CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION TO NANOMATERIALS

Nanotechnology is an emerging technology that enables scientists to develop new materials and products at the molecular level. Nanotechnology is the term used to cover the design, construction and utilization of functional structures with at least one characteristic dimension measured in nanometers. Such materials and systems can be designed to exhibit novel and significantly improved physicochemical and biological properties, as a result of the limited size of their constituent particles. The size of the nanomaterials are in the range of $10^{-9}$ to $10^{-7}$ m (1 to 100 nm) and display physical attributes substantially different and significant from those displayed by either atoms or bulk materials thus leading to a new and novel technological opportunities. Nanomaterials constitute an emerging discipline in chemical, material and biological science. The term ‘nanocluster’ is used to name particles of any kind of matter, the size of which is greater than that of typical molecules, but which is too small to exhibit characteristic bulk properties. Nanoparticles are used to describe the divided metallic state. The study of nanostructured functional materials has attracted a great zeal both in academic and industrial research because of their potential utilities in microelectronics, catalysis, sensors, fuel cell applications, drug delivery etc. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often dependent on its size and shapes. To put this into perspective, a strand of human hair is roughly 75,000 nm across
(Figure 1.1). On the flipside of the concept, ten hydrogen atoms lined up end-to-end to make up 1 nm. A second important aspect of the nanoscale is that as smaller as nanoparticles size decreases, the larger is its relative surface area.
The principle potential applications of these materials stems from their large surface areas. The fraction of surface atoms increases dramatically with a decrease in particle size. A nanoparticle of 1 nm would have ~76% of the atoms on the surface compared to ~45% for a 3 nm particle. Surface plays an important role in catalysis as the reaction takes place at the surface of the catalyst particle.

The special nature of such nanoclusters, whether consisting of atoms or composed of building blocks, is to be traced back to a quantum confinement of electrons leading to a change of the relevant properties compared to the bulk. Even common materials such as water or carbon change their behavior if they become small and the stability of buildings at temperatures below 0°C is guaranteed by a significant decrease of the freezing point of water in the nanopores of cement. Materials reduced to the nanoscale can abruptly exhibit very different properties compared to what they show on a macro scale. For instance, opaque substances become transparent (copper); inert materials become catalysts (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold). Novel properties not exhibited in bulk materials like size-dependent phenomenon namely quantum confinement in semiconductor particles, surface plasmon resonance in metal particles and super paramagnetism in magnetic materials are observed in nanomaterials. Such special properties stems from these unique quantum and surface phenomena at the nanoscale leading to novel applications and to make them interesting materials.

1.1.1 Effects of Length Scale

The small length scale of nano systems directly influences the energy band structure and can lead to changes in the associated atomic
structure. Such effects are generally termed as quantum confinement, which accounts for the size-dependent properties. Reduction of system size can change the chemical reactivity, which is a function of the structure and occupation of the outermost electronic energy levels. Physical properties such as electrical, thermal, optical and magnetic characteristics are also dependent on the arrangement of the outermost electronic energy levels, which may be changed by reducing the size of the system. For example, metallic systems can undergo changes in the metal forbidden energy band gap and other properties such as mechanical strength, which depends on the change in electronic structure. When the dimensions of the material are reduced to nanosize, the transport properties are widely altered, which is governed by quantum mechanics rather than the classical laws.

1.1.2 Changes in the System Structure

To understand the changes observed in systems of reduced dimension, there is a necessity to consider the proportion of atoms, free surface area or an internal interface such as grain boundary in a nanocrystalline solid. Both the surface area to volume ratio (S/V) and the specific surface area (m²g⁻¹) of a system are inversely proportional to particle size and both increase drastically for particles less than 100 nm in diameter. If an atom is located at the surface, then it is clear that the number of nearest neighbour atoms are reduced, giving rise to difference in bonding (leading to the well known phenomenon of surface tension or surface energy) and electronic structure. In a small isolated nanoparticle, a large proportion of the total number of atoms will be present either at the surface or near the surface. Such structural differences in reduced-dimensions would be expected to possess different properties from the bulk.
1.1.3 Thermal Properties

The large increase in surface energy and the change in interatomic spacing as a function of nanoparticle size has a marked effect on thermal properties. For instance, the melting point of gold particles, which is really a bulk thermodynamic characteristic, has been observed to decrease rapidly for particle size less than 10 nm. The smaller particles have high melting point, which evidence that the metallic nanocrystals are embedded in a continuous matrix.

1.1.4 Chemical Properties

The change in structure as a function of particle size is intrinsically linked to the change in electronic properties. The ionization potential (the energy required to remove an electron) is generally higher for small atomic clusters than the corresponding bulk material. Furthermore, the ionization potential exhibits marked fluctuations as a function of cluster size. Nanoscale structures such as nanoparticles and nanolayers have very high surface area to volume ratios and potentially different crystallographic structures, which may lead to an alteration in chemical reactivity. Catalysis using finely divided nanoscale systems can increase the rate, selectivity and efficiency of chemical reactions. Gold nanoparticles smaller than 5 nm are known to adopt icosahedral structures rather than the normal face centered cubic arrangement. This structural change is accompanied by an extraordinary increase in catalytic activity. Furthermore, nanoscale catalytic supports with controlled pore size can select the products and reactants of chemical reactions based on their physical size and thus ease of transport to and from internal reaction sites within the nanoporous structure. Additionally, many new medicines are insoluble in water in the form of micro-sized particles but will dissolve easily in a nanostructured form.
1.1.5 Magnetic Properties

Magnetic properties are used in a wide range of applications, including ferrofluids, color imaging, bioprocessing, refrigeration as well as high storage density magnetic memory media. The large surface area to volume ratio results in a substantial proportion of atoms (those at the surface which have a different local environment) having a different magnetic coupling with neighboring atoms, leading to different magnetic properties.

