticles offer high electrical conductivity and therefore would be used for the electromagnetic shielding and solar control windows by interacting with IR and UV light. Nanoparticles of intermetallics are hardly produced by aqueous solution methods. Most frequently used techniques are mechanical alloying, hydrogen plasma-metal reaction [137-138], condensation from the gas phase and laser-vaporization controlled condensation [139].

iii) Core Shell Nanoparticles:

Sometimes a shell structure around the nanoparticles is formed naturally (sometimes inadvertently) either during the production process or during their utilization. It has to be emphasized that in those cases the naturally formed core-shell structure is not intentional and a distinction must be made from the case of designing core-shell structures. This is a very important fact as in some applications a shell covering the nanoparticles is actually needed [75]. In these cases, a shell is deliberately formed through processing with the main purpose of either protecting the core or enhancing some specific properties. For example, in the first case metal nanoparticles can be covered by inert shells (e.g. oxides) in order to protect them from aggressive environments. In the second case nanoparticles can be covered by catalytically active materials to enhance specific chemical reactions; for example, gold nanoparticles covered by aluminosilicate show excellent catalytic activity in hydrogen reactions [140, 141]. Sometimes a shell is formed for the need of compatibility with the
environment where the nanoparticles are to be used. Some magnetic intermetallic nanoparticles are useful in some medical therapy, as they can be driven efficiently as magnetic probes through organisms. Nevertheless, such materials are generally not fully biocompatible and therefore to become useful, they need to be covered by a shell of biocompatible (generally organic) material. The main aim is in fact to provide ad-hoc sites to which selected molecules can be attached. The whole particle can then be magnetically driven through the organism to a specific sick area. The design of a core-shell structure of nanoparticles depends on their specific application. There are two ways to use nanoparticles. One way is to employ the physical properties (like photoemission or magnetization) of single particles and the other is to make use of collective properties of assemblies of nanoparticles (like colloidal suspension and nanoparticle arrays for electrical applications). An example of application which makes use of the physical properties of single particles is semiconductor nanoparticles which are used for their photoluminescence emission. These particles would have many non-radiative recombination sites on the surface due to dangling bonds or crystal defects which decrease the efficiency of their photoluminescence. This is a deleterious effect in the fabrication of miniaturized opto-electronic devices. By capping the particles with a semiconductor with a wider gap, the efficiency increases as the recombination sites are moved away from the core. CdSe-ZnS core-shell is an example of such multi-layered particles promising as single photon source [142]. Other specific examples of increase in the photoluminescence efficiency of Ge and Si nanocrystals are increased by tailoring shell composition and thickness [143, 144]. Colloidal dispersions of metal nanoparticles in aqueous media generally have a strong tendency to form particle clusters. The primary role of the silica is to avoid coagulation of particles through chemical stabilization. Silica shells are optimal for this sake as they are chemically stable and do not change the optical and electrical properties of the metal core. Furthermore, the thickness
of the shell can be controlled with nanometer precision and this ability implies that the separation between neighboring particles can be tuned, so that the collective (optical, electrical, magnetic) behavior of the particles within the nanostructure can be tailored [145]. Applications of this property are found by nanostructured arrays, nano-patterned and nanocomposite materials. Generally, core-shell nanoparticles are produced in two steps. A core is formed using techniques of the specific systems then a shell is created either in-situ or in a second session, e.g. by layer-by-layer self-assembly method [146], via successive reduction of different metallic salts [147] or by controlled polymer bridging [148].

1.7 SYNTHESIS METHODS:

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. In synthesis and assembly strategies of nanoparticles or nanomaterials, precursors from liquids, solid or gas phase are used. They employ both chemical and physical deposition approach. They rely on either chemical reactivity or physical compaction to integrate nanostructure building blocks.

Generally the manufacturing techniques fall under two categories: ‘bottom-up’ and ‘top-down’ approach. The bottom-up approach refers to the buildup 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. These techniques have been widely used in the formation of structural composite nanomaterials. 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 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 [149]. 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. The different methods for the synthesis of nanoparticles will be discussed under the following categories:

a) **Synthesis of Nanoparticles by Sol-Gel Process:**

The sol-gel method is based on inorganic polymerization reactions. The sol-gel process includes four steps: hydrolysis, polycondensation, drying and thermal decomposition. The size of the sol particles depends on the solution composition, pH and temperature. By controlling these factors, one can tune the size of the particles. This method has been used to synthesize metal oxide nanostructures, such as TiO$_2$ [150], UO$_2$ [151], ZrO$_2$ [152], CeO$_2$ [153], SnO$_2$ [154], SiO$_2$ [155], CuO [156], SnO$_2$ [157] ZnO [158], Al$_2$O$_3$ [159], Sc$_2$O$_3$ [160], ZnTiO$_3$ [161], SrTiO$_3$ [162], BaZrO$_3$ [163], CaSnO$_3$ and other nanostructures [164].
b) **Synthesis of Nanoparticles by Chemical Precipitation:**