1.1.6 Optical Absorption Properties of Nanoparticles

Nanoclusters show large changes in optical properties namely colors as a function of particle size. Metal nanoparticles are the subject of extensive interest because of their unique optical properties, especially nanoparticles of the alkali and the noble metals. Colloidal solutions of noble metals like copper, silver, gold etc. have a broad and an intense absorption band in the visible region of the electromagnetic spectrum. An intense color has been observed for these metal nanoparticles, which is absent for the bulk material as well as for the atom. In noble metals, the decrease in size below the electron mean free path (the distance the electron travels between scattering collisions with the lattice centers) gives rise to an intense absorption in the visible region near UV called as the ‘surface plasmon resonance’, which is collective oscillation of the conduction electrons resulting from the interaction with electromagnetic radiation i.e. the band results when the incident photon frequency is resonant with the collective oscillation of the free conduction electrons. The oscillation wavelength and size of the surface plasmons depend on a number of factors, among which particle size and shape, as well as the nature of the surrounding medium plays the major role.
Colloidal solutions of gold nanoparticles have a deep red color, which becomes progressively more yellow as the particle size increases; indeed gold colloids have been used as a pigment for staining glasses since the seventeenth century. Another interesting phenomenon was observed in the plasmonic absorption with different particle shapes. A pronounced effect on surface plasmon absorption was found if the nanoparticles shape is changed. In the case of spherical particles, a single band is observed while for nonspherical particles, such as rods, the resonance wavelength depends on the orientation of the electric field. Therefore, the plasmon resonance for nanorods splits into two modes of oscillations, one longitudinal mode along the axis of the rod and a transverse mode perpendicular to the first. The transverse mode shows a resonance at about 520 nm, while the longitudinal mode is red shifted (shows a resonance at about 600 nm to 900 nm) in the case of gold nanoparticles. As the particle size is increased, red shift in the wavelength is also observed. It has been shown theoretically and experimentally that aggregation of metal nanoparticles leads to another plasmonic absorption at longer wavelengths when the individual nanoparticles are electronically coupled to each other. The oscillating electrons in one particle feel the electric field due to the oscillation of the free electrons in a second particle that can lead to a collective plasmonic oscillation of the aggregated system. The more particles that are in contact, the longer the range of the plasmon coupling. Very long-range coupling can lead to absorbance that is red shifted to several hundred nanometers from that of the individual particles.

1.2 STABILITY OF METAL NANOPARTICLES

The prime significance of nanoparticles is its small size. This factor becomes detrimental, as the particles often tend to fall out of solution due to its small size leading to agglomeration. In most cases, this aggregation leads
to loss of properties associated with the colloidal state of these metallic particles. For example, during catalysis the coagulation of colloidal particles used as catalyst leads to a significant loss of activity. Hence the nanoparticle stabilization is an imperative issue that should be taken into account to preserve its identity. Hence the stabilization of metallic colloids and the means to preserve their finely dispersed state is a crucial aspect to be considered during their synthesis. In general the role of the stabilizers are (i) prevents uncontrollable growth of particles (ii) prevents particle aggregation (iii) controls growth rate (iv) controls particle size and (v) allows particle solubility in various solvents.

The short interparticle distances between the metal particles and the van der Waals forces favour the attraction towards each other. These forces vary inversely as the sixth power of the distance between their surfaces. Aggregations of the particles occur in the absence of repulsive forces against the van der Waals forces. Consequently, the use of a stabilizing agent induces a repulsive force opposed to the van der Waals forces, which is essential to produce stable nanoparticles in solution. Based on the stabilizing agents used, there are four kinds of stabilization procedures namely (i) the electrostatic stabilization caused by the surface adsorbed anions, (ii) the steric stabilization by the presence of bulky groups, (iii) the combination of these two kinds of stabilization known as electrosteric stabilization caused by the surfactants and (iv) the stabilization with a ligand. Electrostatic stabilization arises when the metal particles are adsorbed by ions creating a double layer (Figure 1.2). Due to the formation of electric double layer around the metal particles, cumbinic repulsion is created between the particles thereby preventing them from agglomeration. The ionic compounds such as halides, carboxylates, or polyoxoanions, dissolved in (generally aqueous) solution generate electrostatic stabilization. One of the most popular methods for stabilizing nanomaterials is steric stabilization, wherein macromolecules such as
oligomers or polymers are generally employed (Aymonier et al. 2002, Pastoriza-Santos and Liz-Marzan 2002).

A protective layer is formed around the nanoparticle surfaces (Figure 1.2). The adsorbed molecules will be restricted in motion in the interparticle space, which causes a decrease in entropy and thus an increase in free energy. In contrast to the electrostatic stabilization, which is mainly used in aqueous media, the steric stabilization can be used both in organic or in aqueous phase.

Figure 1.2  A schematic representation showing the (a) electrostatic stabilization and (b) steric stabilization of metal nanoparticles

The third type of stabilization, which is a combination of both electrostatic and steric type of stabilization, is electrosteric stabilization obtained by ionic surfactants. Such kind of surfactants has a polar head group (hydrophilic), which aids in generating an electric double layer and a hypophilic side chain providing steric repulsion. Some of the compounds generating electrosteric stabilization are polyoxoanions such as the couple ammonium (Bu₄N⁺)/polyoxoanion (P₂W₁₅Nb₃O₆₂⁹⁻). One of the most currently employed stabilizers for metal nanoparticles is the ligands notably called as ‘ligands stabilized metal nanoparticles’. Ligands such as
phosphines, thiols, amines, carbon monoxide, citrate ions etc., have been invariably used for the protection of various metal nanoparticles. Such type of stabilization occurs through coordination between the ligand moiety and metal nanoparticles. It has recently been reported that solvent molecules can stabilize the nanoparticles more efficiently. Thus metal nanoparticles can be synthesized in tetrahydrofuran or thioethers without adding steric or electrostatic stabilizers (Lin and Finke 1994, Duteil et al 1995, Amiens et al 1993 and Dassenoy et al 1998).