The kinetics of nucleation and particle growth in homogeneous solutions can be adjusted by the controlled release of the anions and cations. Careful control of the kinetics of the precipitation can result in monodisperse nanoparticles. Thus it is essential to control the factors that determine the precipitation process such as the pH and the concentration of the reactants and ions. Organic molecules are used to control the release of the reagents and ions in the solution during the precipitation process. The particle size is influenced by the reactant concentration, pH and temperature. By engineering these factors, nanoparticles with narrow size distributions can be synthesized. Zr(OH)$_4$ [165], Ba-TiO$_3$ [166], CdS [167], HgTe [168], HgTe [169] and CdTe [170], AuAg nanoparticles have been produced by this approach. Sordelet and Akinc reported the utilization of urea to control the nucleation process in the synthesis of Y$_2$O$_3$:Eu nanoparticles [171]. Henglein et al. demonstrated the preparation of CdS nanocrystals with a relatively narrow size distribution of 4–6 nm by precipitating Cd$^{2+}$ ions with the addition of stoichiometric amount of H$_2$S at higher pH. Yamamura et al. described the preparation of barium titanate nanoparticles by addition of ethanolic oxalic acid solution to barium titanium mixed aqueous solution at room temperature [172]. Although the method of using precipitation to prepare nanoparticles is very straightforward and simple, very complicated nanostructures can also be constructed using this method such as CdS/HgS/CdS [173], CdS/(HgS)$_2$/CdS [174] and HgTe/CdS [175] quantum well systems and other core/shell structures.

c) **Bottom Up Synthesis:**

This involves the building of structures atom by atom or molecule by molecule. The formation of structures in this approach is governed by the polarity and reactivity of the nanoparticle surface [176]. This is
derived from the functionalization of particle surface. The functionalities [177] determine the binding capabilities of the nanoparticles with other molecules, particles and surface. The bottom up approach for fabrication of nanostructures from stable building blocks has become popular in current science and engineering. This construction principle mimics biological systems by exploiting the order inducing factors that are imminent to the system [178]. The bottom up methods may in future offer a number of potentially very attractive advantages. These include experimental simplicity down to the atomic size scale, the possibility of three dimensional assemblies and the potential for inexpensive mass fabrication.

Bottom up approaches use single atoms or ions to grow clusters and nanoparticles with chemically of rather precise composition, size and structure. In order to prevent agglomeration the nanosized entities have to be protected by appropriate ligand molecules serving as a protecting sphere. Thus special conditions are required for the generation of identical species.

Figure 1.7.c.1 Bottom up approach for nanoparticle preparation

Top Down Synthesis:

This approach of synthesis involves starting with a larger piece of material and etching, milling or machining a nanostructure from it by removing material (for example in circuits on microchips). This can be
done by using techniques such as precision engineering and lithography and has been developed and refined over the last 30 years. Such methods offer reliability and device complexity, although they are higher in energy usage and produce more waste than bottom up methods. The disadvantage of this method is the manipulation of small amounts of atoms at a time resulting in low fabrication throughout.

![Top-down approach for nanoparticle preparation](image)

**Figure 1.7.c.2** Top down approach for nanoparticle preparation

d) **Synthesis of Nanoparticles by Hydrothermal Method:**

Hydrothermal synthesis is a common method to synthesize zeolite/molecular sieve crystals. This method exploits the solubility of almost all inorganic substances in PbS and water at elevated temperatures and pressures and subsequent crystallization of the dissolved material from the fluid. Water at elevated temperatures plays an essential role in the precursor material transformation because the vapor pressure is much higher and the structure of water at elevated temperatures is different from that at room temperature. The properties of the reactants including their solubility and reactivity also change at high temperatures. The changes mentioned above provide more parameters to produce different high-quality nanoparticles and nanotubes which are not possible at low temperatures. During the synthesis of nanocrystals, parameters such as pressure, temperature, reaction time, and the respective precursor-
product system can be tuned to maintain quite high rate of simultaneous nucleation and narrow particle size distribution. Different types of nanoparticles such as TiO$_2$ [179], LaCrO$_3$ [180], ZrO$_2$ [181], BaTiO$_3$ [182], SrTiO$_3$ [183], Y$_2$Si$_2$O$_7$ [184], Sb$_2$S$_3$ [185], CrN [186], SnS$_2$ [187], Ni$_2$P [188] and SnS$_2$ nanotubes [189], Bi$_2$S$_3$ nanorods [190] and SiC nanowires [191] have been successfully synthesized using this methodology. Different types of nanostructures have also been obtained by solvothermal synthesis using supercritical fluids as solvents. Ag [192] Cu [193], Ni [194], Co, Pt, Ge [195], ZnS [196] and CdS [197], nanowires and carbon nanotubes have also been synthesized. In addition various shapes of nanostructures have been synthesized including Cu$_2$S nanoparticles, nanorods, nanodisks, nanoplates, NiS nanorods [198a,b] and triangular nanoprisms [199] by a new method named solventless synthesis.

e) **Synthesis of Nanoparticles by Pyrolysis:**

Pyrolysis is a chemical process in which chemical precursors decompose into solid compound and unwanted waste evaporates away. Upon completion, the desired new substance is obtained. Generally the pyrolytic synthesis of compounds leads to powders with a wide size distribution in the micrometer regime. To get a uniform nanosized material, some modifications or revisions of the pyrolytic preparation procedure and reaction conditions need to be changed such as slowing of the reaction rate or decomposition of the precursor in the inert solvent. Pyrolysis can be used to prepare different kinds of nanoparticles including metals, metal oxides, semiconductors and composite materials such as Ag [200], Au [201], Al$_2$O$_3$ [202], TiO$_2$ [203], Ni [204] and carbon nanotubes [205].

The pyrolysis of organic precursors seems to provide a direct and effective method of producing nanotubes of various kinds such as the one-step synthesis of aligned carbon nanotubes and Y-junction nanotubes. Carbon nanotubes produced from organometallic
precursors can be used to further prepare gallium nitride nanowires, silicon nitride nanotubes and boron nitride nanotubes [206].

**f) Synthesis of Nanoparticles using Chemical Vapor Deposition:**

In chemical vapor deposition (CVD) technique, the vaporized precursors are introduced into a CVD reactor and adsorb onto a substance held at an elevated temperature. These adsorbed molecules will either thermally decompose or react with other gases/vapors to form crystals. The CVD process consists of three steps: (a) mass transport of reactants to the growth surface through a boundary layer by diffusion, (b) chemical reactions on the growth surface and (c) removal of the gas-phase reaction byproducts from the growth surface. There are many good examples of the application of this method in the recent literature. Ostraat et al. [207] have demonstrated a two-stage reactor for producing oxide-coated silicon nanoparticles that have been incorporated into high-density non-volatile memory devices. This is one of the few examples of a working microelectronic device in which vapor-phase synthesized nanoparticles perform an active function. In other recent examples of this approach, Magnusson et al. [208] produced tungsten nanoparticles by decomposition of tungsten hexacarbonyl and Nasibulin et al. [209] produced copper and copper oxide nanoparticles from copper acetylacetonate.

Another key feature of chemical vapor synthesis is that it allows formation of doped or multi-component nanoparticle by use of multiple precursors. Schmechel et al. [210] prepared nanocrystalline europium doped yttria (Y$_2$O$_3$:Eu$^{3+}$) from organometallic yttrium and europium precursors. Senter et al. [211] incorporated erbium in silicon nanoparticles using disilane and an organometallic erbium compound as precursors. Srdic et al. [212] prepared zirconia particles doped with alumina. It is also possible to make composite nanoparticles where one material is encapsulated within another. A particularly promising approach to this is the sodium metal/metal
halide chemistry used by Ehrman et al. [213]. In this approach, a halide such as SiCl$_4$ is reacted with sodium vapor in a heated furnace to produce NaCl-encapsulated particles. For example, SiCl$_4$ reacts with sodium to produce NaCl-encapsulated Si particles. The salt-encapsulation can potentially be used to prevent agglomeration of particles and the salt can then be washed away in a post-processing step.

A wide variety of nanoparticles can be synthesized using other techniques, which fall under the vapor phase process viz. inert gas condensation [214], pulsed laser ablation [215], ion sputtering [216], thermal plasma synthesis [217] and flame synthesis [218].

**g) Microemulsion Synthesis:**

The preparation of metal nanoparticles using the microemulsion system, where ionic and non ionic surfactants are used has been well reported [219]. Microemulsions are colloidal “nanodispersions” of water in oil (W/O) or oil in water (O/W) stabilized by surfactant film. In case of water in oil microemulsions, the size of the water droplet is varied by changing only one parameter $W_0$ ($W_0 = \text{Water to Surfactant molar ratio}$). The size of the nanoparticles is controlled by the size of the water droplets of the micro emulsion.

In the preparation of non ionic surfactant, Triton X-100 and cyclohexane as bulk phase and 1-hexanol as a co surfactant have been used. The metallic and bimetallic nanoparticles are synthesized at room temperature through the reduction of metal salts using sodium borohydride as a reducing agent. The nanoparticles synthesized by this technique are stable for about 6 months. Two reverse micelle system are prepared at room temperature, one contained reducing agent and the other contained metal salt solutions as a water domain in the reverse micelle. Then the two reverse micelles are mixed with continuous stirring. A change in the color
occurred almost immediately after mixing the two reverse micelles. The size of the nanoparticles was in the range of 5 to 50 nm.

**h) Templated Synthesis:**

The synthesis of nanoparticles on templates has generated an increasing amount of attention in the past few years. Techniques on heterogeneous nucleation in which seed crystals serve as nucleation site for further deposition and growth of crystallites can essentially be considered one of the simpler forms of a template synthesis. This technique [220,221] can be used to increase the average particle size of nanoparticles such as aqueous Au (III) is deposited on colloidal Au or Ag(I) is deposited on colloidal Ag. This method can also be used for the synthesis of core shell and onion like structure such as deposition Pd, Bi, Sn, or In on colloidal Au [222,223]. To maintain the narrow size distribution of the nanoparticles care must be taken to ensure that small particles do not nucleate from the solution during the deposition process. Several new techniques have recently emerged to prevent this occurrence. Brown [224] et al. used hydroxyl amine for the seed mediated growth of colloidal Au which led to increase in the average diameter from 12 to 50 nm. The use of hydroxylamine is critical to this process.

**i) Electrochemical Reduction Method:**

Elucidating the electronic structure of metallic nanoparticles is attractive to scientists. The development of preparative method to obtain enough amounts of the monodispersed metallic nanoparticles is essential for the observation of different analytical tools. Many researchers have developed the synthetic methods of monodispersed metal nanoparticles in the presence of linear polymer [225], ligands [226] and so on. In general the control of nanoparticles size and shape constitutes a preparative challenge. Some methodologies have been demonstrated by chemical reduction methods either by adjusting the water contents at a certain interconnected microemulsion phases for
the production of rod like nanoparticles or through using capping polymers in the preparation of cubic tetrahedral Pt nanoparticles [227].