1.3 SYNTHESIS OF METAL NANOPARTICLES

In general two broad categories are available for the synthesis of nanostructured metal particles called as ‘top down method’, i.e. by the mechanical grinding of bulk metals, or via ‘bottom-up method’ which rely on the wet chemical reduction of metal salts (nucleation and growth of metallic atoms) (Figure 1.3). As previously explained, a variety of stabilizers supplement the synthesis reaction, e.g. donor ligands, polymers and surfactants are used to control the growth of the initially formed nanoclusters and to prevent them from agglomeration.

Compared to chemical mode of synthesis, a broad particle size distribution is obtained from the physical methods. Traditional colloids are typically larger (>10 nm) giving irreproducible catalytic activity. Chemical methods such as the reduction of transition metal salts by reducing agents are the most convenient method to control the size of the particles. The basic properties that a nanocluster should possess are (i) specific size (1-10 nm), (ii) well defined surface composition, (iii) reproducible synthesis and properties, and (iv) should be isolable and redispersible. Colloidal suspensions can be obtained by various methods leading to various particle size distributions. Nevertheless, whatever the method used, a stabilizing agent
is always essential to prevent the colloids from aggregation. Four general synthetic methods are mainly cited in the literature to synthesize transition metal colloids: (i) chemical reduction of transition metal salts, (ii) thermal, photochemical, or sonochemical decomposition, (iii) ligand reduction and displacement from organometallics, and (iv) electrochemical reduction, which are briefly outlined in the following sections.

1.3.1 Chemical Reduction of Metal Salts

The synthesis of metal nanoparticles via chemical reduction can be divided into two sections (i) synthesis of metals from aqueous solutions and (ii) synthesis of nanoparticles from non-aqueous solutions. A general pictorial representation for the synthesis of metal nanoparticles by chemical pathway is shown in Figure 1.3.
1.3.1.1 Synthesis of metal nanoparticles from aqueous solutions

Due to their widespread application as catalyst materials, metal nanoparticles synthesized from aqueous solutions continue to be a thoroughly investigated subject among the researchers. The synthesis of metal nanoparticles from aqueous or nonaqueous solutions typically requires the chemical reduction of a metal cation. Reducing agents take many forms, the most common of which are gaseous $\text{H}_2$, solvated $\text{ABH}_4$ ($\text{A}=\text{alkali metal}$), hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$), and hydrazine dihydrochloride ($\text{N}_2\text{H}_4\cdot2\text{HCl}$). For a typical reduction reaction of a transition metal cation is

$$\text{M}^{n+} + \text{n}e^- \rightarrow \text{M}^0 \quad (1.1)$$

And the corresponding oxidation process of some species $\text{X}$ is

$$\text{X}^{m-} - \text{n}e^- \rightarrow \text{X}^{m-n} \quad (1.2)$$

In order to obtain electron transfer, the free energy change ($\Delta G$) should be favorable. As a matter of convention, the feasibility of oxidation-reduction processes was reflected in the standard electrode potential ($E^\circ$) of the corresponding electrochemical half cell-reaction. Numerous metal ions can be reduced from aqueous solution to the metallic state in the presence of gaseous $\text{H}_2$ with proper adjustment of pH. For example, the electrochemical half cell-reaction and $E^\circ$ for borohydride ion are given by

$$\text{B(OH)}_3 + 7\text{H}^+ + 8\text{e}^- \equiv \text{BH}_4^- + 3\text{H}_2\text{O} \quad E^\circ = -0.481 \text{ V} \quad (1.3)$$

Borohydride ions, however, should be employed judiciously, as they are known to reduce some cations to metal borides, particularly in
aqueous systems. Hydrazine hydrate is freely soluble in water, since \( N_2H_4 \) is basic and the chemically active free-ion is normally represented as \( N_2H_5^+ \),

\[
N_2H_4.H_2O \rightarrow N_2H_5^+ + OH^- \tag{1.4}
\]
in the case of hydrazine dihydrochloride,

\[
N_2H_4.2HCl \equiv N_2H_5^+ + H^+ + 2Cl^- \tag{1.5}
\]

The standard reduction potential for the hydrazinium ion, \( N_2H_5^+ \), is

\[
N_2 + 5H^+ + 4e^- \equiv N_2H_5^+ \ E^0 = -0.23 \text{ V} \tag{1.6}
\]

According to the theory of reduction, any metal can be reduced at 25°C when the potential \((E^0)\) of metal is more positive than the potential of reducing agent, provided a sufficient excess of reducing agent and proper control of pH is maintained. A brief survey of nanoparticles prepared by reduction from aqueous solutions is summarized in Table 1.1. Tan et al (1987) have recently reported the synthesis of Au, Pt, Pd, and Ag nanoparticles by reduction with potassium bitartrate, which were found stable with the addition of a suitable stabilizing agent. In many cases, an organic capping agent that is normally used to prevent agglomeration can also serve as the reducing agent. Turkevich et al (1951) described a synthetic method for colloidal gold prepared by boiling a mixture of dilute \( HAuCl_4 \) and sodium citrate where the citrate ions are used as capping agents. They have a negative surface charge as a consequence of weakly bound citrate coating. Nanoparticles of other metals can also be prepared by citrate reduction (citrate anion is an innocent ligand), such as silver nanoparticles from \( AgNO_3 \), palladium from \( H_2PdCl_4 \), platinum from \( H_2PtCl_6 \) and iridium nanoparticles from \( IrCl_4 \). Yonezawa et al (1987) have demonstrated the formation of gold nanoparticles by reduction of
AuCl$_4^-$ with citrate in the presence of a thiol. Gold colloids with 2-10 nm dimensions are achievable with this method, and narrow size distributions are possible at high [thiol/Au] ratios. The reduction of metals with high negative reduction potentials require reducing agents with considerably stronger reducing ability than that afforded by most amines, hydroxycarboxylic acids, or alcohols.