All of the methodologies developed for the production of metal nanoparticles the electrochemical methods offer an alternative simple means within reverse micelles in organic solvent systems. We have now successfully applied it to the preparation of Cu, Ag and Mo mono and Cu-Ag and Cu-Mo bimetallic nanoclusters within a suitable mixture of organic solvents and have developed a unique synthetic route in preparing sufficient yield of these nanoparticles. Our synthetic approach is to control the growth and particle size by introducing size control reagent into the electrochemical systems in which appropriate surfactants or ligands are employed. These act as a supporting electrolyte and a stabilizer for the resulting nanoparticles. Other parameter for controlling the size of the nanoparticles is current density in electrochemical reduction method.

Pure and size selective nanoparticles can be prepared by electrochemical reduction method. The process makes the use of an inexpensive two electrode set up for 25 to 50 ml electrolyte solution. During the synthesis, the bulk metal anode is oxidised and converted into metal cations [228]. These cations migrate to the cathode and the reduction takes place with the formation of the metal atom in zero oxidation state.

The noble metal cluster in the 1 to 30 nm range has been prepared by this method for fundamental and practical reason. In order to prevent agglomeration of metal particles in solution, synthesis is done in presence of stabilizer such as ligand (phenanthroline), polymers (PVP) or surfactants such as tetra alkyl ammonium salts.
The particle size of the nanostructured metal clusters can be controlled by varying parameters such as types of ligands, concentration of ligands, solvent and current density. “True control of particle size remains the most attractive goal for the synthetic chemist”. The first report of stabilization of metal colloids by tetra alkyl ammonium salt, Pt/acetyl trimethyl ammonium chloride is due to Gratzel [229] in 1979. Thereafter the research in the area of ammonium salt stabilized metal clusters was intensified by Toshima [98] et al. Recently Bollemen [230] synthesized stabilized metal cluster by reduction of metal salt with tri alkyl boron hydride. Quaternary ammonium compounds are a group of ammonium salt in which organic groups are substituted for all the four hydrogen of the original ammonium cation. They have central nitrogen atom which is joined to four organic groups. The organic group is mainly alkyl or aryl and the nitrogen can be a part of the ring system. They show a variety of physical, chemical and biological properties and most compounds are soluble in water and act as strong electrolyte.

In electrochemical synthesis, the choice of the tetra alkyl ammonium surfactant is governed by the following constraints,

1. It should be adsorbed at the metal surface to stabilize the synthesized nanoparticles.
2. It should be highly soluble and dissociated in the solvent to play the role of an electrolyte.
3. Hydrophylic-Liophilic balance of the chosen surfactant should be sufficiently high to prevent any precipitation due to the presence of water even in the presence of small quantities in the medium.

The surfactant that satisfied the above constraints, such as tetra ethyl ammonium bromide (TEAB), tetra propyl ammonium bromide (TPAB) and tetra butyl ammonium (TBAB) are used in the present work.
A controlled current electrolysis is used throughout the synthesis process. Solvent selection is made (either single or mixture) depending on the solubility of the ligand or surfactant. The basic principle is simple viz. electrochemical reduction of metal ion in the presence of surfactants serves as an electrolyte and also as a stabilizer. The salient feature of the process includes high yield, absence of any side products, easy isolation of the nanoparticles, variation and choice of ligands and control of particle size by controlling current density. The metal aggregates synthesized do not coalesce during the process.

**j) Photochemical Synthesis:**
Recently a radiolytical and chemical size controlled with improved mono dispersity via seed mediated growth of colloidal nanoparticles has been reported [231]. They have followed iterative growth method, i.e. particles were grown in the immediately previous steps which were used as seeds in the next growth step. Here particles of various size ranging from an average diameter of 5–20 nm could be obtained within a few minutes by UV irradiation at room temperature in the presence of air. Furthermore larger size particles (25 to 100 nm) were produced directly from the original seed particles by varying the ratio of original [seed] to Au (III) and using ascorbic acid as reductant. It should be noted that ascorbate ion is frequently used as a reducing agent for reduction Au (III) or Ag (I) ions. In a variation of this method at pH dependent condition large spherical gold nanoparticles were synthesized directly from Au (III) ions [232].

**k) Ultrasound Technique (Sonochemical Reduction):**
Ultrasonic irradiation treatment is done by means of high density ultrasonic probe consisting of multiwave ultrasonic generator and barium titanate oscillator. This technique has been proved useful for preparation of novel materials [233]. The chemical effect of ultrasound cavitation that is formation, growth and implosive collapse of bubbles in liquid produces unusual chemical environments [234].
Radical species are generated from water molecules due to the absorption of ultrasound.

\[ \text{H}_2\text{O} \xrightarrow{\text{Ultrasound radiation}} \text{H}^* \text{OH}^* \text{(sonolysis)} \]

\[
\begin{align*}
M^{2+} + 2\text{H}^* & \rightarrow M^0 + 2\text{H}^+ \\
nM^0 & \rightarrow (M^0)_n \text{ (aggregates)}
\end{align*}
\]

The OH* radical produces hydrogen peroxide which oxidizes the metallic cluster. In the presence of hydrogen the OH* radicals can be scavenged out. In this method stable fine particles are produced in the presence of the protecting agent such as surfactant or water soluble polymer.

Silver nanoparticles with a size of 5 nm have been prepared by this technique [235]. An argon/hydrogen environment produced more H* radicals and prevented the oxidation of silver nanoparticles.

1) **Laser Ablation Method:**

Wet chemical methods used to prepare metal nanoparticles are based on the reduction of suitable metal salts in the presence of stabilizers. Laser ablation [236] on the other hand is an alternative route to the chemical synthesis for the preparation of small metal particles. The main advantage of laser ablation is the high purity of the nanoparticles wherein pure bulk material and solvents can be used in the preparation. Another advantage of this method includes its simplicity and versatility with respect to metals or solvents in the absence of chemical reagents or ions in the final solution.