**Table 1.1 Nanoparticulate metals synthesized from aqueous solutions**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Starting Material</th>
<th>Reducing Agent</th>
<th>Stabilizer</th>
<th>Avg. Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>Co(OAc)$_2$</td>
<td>N$_2$H$_4$.H$_2$O</td>
<td>None</td>
<td>20</td>
</tr>
<tr>
<td>Ni</td>
<td>NiCl$_2$</td>
<td>N$_2$H$_4$.H$_2$O + NaOH</td>
<td>CTAB</td>
<td>10-36</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(OAc)$_2$</td>
<td>N$_2$H$_4$.H$_2$O + NaOH</td>
<td>None</td>
<td>(10-20) × (200-300) rods</td>
</tr>
<tr>
<td>Cu</td>
<td>CuSO$_4$</td>
<td>N$_2$H$_4$.H$_2$O</td>
<td>SDS</td>
<td>35</td>
</tr>
<tr>
<td>Ag</td>
<td>AgNO$_3$</td>
<td>NaBH$_4$</td>
<td>TADDD</td>
<td>3-5</td>
</tr>
<tr>
<td>Pt</td>
<td>H$_2$PtCl$_6$</td>
<td>Potassium bitartrate</td>
<td>TDPC</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>Au</td>
<td>HAuCl$_4$</td>
<td>Trisodium citrate</td>
<td>S3MP</td>
<td>not stated</td>
</tr>
</tbody>
</table>

CTAB - cetyltrimethylammonium bromide; SDS - sodium dodecyl sulfate; Daxad TADDD-bis(11-trimethylammoniumdecanoylamino ethyl)-disulfide dibromide; TDPC-3,3'-thiodipropionic acid; S3MP - sodium 3-mercaptopropionate.

**1.3.1.2 Synthesis of metal nanoparticles by reduction from nonaqueous solutions**

The stabilization of Au nanoparticles against agglomeration in aqueous solutions by capping ligands such as citrate is a well-documented process. Brust et al (1994) however, reported the synthesis of alkanethiol stabilized colloidal Au nanoparticles that are almost indefinitely stable in
nonpolar solvents. Starting from an aqueous solution of AuCl$_4^-$, the
tetrachloroaurate ions were transferred to an organic phase by vigorously
mixing the aqueous solution with a solution of tetraoctylammonium bromide
(TOAB) dissolved in toluene (TOAB is a well known phase-transfer catalyst).
After the addition of dodecanethiol to the organic phase, an aqueous solution
of NaBH$_4$ was subsequently introduced into the mixture with rapid stirring.
Colloidal gold (1-3 nm) was formed in the organic phase and subsequently
isolated by vacuum evaporation or by precipitation with methanol. Once the
products were isolated as dry powders, stable colloidal suspensions could be
reconstituted in any number of nonpolar or weakly polar solvents, including
toluene, pentane, and chloroform, but not alcohol or water. The results of
Brust et al (1994) triggered a spell of research into the thiol-based
stabilization of colloidal nanoparticles. Among the more significant results
from these investigations, numerous new thiols, amines, silanes, phosphines,
and disulfide-based capping ligands have been identified, and several
techniques have emerged for the exchange of capping ligands.
Poly(vinylpyrrolidone) (PVP) has been used as a stabilizer for 30 nm Ag
nanoparticles and the synthesized nanoparticles exhibited a narrow size
distribution. In a similar reaction, silver nanoparticles have been prepared by
the reduction of AgNO$_3$ or AgClO$_4$ by $N,N$-dimethylformamide (DMF),
where 3-(aminopropyl) trimethoxysilane served as the stabilizing agent. The
reaction probably involves the oxidation of DMF to a carboxylic acid.

$$\text{HCONMe}_2 + 2\text{Ag}^+ + \text{H}_2\text{O} \rightarrow 2\text{Ag}^0 + \text{Me}_2\text{NCOOH} + 2\text{H}^+ \quad (1.7)$$

In this case, the size of the silver nanoparticles could be varied from
6 to 20 nm by adjustment of the temperature as well as the [DMF/Ag$^+$] molar
ratio. The ability of alcohols such as ethanol to act as reducing agents for
strongly oxidizing cations is well known. Table 1.2 summarizes the various
nanoparticles synthesis in organic phase.
Table 1.2  Details of nanoparticulate metals and alloys synthesized by reduction from nonaqueous solutions

<table>
<thead>
<tr>
<th>Metal</th>
<th>Starting Material</th>
<th>Solvents</th>
<th>Reducing Agent</th>
<th>Stabilizer</th>
<th>†Avg.Diameter(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe(Oet)$_2$</td>
<td>THF</td>
<td>NaBEt$_3$H</td>
<td>THF</td>
<td>10-100</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(acac)$_3$</td>
<td>THF</td>
<td>Mg*</td>
<td>THF</td>
<td>~8</td>
</tr>
<tr>
<td>Fe$<em>{20}$Ni$</em>{80}$</td>
<td>Fe(OAc)$_2$ Ni(OAc)$_2$</td>
<td>EG</td>
<td>EG</td>
<td>EG</td>
<td>6 (A)</td>
</tr>
<tr>
<td>Co</td>
<td>Co(OH)$_2$</td>
<td>THF</td>
<td>NaBEt$_3$H</td>
<td>THF</td>
<td>10-100</td>
</tr>
<tr>
<td>Co</td>
<td>CoCl$_2$</td>
<td>THF</td>
<td>Mg*</td>
<td>THF</td>
<td>~12</td>
</tr>
<tr>
<td>Co$<em>{20}$Ni$</em>{80}$</td>
<td>Co(OAc)$_2$ Ni(OAc)$_2$</td>
<td>EG</td>
<td>EG</td>
<td>EG</td>
<td>18-22 (A)</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(acac)$_2$</td>
<td>HDA</td>
<td>NaBH$_4$</td>
<td>HDA</td>
<td>3.7 (C)</td>
</tr>
<tr>
<td>Ni</td>
<td>NiCl$_2$</td>
<td>THF</td>
<td>Mg*</td>
<td>THF</td>
<td>~94</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(OAc)$_2$</td>
<td>EG</td>
<td>EG</td>
<td>EG</td>
<td>25 (A)</td>
</tr>
<tr>
<td>Ru</td>
<td>RuCl$_3$</td>
<td>1,2-PD</td>
<td>1,2-PD</td>
<td>Na(OAc) &amp; DT</td>
<td>1-6 (C)</td>
</tr>
<tr>
<td>Ag</td>
<td>AgNO$_3$</td>
<td>methanol</td>
<td>NaBH$_4$</td>
<td>MSA</td>
<td>1-6 (C)</td>
</tr>
<tr>
<td>Ag</td>
<td>AgClO$_4$</td>
<td>DMF</td>
<td>DMF</td>
<td>3-APTMS</td>
<td>7-20 (C)</td>
</tr>
<tr>
<td>Au</td>
<td>AuCl$_3$</td>
<td>THF</td>
<td>K(15C5)$_2$K$^-$</td>
<td></td>
<td>6-11 (C)</td>
</tr>
<tr>
<td>Au</td>
<td>H AuCl$_4$</td>
<td>formamide</td>
<td>formamide</td>
<td></td>
<td>30 (C)</td>
</tr>
</tbody>
</table>

EG - ethylene glycol; DMF - N, N dimethylformamide; HDA - hexadecylamine; THF - tetrahydrofuran; 1,2-PD - 1,2-propanediol. MSA - mercaptosuccinic acid; 3-APTMS-3-(aminopropyl) trimethoxysilane; PVP - poly(vinyl pyrrolidone); DT - dodecanethiol. (A) - agglomerated; (C) - colloidal/monodispersed; †Estimated from BET surface area assuming spherical shape. Mg* - solvated magnesium

Reactions were carried out in polyalcohols such as ethylene glycol or 1,2-propanediol tends to yield more monodispersed products. Such polyols effectively act as bidentate chelating agents for the solvated metal cations and in some cases, also serve as reducing and/or stabilizing agents. In these cases,
solvents that are more stable must be employed. The trialkylborohydride (ABEt₃H), (A = Li, Na, or K) and solvated magnesium (Mg*) also act as powerful reducing agents. Bonnemann et al (1997 and 1998) have demonstrated that these reagents reduce an impressive array of electropositive metals from their various salts in nonpolar organic solvents such as toluene, dioctyl ether or THF etc.,

\[ xM \text{X}_y + y\text{ABEt}_3\text{H} \rightarrow x\text{M}(0) + y\text{AX} + y\text{BEt}_3 + \frac{3y}{2}\text{H}_2 \]  

(1.9)

where \( M^{y+} = \text{Cr}^{3+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Ru}^{3+}, \text{Rh}^{3+}, \text{Pd}^{2+}, \text{Ag}^+, \text{Cd}^{2+}, \text{In}^{3+}, \text{Sn}^{2+}, \text{Re}^{3+}, \text{Os}^{3+}, \text{Ir}^{3+}, \text{Pt}^{2+}, \text{or Au}^+; \ A = \text{Li or Na}; \) and X represents the counter ion.

1.3.2 Synthesis of Metal Nanoparticles by Electrochemical Reduction

The electrochemical mode of synthesis has gained lots of popularity after developed by Reetz et al (1998) for the synthesis of nanostructured materials. This large-scale synthetic procedure produces size-controlled particles. A sacrificial anode is used as a metal source. This anode is oxidized in the presence of quaternary ammonium salt, in which it acts both as the electrolyte and stabilizing agent. The ions are then reduced at the cathode to yield metallic nanoparticles. A schematic representation showing the mode of electrochemical synthesis is depicted in Figure 1.4. A generalized mechanism for the electrochemical synthesis of metal nanoparticles can be represented in Figure 1.4.

An overview of the reactions occurring in the electrochemical cell can be summarized as follows (i) oxidative dissolution of the sacrificial \( \text{M}_{\text{bulk}} \) anode (ii) migration of \( \text{M}^{n+} \) ions to the cathode (iii) reductive formation of zerovalent metal atoms at the cathode (iv) formation of metal particles by
nucleation and growth and (v) arrest of the growth process and stabilization of the particles by colloidal protecting agents e.g. tetraalkyl ammonium salts and (vi) precipitation of the nanostructured metal colloids.

Figure 1.4  (a) Formation scheme of electrochemically produced metal nanoparticles and (b) Electrochemical setup for the synthesis of bimetallic nanoparticles

Reetz et al (2000) have reported that the Pd metal was deposited from 0.1 M solution of tetraoctylammonium bromide dissolved in a mixture of acetonitrile-THF (4:1) by applying 0.1 mA/cm² current at 1 V using a potentiostat. The monodispersed 4.8 nm particles were collected by decantation/drying and were redispersable in THF or toluene. The authors also noted that an increase in the current density resulted in a substantial decrease in particle size i.e., 1.4 nm particles were obtained at 5.0 mA/cm². For less easily oxidized metals such as Pt, Rh, or Ru, the anode and cathode used are made of Pt and the metallic precursor is a transition metal salt reduced by electrolysis in the presence of a quaternary salt. The Pd-Pt, Ni-Pd, Fe-Co and Fe-Ni bimetallic nanoparticles could be also obtained by this method. Bulk plates of two metals were immersed as anodes into the
electrolyte containing a stabilizer (tetraalkylammonium salt) and a Pt plate acted as cathode. From the anode, the corresponding metal ions were generated, and the formed ions were reduced by electrons from the Pt cathode to produce tetraalkylammonium salt-stabilized bimetallic nanoparticles (Figure 1.4b).

Advantages of electrochemical methods: Some of the advantages of synthesizing nanoparticles using electrochemical methods are (i) The products can be easily isolated from the precipitate without any contamination of byproducts. (ii) The electrochemical preparation provides size-selective particle formation. (iii) The particle sizes can be controlled by varying the current intensity (higher current intensity gives smaller particles). (iv) The isolation of nanoparticles is simple and they can be easily separated from the solvent when formed. An appreciable yield of about 95% can be achieved.