Metal nanoparticles are produced by focusing Q switched Nd YAG laser (1064 nm, 8 nsec. pulses) as the radiation source on a metal wire. The laser used has an energy output of 5 – 15 mJ operated at 50 Hz. A 1064 laser beam is focused by a lens with 50 cm focal length on the metal wire suspended in solvent. Typical ablation time was 10 minutes.
m) Microwave Heating:

Recently microwave irradiation as a heating method has been used in the synthesis of nanoparticles. In principle this is a high temperature synthesis method. The generation of nanoparticles originates from the heating effect rather than the quantum energy of microwave. Polar molecules can be heated quickly under the microwave irradiation. In comparison with conventional heating, the microwave synthesis is quite fast, simple, very energy efficient and also achieves uniform nucleation in shorter crystallization time. In a microwave heating process one precursor can be heated at much higher heating rates and reach a higher temperature than its surrounding. A quick simple and energy efficient method based on microwave [237] heating has been developed and is widely used in synthesis of solid materials. Silver nanoparticles have been synthesized using the non conventional reducing agent, N,N diphenyl benzamidine and the microwave irradiation method [238]. Silver nanoparticles of different sizes of interesting colors were synthesized.

n) Chemical Reduction Method:

It is the most widely used method for nanoparticle synthesis. Metal ion in aqueous solution is reduced by reducing agents such as hydroquinone, sodium borohydride, hydrazine, sodium citrate, ascorbic acid etc. to produce nanoparticles. An electric charge on the reductant particle was found to exert large effect on the process of nanoparticle formation. The most highly dispersed and stable colloidal nanoparticles are formed by using anionic reductant [239].

One of the best known technique is described by Turkivech [240], where an aqueous solution is brought to boil and sodium citrate is used as both as a capping material and reducing agent. The order of addition of the metal salt and sodium citrate as well as the temperature, mole ratio of citrate to metal salt and volume of the solution determined the size of the nanoparticle generated. This
synthesis is easy, quick and reproducible and generates mono
dispersed population of nanoparticles around 20 nm in diameter. This
synthesis is widely used to generate metal nanoparticles for many
systems where 20 nm is a desirable diameter or a seed for further
growth. The use of sodium citrate as a capping material allows easy
surface modification for a variety of applications. Sodium citrate is a
weak reducing agent which does not reduce the metal ion at room
temperature. Thus the strength of the reducing is controlled by the
temperature of the solution.

A very popular technique of generating gold nanoparticles has been
reported by Burst [241]. The technique is often referred to as creating
monolayer protected clusters due to the formation of monolayer of
thiol molecules on the surface of the gold nanoparticles. These
particles are extremely stable due to the high strength of the gold–thiol
bond. A two phase systems is used where the gold ion is first
transferred to the organic phase by employing a phase transfer agent,
typically tetra octyl ammonium bromide (TOAB). Then sodium
borohydride is used to reduce the gold ions. This reduction is
accomplished slowly when the gold ions from the organic phase come
in contact with sodium borohydride from the aqueous phase. Then
thiols can be used to protect the gold ions after they are reduced. This
technique is able to glow clusters around 1.5 nm diameter that are
very stable.

Other reducing agents that have been used to synthesis noble metal
nanoparticles are formamide [242], sucrose [243] and glucose [244].
o) **Gamma (γ) Irradiation Technique:**

The radiation induced synthesis is one of the most promising strategies because there are some important advantages to use of irradiation [245] techniques compared to conventional chemical and photochemical methods these are:

- The process is simple and clean.
- The gamma ray irradiation has harmless future.
- Controlled reduction of metal ions can be carried out without using excess reducing agent or producing undesired oxidation product of the reductant.
- The method provides metal nanoparticles in a fully reduced, highly pure and highly stable state.
- No disturbing impurities like metal oxides are produced.

Radiolytic reduction generally involves radiolysis of aqueous solutions that provides an efficient method to reduce metal ions and form homo and hetero nuclear clusters of metals. In the radiolytic method aqueous solutions are exposed to gamma rays creating solvated electrons, e-aq. These solvated electrons in turn, reduce the metal ions and the metal atoms eventually coalesce to form aggregates as depicted by following reactions

\[
\begin{align*}
\text{H}_2\text{O} \xrightarrow{\text{radiation}} & \text{H}_3\text{O}^+, \text{H}^*, \text{H}_2\text{O}, \text{H}_2\text{O}_2 \\
\text{e}^{-}\text{aq} + \text{M}^{m+} & \rightarrow \text{M}^{(m-1)+} \\
\text{e}^{-}\text{aq} + \text{M}^{m+} & \rightarrow \text{M}^0 \\
n\text{M}^0 & \rightarrow \text{M}_2 \rightarrow \text{M}_n \rightarrow \text{M}_{\text{agg}}
\end{align*}
\]

The gamma irradiation based strategies have been used to synthesize gold and silver [246] nanoparticles. Silver nitrate or hydrogen tetra chlorate aurate was dissolved in water with 2 propanol and PVP to form primary solution with predetermined concentration of the metal.
salts. The mixture solution was bubbled with pure nitrogen for about 20 minutes to remove oxygen and then irradiated in field of $^{60}\text{Co}$ which is $\gamma$ ray source at certain irradiation dose rates. Dark brownish silver colloids or reddish gold colloids were prepared. The addition of PVP and small amount of 2-propanol did not lead to any thermal reduction of the Ag or Au salt. This technique has also been used to prepare bimetallic alloy metal clusters of Ag-Pd.

1.8 APPLICATIONS:

Nanotechnology offers an extremely broad range of potential applications for 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. gold nanoparticles are used as an inorganic dye for coloration of glass, (ii) the large surface area, such as gold nanoparticles supported on metal oxide are used as low temperature catalyst and 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 [247]. Some of the applications of nanostructures and nanomaterials are highlighted in the following ways:-

Metal nanoparticles have many unique properties. These include large surface to volume ratio, high surface reaction activity, high catalytic efficiency and strong adsorptions ability. Thus they have many possible applications in areas such as non-linear optical switching [248a], immunoassay labeling [248b] and Raman spectroscopy [248c] enhancement. Thus the nanoparticles do not have only exceptional scientific attractions but have increasing practical relevance in numerous disciplines like Physics, Chemistry, Biology, Medicine and Material Science. The nanoparticles are classified as two types i.e.
Engineered or Non-Engineered. Engineered nanoparticles are intentionally designed and created with physical properties tailored to meet the need of specific application. They can be end product in themselves as in the case of quantum dots or pharmaceutical drugs, sensors for special purpose, or they can be later incorporated, such as carbon black in rubber products.

a) **Catalytic Application:**

Any material to show good catalytic activity must possess high surface area. Nanomaterials have tremendous implications in catalysis since the surface area of nanomaterials markedly increases with the reduction of their size. For example, a nanocrystal of 10 nm diameter will have ~15 % of its atoms on the surface while nanocrystal of 1 nm diameter will have ~100 %. Thus, a small nanocrystal with a higher surface area would be more catalytically active. Furthermore, the change in electronic properties arising due to quantum confinement in small nanocrystals will also bestow unusual catalytic properties on these particles [249a]. Yates et al. demonstrated that there is decrease in catalytic activity per unit surface area of nickel with the increase in particle size in the hydrogenation reaction of ethane [249b]. In a series of papers, Corrolleur, Gault and their co-workers demonstrated the effect of particle size on mechanisms and product distributions of hydrogenolysis reactions over platinum catalysts [249c]. There have been quite a few interesting examples of nanostructured metal oxides and sulfides exhibiting unusual catalytic properties [249d]. Ying et al. reported the use of cerium oxide nanoparticles in the selective reduction of SO₂ by CO with excellent poisoning resistance towards H₂O and CO₂ [249e]. Catalysis drives many reactions with the ability to lower the activation energy of the reaction and thus increases the rate of reaction and the yield. The use of nanoparticles as catalyst has increased as nanoparticles properties and reactions are better understood. The possibility of using less material and having different properties for different shapes of
nanoparticles is very attractive. Nanoparticles catalysis has been investigated [250] for both homogenous and heterogeneous systems. Small clusters are also found to be catalytically active [251] even for materials that display very limited reactivity on the bulk scale. They include the electronic and chemical properties of nanoparticles or the shape, size and oxidation state of the nanoparticles. The surface support is also suggested to be responsible for the catalytic activity.

Bimetallic nanoparticles are also applied to hydrogenation catalysts. PVP stabilized Au–Pd [252] bimetallic nanoparticles with various compositions are used as catalysts for the selective hydrogenation of 1, 3-cyclooctadiene to cycloctane. In these bimetallic nanoparticles, with palladium content of 80% showed the highest activity which is greater than Pd nanoparticles themselves.

The greatest attraction of copper nanoparticles catalysis is their green credentials. They offer the possibility of catalytic oxidation, that use atmospheric air as the oxidant and form pure water as the only by product. Recently the aerobic oxidation of methanol to industrially important chemical, methylformate using an unsupported nano-porous copper catalyst has been reported [253].

b) Nanofluids:

Nanofluids are engineered by dispersing nanometer size solid particles in traditional heat transfer fluids to increase thermal conductivity and heat transfer performance. The primary function of nanofluid is to dramatically enhance thermal conductivity in conventional fluids. Since thermal conductivity of solid nanoparticles is much higher than that of fluids the suspended particles are expected to increase the thermal conductivity and heat transfer performance. In fact many factors (such as shape, size, volume, fraction, thermal conductivity of nanoparticles, viscosity as well as
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membrane of liquid molecules around the nanoparticles etc.) may influence the thermal conductivity of nanofluids.

Experimental result showed that the enhanced thermal conductivity ratio increases with the increase of volume fraction of Al$_2$O$_3$ nanoparticles in nanosuspensions [254]. The results of Zhang [255] showed that the effective thermal conductivity and thermal diffusivity of Au/toulene, Al$_2$O$_3$/water and CNT/water nanofluids at different temperature increases with the increase in the particle concentration. Another important factor that may influence the thermal conductivity of nanofluids is the liquid-solid interface. Liquid molecules close to the liquid solid surface are known to form a layered structure. A liquid in contact with a solid interface is more ordered than a bulk liquid. Since crystalline solids (which are obviously ordered) display much better thermal transport than liquids such as liquid layering is expected to lead to a higher thermal conductivity.

c) Cosmetics:

ZnO nanoparticles [256] have received considerable attention due to their unique properties. They are well known as UV blocking materials especially of light in the UV region and as such are used widely in cosmetics, paints and fibers. But their high catalytic activity in oxidation and photochemical reactions restrict their application as UV blocking materials. Particle surface modification is regarded as an effective way to restrain the ultrafine particles from high oxidative and photochemical activity.