1.3.3 Synthesis of Metal Nanoparticles by Radiation-assisted Reduction

The most obvious example of radiation-assisted reduction is the photo reduction of aqueous AgNO₃ solutions upon exposure to UV light. Huang et al (2002) used this method for the synthesis of Ag nanoparticles by exposing a solution of AgNO₃ to 243 nm radiation in the presence of poly(vinylpyrrolidone) (PVP) as stabilizer. The average particle size can be tuned from 15 to 22 nm by adjusting the [PVP/Ag⁺] ratio. At the extreme end of radiation-assisted reductions, all the noble metals, as well as many other electronegative metals, can be reduced in aqueous solutions by exposure to γ radiation. γ-rays decompose H₂O to H₂, H₂O₂, OH, H radicals, H₃O⁺ and solvated electrons. These species can react with the molecules in solution to give new radicals, which in turn were able to reduce the metal salts as shown below.
Active species generation

\[ H_2O \rightarrow H, OH^-, e_{aq}^-, H_3O^+, H_2, H_2O_2 \] (1.10)

\[ OH^- (H) + RH \rightarrow R^- + H_2O (H_2) \] (1.11)

Metal reduction

\[ M^{n+} + nR^- \rightarrow M^0 + nR^+ + nH^+ \] (1.12)

\[ M^{n+} + ne^- \rightarrow M^0 \] (1.13)

Growth of colloids

\[ nM^0 \rightarrow M^0_{\text{Colloids}} \] (1.14)

The reactions are usually performed under a nitrous oxide atmosphere that acts as a scavenger for the hydrated electrons (\(e_{aq}^-\)):

\[ N_2O + e_{aq}^- + H_2O \rightarrow N_2 + OH^- + OH^- \] (1.15)

The \( \cdot OH \) and \( \cdot H \) radicals are subsequently scavenged by short-chain alcohols such as methanol:

\[ OH^- + CH_3OH \rightarrow H_2O + CH_2OH \] (1.16)

\[ H^- + CH_3OH \rightarrow H_2 + CH_2OH \] (1.17)

The \( \cdot CH_2OH \) radical then serves as a reducing agent for the metal accompanied by the oxidation of the radical to an aldehyde:

\[ M^{n+} + nCH_2OH^- \rightarrow M^0 + nCH_2O + nH^+ \] (1.18)

Metal nanoparticles are produced by radiolytic reduction, which includes Au (2 nm) stabilized in poly (vinyl alcohol) or poly (vinylpyrrolidone), Co (2-4 nm) stabilized by polyacrylate and
Cu (20-100 nm) in poly(vinyl sulfate). The radiolytic reduction method is the most useful method for enlarging colloidal metals in order to (or layering dissimilar metals over one another) form core shell type arrangements. In these reactions, a metal colloid is usually prepared by a conventional chemical route such as the Turkevich (citrate) method. The metal colloids are then used as seed particles for subsequent growth of the same or a different metal from aqueous solutions. For instance, starting from a solution of 15 nm Au prepared by the citrate method, Henglein (1999) enlarged the Au particles sequentially up to diameters of 120 nm by adding aqueous Au(CN)$_2^-$ and methanol to the colloidal solution and irradiating with Co source. In Henglein’s method, rather than the organic radicals directly reducing the metal cations, they instead charge the colloidal Au particles that subsequently act as reducing agents for the aqueous Au(CN)$_2^-$ ions. This mechanism is demonstrated schematically in Figure 1.5.

![Figure 1.5](image)

**Figure 1.5** (a) Mechanism of Au nanoparticles enlargement by $\gamma$ radiation and (b) TEM image of 20 nm Au nanoparticles (left) produced by the Turkevich method and (right) after coating with Ag by a radiation-assisted reduction method

There is, of course, no requirement that the nanoparticle seeds and aqueous metal ions consist of the same metals. A dissimilar metal cation dissolved in the aqueous solution would essentially coat the surfaces of the
existing metal colloid particles, creating a core-shell type composite. Henglein et al (1981, 1993, 1998, 1999 and 2000) have studied extensively on $\text{Au}_{\text{core}}\text{Pt}_{\text{shell}}$, $\text{Pt}_{\text{core}}\text{Au}_{\text{shell}}$, $\text{Au}_{\text{core}}\text{Hg}_{\text{shell}}$, $\text{Au}_{\text{core}}\text{Pb}_{\text{shell}}$, $\text{Au}_{\text{core}}\text{Ag}_{\text{shell}}$ and $\text{Pd}_{\text{core}}\text{Au}_{\text{shell}}\text{Ag}_{\text{shell}}$ nanocomposites (Figure 1.5).

1.3.4 Synthesis of Nanoparticles by Decomposition of Organometallic Precursors

The thermolysis of organometallic precursors in the presence of polymer is one of the oldest methods of preparing colloidal metals. Typically, a metal complex such as cobalt carbonyl $[\text{Co}_2(\text{CO})_8]$ is decomposed at 130-170°C under inert atmosphere in decalin or ethylene glycol solvents to obtain cobalt metal nanoparticles.

$$\text{Co}_2(\text{CO})_8 \rightarrow 2\text{Co(s)} + 8\text{CO}↑ \quad (1.19)$$

Cobalt particles of size 45 nm have been prepared by this approach using poly(vinylpyrrolidone) (PVP) as stabilizing agent. The nitrogen-containing polymer (i.e. PVP) chains were found to effectively serve as nucleophiles (Nu), leading to the formation of legated metal-cluster macromolecules:

$$(n+1)\text{Fe(CO)}_5 + x\text{Nu} \rightarrow [\text{Fe(Nu)}_x][\text{Fe}_n(\text{CO})_m] \quad (1.20)$$