d) Industrial Applications:

Silver is amongst the widely used metal in the world. Its metallic properties make it a great conductor. Its antimicrobial property has also been exploited in several applications. Reducing silver to nonosized particles helps to make the element highly effective, making it more in demand for several uses in the industry of medicine and
technology. Currently there are many uses of silver nanoparticles in industries that have resulted in a boost in its demand and production. Silver nanoparticles can be used as an ingredient for water purifiers and even as an ingredient for inks used in inkjets. A potential industrial use of silver nanoparticles is making it as coating on polyurethane foams. The material is ideal as it can be washed, dried and stored for long period of time and yet retained same number of nanoparticles. The material is also tested as an element for water filtration to eliminate bacteria. It is also possible to use it in the air filtration, air quality management and industrial settings as well as antibacterial packing semiconductor nanoparticles.

e) **Semiconductor Nanoparticles:**

A decrease in the size of semi-conductor nanoparticles results in the shift of the conduction and valence bands towards more negative and more positive potentials respectively. The small size of semi conductor nanoparticles can provide high efficiency of detrapping of light generated electrons and holds the increasing probability of the photocatalytic process on the surface of the conductor. The idea of using nanoparticles for photocatalytic water decomposition was first proposed by Henglein [257a] and Duonghong [257b] who demonstrated the possibility of photoreduction of methylviologen in colloidal solutions of semi-conductors. The photo reduction of methylviologen on the surface of nanoparticles was studied by laser flashed photolysis in colloidal solutions of TiO$_2$ and metal chalcogenides. When Cd-Se is electrochemically deposited on electrically conducting glass, agglomerated Q particles are formed and such electrodes in photochemical cells exhibit photocurrent arising from the Q particles. In order to absorb significant quantities of the incident light, 10-20 coatings of Q particles are deposited one over the other and thus the released electrons must be transported over many particles to the back contact. Energy is lost with every jump of the electrons from one particle to another so that the photocurrent and
voltage attainable with such systems are relatively low. This problem can be overcomed by depositing the $Q$ particles on a porus TiO$_2$ electrode to which the electrons are transferred after light absorption.

f) **Solar Cells:**

Electrochemical studies have demonstrated the electron storing properties of gold nanoparticles and their ability to act as an electric relay on a nanotemplate structure. Beneficial role of gold nanoparticles in photocurrent generation has been reported by Kuwahara [258] in tris 2, 8 bipyridilede ruthenium (II) vilogen linked thiol.

g) **Nanodiagnostic:**

Molecular recognition is fundamental for the development of clinical diagnostic tools and therapeutic modalities. Various organic molecules possessing unique properties have been used to achieve the recognition of different targets. The possibility of combining the ease of handling DNA based modification with different modification strategies of nanomaterials has shown its applicability [259] in spectroscopy, electrochemistry, magnetism (imaging, purification, detecting, etc). The incorporation of nanomaterials (e.g. Au NPs) facilitates signal transduction as the signal of recognition can be amplified by several orders of magnitude making recognition more effective. They can be modified according to the function of the designated DNA probe and make applications of functional DNA more practical for molecular recognition in medical diagnostics by taking advantage of the unusual interaction between the nanomaterials and the living systems [260]. This increase in sensitivity and flexibility present numerous advantages over more traditional procedure like fluorescence and chemi-luminescence.
h) Drug Delivery:

In recent years nanocapsules and nanospheres surrounded by a polymer matrix into which the drug is physically and uniformly dispersed are used as drug delivery devices. These have the ability to circulate for a prolonged period of time, target a particular organ as carriers [261] of DNA in gene therapy and have the ability to deliver proteins, particles and genes.

The advantages of using nanoparticles as delivery systems include:

- Particle size and surface characteristics can be easily manipulated to achieve passive and active drug targeting after parental administration.
- They control and sustain release of the drug during transportation and at the site of localization, altering organic distribution of the drug and subsequent clearance of the drug so as to achieve increase in drug efficiency and avoid side effects.
- Drug loading is relatively high and drugs can be incorporated into the system without any chemical reaction thus preserving drug activity.
- Site specific targeting can be achieved by attaching targeting ligands to the surface of the particles or use of magnetic guidance.
- The system can be used for various routes of administration including oral, parental, intra-ocular etc.

The delivery of the drug Doxorubicin [262] into the mononuclear phagocytic system rich organs/tissues like liver, spleen and lungs is helpful for treatment of hepatic-carcinoma, hepatic metastasis, gynecological cancers, bronco pulmonary tumors, myeleoma and leukemia. Bioactive molecules and vaccines based on peptides and protein can also be encapsulated and delivered. The insulin loaded
nanoparticles were found to reduce blood glucose for a longer period [263]. Polynucleotide vaccines and therapeutic genes are also delivered to produce immune response and treatment of bone healing [264]. Several drugs have also been delivered to the brain by crossing the blood-brain barrier system. The nanoparticles, containing the drugs, were transported to the brain by receptor mediated transcytosis [265].

i) Nanomedicines:

Some of the challenges facing conventional therapies are poor bioavailability and intrinsic toxicity. These have seriously compromised the therapeutic efficiency of many otherwise beneficial drugs. Thus innovative nanodevices and nanostructures have been developed for applications [266] in the fields of diagnostics, biosensing, therapeutics, drug delivery and targeting.