Smith and Wychick (1980) selectively prepared 5-15 nm colloidal Fe particles in this manner. Thermal decomposition of Fe(CO)$_5$ combined with the polylol reduction of Pt(acac)$_2$ resulted in the formation of intermetallic Fe-Pt nanoparticles.
1.3.5 Microwave-assisted Synthesis of Nanoparticles

Of the various techniques used for the synthesis of metal nanoparticles, microwave mode has attracted a wide attention due to its potential advantages. The microwave processing of nanoparticles results in rapid heating of the reaction mixtures, particularly those containing water and subsequently leads to simultaneous precipitation. This method provides the formation of very small particle size, narrow size distribution and requires very short reaction time. Pastoriza-Santos and Liz-Marzan (1999 and 2002) described Ag and Au nanoparticles prepared by both reflux-induced precipitation and microwave-assisted precipitation. In both the cases, the metals were reduced by the solvent (DMF). They found that, generally, the microwave method offered better control of particle size and morphology. Many colloidal metals can be prepared by microwaving mixtures of metal salts and polyalcohols. This method, originally developed by Fievet et al (1989) is now referred to as the microwave-polyol process. Recently, Yu et al (1999) prepared 2-4 nm colloidal Pt particles by irradiating a mixture of poly(N-vinyl-2-pyrrolidone), aqueous H\textsubscript{2}PtCl\textsubscript{6}, ethylene glycol, and NaOH with 2450 MHz microwaves in an open beaker for 30s. Tsuji et al (2002) have prepared PVP-stabilized, nanoparticulate Ni in ethylene glycol by a similar method.

1.3.6 Sonication-assisted Synthesis of Nanoparticles

Like microwave-induced heating, sonication of liquid also results in rapid heating, although the mechanism is fundamentally different. The sonication of a liquid results in cavitation (the implosive collapse of bubbles) that creates localized ‘hot spots’ with effective temperatures of 5000 K and lifetimes on the order of a few nanoseconds or less. As such, the chemical reactions largely take place inside the bubbles. The extremely rapid cooling
rates encountered in this process, however, strongly favor the formation of amorphous products. Many of the methods reported in the literature for sonochemical synthesis of nanoparticles involve the decomposition of carbonyl precursors. Suslick et al (1990, 1991 and 1996) have studied extensively on the use of ultrasound in chemical synthesis for the preparation of amorphous Fe, Co and several Fe-Co nanoparticulate alloys. Typically, the corresponding metal carbonyls were dissolved in decane and irradiated at 20 kHz for 3 h under an inert atmosphere to produce well-dispersed 8 nm particles.

1.4 CHARACTERIZATION OF NANOMATERIALS

The current revolution in nanoscience was brought about by the concomitant development of several advances in technology. One of them has been the progressive ability to fabricate smaller and smaller structures, and another has been the continual improvement in the precision with which such structures are made. Another major factor responsible for the nanotechnology revolution has been the improvement of old and the introduction of new instrumentation techniques for evaluating and characterizing nanostructures. Nanoparticle characterization is indispensable to establish understanding and control of nanoparticle synthesis and applications. The nanomaterials characterizations are done using a variety of techniques, mainly drawn from material sciences. Common techniques are electron microscopy (TEM, SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), UV-visible and fourier transform infrared spectroscopy (FTIR). Many techniques have been used to reveal the size and homogeneity of metal nanoparticles obtained by chemical methods. In general, characterization can be broadly grouped into two categories (a) Spectroscopic analysis and (b) Microscopic analysis.
1.4.1 Spectroscopic Analysis

The world of the very tiny is a constant bustle of activity. Things absorb, emit, bond, break up, vibrate and travel, but they almost never stand around doing nothing. Since nano-size particles are too tiny to observe with naked eyes, studying such things requires special clever instruments that measure certain properties of matter for example, HR-TEM, AFM, SEM etc.

1.4.1.1 UV/Vis spectroscopy

Metal nanoparticles are mainly recognized due to their brilliant color in solution. Faraday’s classical Au solution shows clear ruby-red color. Ruby glasses, with incorporated Au nanoparticles, are very famous. Indeed, Au, Ag and Cu (Group 1B metal) nanoparticles all have characteristic colors related with their particle size. Thus, for these metals, observation of UV/Vis spectra can be a useful complement to other methods in characterizing metal particles. Nanoparticles have generally unique absorptions in the UV-Vis region also called as ‘plasmon absorptions’. From UV-Vis spectrum, particle size could be calculated. UV-Vis spectroscopy plays a major role in the creation of nanosensors that can detect a material and identify its composition by bonding with it, which changes the nanosensor’s properties in specific ways.

1.4.1.2 FTIR spectroscopy

Infrared spectroscopy has been widely applied for the investigation of the surface chemistry of adsorbed small molecules, functional groups of ligands or polymers adsorbed on the nanoparticle surfaces. For chemistry of nanoparticles, IR spectroscopy is used to examine the structure of coordinations of ligands or protective polymers attached to the surface of
nanoparticles. In the chemistry of catalysis by nanomaterials, absorption of CO and H\textsubscript{2} has been widely applied to investigate the surface. An IR spectrum is produced when CO gets adsorbed onto the metal nanoparticle surface. The absorption structure of C=O depends on the size of the particles. Smallest particle absorb in an exclusively linear mode, giving a fairly sharp absorption band at 2,037 cm\textsuperscript{-1}. As particle size is increased, the ratio of terminal CO to bridging CO is decreased. The C=O bond frequency occurs in different regions between 2000 cm\textsuperscript{-1} and 1700 cm\textsuperscript{-1} depending upon the geometry of CO molecule binding to the surface.

1.4.1.3 X-ray photoelectron spectroscopy

XPS is a powerful tool for investigating the catalytic properties, the surface composition and structure of metal nanoparticles. An XPS measures the photoelectron emitted by X-ray irradiation and elements located near the surface can preferentially be detected. By a quantitative analysis of XPS spectra of bimetallic nanoparticles, the presence of elements in the surface region of the nanoparticles could be clearly seen, i.e. it is an efficient tool to reveal their surface composition. XPS spectra are also used to calculate the binding energy of the coordinating group. If the coordinating group (through which it gets binded to the surface of the nanoparticles) have more than two coordinating site, the exact coordinating sites can be detected from the difference in binding energy of the coordinating sites.