Drug delivery with nanotechnological products takes advantage of the patho-physiological conditions and anatomical changes within diseases tissues to achieve site specific and targeted delivery. The nanosystems are accumulated at higher concentration thus enhancing bioavailability at the targeted site. This leads to less systemic toxicity. The unique property of the nanosystem has helped to deliver drugs to harder-to target sites such as the brain, where blood-brain barrier exists [267]. Some nanoparticles can penetrate smaller capillaries and are taken up by cells. Many of the metal nanoparticles are known to be biocompatible, undetected by the immune system and biodegradable. In addition some may possess unique optical and electrical properties e.g. gold NPs, making it possible to track their systemic movement and localization. Recent advances in the use of nanoparticles in medicine include delivery of antigens for vaccinations, gene delivery for treatment or prevention of genetic disorders, in cardiac treatment, in dental care and orthopedic applications.
Chrysotherapy the use of gold in medicine has been practiced since antiquity. Ancient cultures in Egypt, India and China have used gold to treat diseases like smallpox, skin disorders, syphilis and measles. In India, Ayurved an ancient medical science makes use of various Bhasma. One of them Suvarna Bhasma (Gold Ash) is a therapeutic form of gold metal nanoparticles. In the past few decades, several organogold complexes have emerged with antitumor, antimicrobial, antimalarial and anti-HIV activities. It is also used in the treatment of rheumatoid arthritis. Gold nanoparticles of various shapes have been found to be effective in this treatment. Proteins grafted into gold nanoparticles have also been used to kill cancer cells [267].

The antibacterial effects of Ag salts have been noticed since antiquity and Ag is currently used to control bacterial growth in a variety of applications [268,269] including dental work, catheters and burn wounds. It is well known that Ag ions and Ag-based compounds are highly toxic to micro-organisms showing strong biocide effects on a number of bacterial species. The hybrids of Ag nanoparticles with amphiphilic hyper branched molecules exhibit effective antimicrobial activity in surface coating agents [270].

1.9 MOLECULAR ELECTRONICS AND NANOELECTRONICS:

The last few years have been witnessing a tremendous progress in the molecular electronic and nanoelectronics [271]. In molecular electronics single molecules are designed to control electron transport which offers the promise of exploring the vast variety of molecular functions for electronic devices. The control over electronic energy levels at the surface of conventional semiconductors and metals is achieved by assembling on the solid surfaces and molecules can be designed into a working circuit. If molecules are biologically active, then bioelectronic devices could be developed [272].
Many nanoelectronic devices have been developed which include tunneling junctions [273a], electrically configurable switches [273b], carbon nanotube transistors [273c], single molecular transistors [273d] etc. Various techniques have been used in the fabrication of nanoelectronics such as focused ion beam (FIB) [274a], electron beam lithography [274b] and imprint lithography [274c].

Molybdenum nanoparticles 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 [275].
CHAPTER-I

1.10 SCOPE AND OBJECTIVE OF THE THESIS:

Nanotechnology involves the tailoring of materials at atomic level to attain unique properties which can be suitably manipulated for the desired applications.

In the present work, synthesis and characterization of copper, silver and molybdenum monometallic, bimetallic clusters and colloids are studied along with their antibacterial effect. The particles in the range of 1 to 10 nm have been seen to have unusual electronic properties which may lead to new technologies based on advanced materials. Some progress has been made to control the particle size of the nanostructured metal clusters. However true control of the particle size, still remains the most attractive goal in this field.

The electrochemical reduction method has been reported to synthesize metal colloids and nanoparticles in the nanometer regime and that the particle size can be controlled in a simple manner by the variation in the current density. Apart from this important aspect the method is simple, easy to operate, cost effective, allows high purity of the products, allows reproducible results and is environment friendly since it does not make use of toxic chemicals.

In the preparation of nanoclusters, capping agents are required to stabilize them and prevent their aggregation. The surfactants used in the present study are a group of tetra alkyl ammonium salts, which include TEAB, TPAB and TBAB. The tetra alkyl ammonium ion forms a monolayer around the nanoparticles and is weakly bonded with it.

The electrochemical reduction method is used for the synthesis of the nanoparticles in the non polar organic solvent in the form of a mixture of acetonitrile and tetrahydroforan (4:1). The advantages in using the
non polar organic solvent include control over the size of the nanoparticles, monodispersity and the chemical nature of the nanoparticles surface (via capping agent). Synthesized metal nanoparticles are characterized by different characterization techniques like UV-Visible spectrophotometer, FTIR spectroscopy, XRD, SEM-EDS, TEM, XPS etc.

In order to facilitate the nanoparticles loading and reduce health risks, the bacterial effectiveness of metal nanoparticles has been suggested to be due to both their size and high surface-to-volume ratio. Such characteristics should allow them to interact closely with bacterial membranes but bactericidal property of metal nanoparticles depend on their stability in the growth medium, since this imparts greater retention time for bacterium nanoparticles interaction. There lies a strong challenge in preparing nanoparticles of metal oxides stable enough to significantly restrict bacterial growth. Thus the copper, silver and molybdenum monometallic and bimetallic nanoparticles show excellent antibacterial activities against gram positive and gram negative bacteria.

Thus the present work can be pursued in a systematic and result oriented manner with definite information being obtained for the monometallic and bimetallic nanoclusters of copper, silver and molybdenum capped with different capping agents like TEAB, TPAB and TBAB and their antimicrobial activities. Results can be obtained for the effect, on the variation of the current density as well on the variation of the bulkiness of the capping agent on the synthesis of the nanoparticles.
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