1.4.1.4 Energy dispersive X-ray analysis

One of the most revealing analytical methods mainly used for investigating the composition of bimetallic nanoparticles is energy dispersive X-ray spectroscopy (EDX), which is usually coupled with a transmission electron microscope with high resolution. EDX is a kind of EPMA (electron
probe microanalysis) or XMA (X-ray microanalysis), which has higher sensitivity than the usual EPMA or XMA techniques. The electron beam can be focused on a single particle by TEM, to get information from individual particles. Each element in the chosen nanoparticle emits X-rays at characteristic energies by electron beam irradiation, and their intensity is proportional to the concentration of each element in the particle. This method provides analytical data that cannot be obtained by the other three methods (UV/Vis, XPS and FTIR Spectroscopy). For sufficiently large particles, the electron beam can be spotted on the surface area or on the center of the particle, to investigate the regional composition, which often reveals non-uniformity in the composition. Such variations of each particle are important when we consider the structure or the preparative process of these bimetallic nanoparticles.

1.4.2 Microscopic Analysis

1.4.2.1 Scanning electron microscopy and Transmission electron microscopy analysis

Electron beams are not only capable of providing crystallographic information about nanoparticle surfaces but also can be used to produce images of the surface, and they play this role in electron microscopes. Scanning electron microscope (SEM) creates images of invisibly tiny things by bombarding with a stream of electrons to look at features on a scale as small as 10 nm. A SEM shoots a beam of electrons to the samples, which further breaks off the electrons in the specimen. These dislodged electrons are then pulled onto a positively charged grid, where they are translated into a signal. Moving the beam around the sample generates a whole bunch of signals, after which the SEM can build an image of the surface of the sample. In general, SEMs can ferret out quiet a bit of information about the sample
like (i) topography-surface features such as texture. (ii) morphology - shape, size and arrangements of the particles that compose the object’s surface and (iii) composition - elements that make up the sample.

Transmission electron microscopy (TEM) is another very valuable and indispensable technique used for the precise characterization of metal nanoparticles. Metal nanoparticles, especially those consisting of heavy and precious metal elements, give high contrast when the particles are dispersed on thin carbon films supported by metal grids. When compared to SEM, a TEM can achieve a resolution of approximately 0.2 nm, roughly the size of many atoms. Because most atoms have diameters of at least 0.2 nm, a TEM can produce images that can reveal how the atoms are arranged in a material. Typically, TEMs are used to analyze the morphology, crystallographic structure (arrangement of atoms in a crystal lattice) and composition of the sample. The main advantage in TEM measurements lies in sample preparation involving evaporation of a small drop of metal nanoparticle dispersion onto a carbon coated micro grid provided the carbon coating must be thin enough to obtain a good contrast. An advanced technology, high resolution TEM (HRTEM) can now provide information not only on the particle size and shape but also on the crystallography of monometallic and bimetallic nanoparticles.

HR-TEM can provide the area composition by the fringe measurement, giving crystal information of nanoparticles observed in the particle images. When energy disperse X-ray microanalysis (EDX) is used in conjunction with TEM, localized elemental information can be obtained. Some of the important properties of TEM are that it provides direct visual information of size, shape, dispersity, structure and morphology with routine magnifications $\geq 40,000$ to 0.2 nm. Some of the limitations of TEM studies are (i) samples are dried and examined under high vacuum conditions and
therefore, no direct information is gained on how particles exist in solution. (ii) only a finite number of particles can be examined and counted, which may not be a representative of the sample as a whole and (iii) requires electron beam in which case, some nanoparticles may undergo structural rearrangement, aggregation or decomposition.

1.4.2.2 Atomic force microscopic analysis

AFM is a breakthrough technology that allows three-dimensional imaging and measurement of unstained and uncoated structures in air or fluid from molecular to micron scales. The advantage of AFM is that it can get images of samples in air and underneath liquids. An AFM probes the surface of a sample with a sharp tip. Tip located at the free end of cantilever that is 100-200 mm long. Forces between the tip and cantilever will cause the cantilever to bend and/or twist. This deflection is measured as the tip is scanned over the surface, providing a map of the surface topography. AFMs can be operated in air, vacuum, and in liquids. Biological measurements, in particular, are often carried out in vitro in biological fluids. Now research is undertaken to change the AFM tips with carbon nanotubes because nanotube tips are assure to make AFMs even more valuable tools for evaluating nanomaterials.

1.5 APPLICATIONS OF NANOMATERIALS

1.5.1 Nanotechnology in Medicine

Nanotechnology is an emerging reality that can help us to modify and create particles that circulate through the body with effective control. The building blocks of life including proteins, nucleic acids, lipids and carbohydrates are examples of materials that possess the unique properties
determined by their size, shape folding and pattern at the nanoscale. Living organisms are built up of cells that are typically 10 µm across. However, the cell parts are much smaller and are in the sub-micron size domain. Even smaller are the proteins with a typical size of just 5 nm, which is comparable with the dimensions of smallest manmade nanoparticles. Because of such small size, nanoparticles can be used as a probe, which would allow to spy at the cellular machinery without involving too much interference. Understanding of biological processes on the nanoscale level is thus a strong driving force behind the development of nanotechnology. Nanomedicine is the medical application of nanotechnology and related research. It covers areas such as nanoparticle drug delivery and possible future applications of molecular nanotechnology (MNT). Some of the applications of nanomaterials to biology or medicine are fluorescent biological labels, drug and gene delivery, bio detection of pathogens, detection of proteins, probing DNA structure, tissue engineering, tumor destruction via heating (hyperthermia), separation and purification of biological molecules and cells.

1.5.1.1 Nanotechnology for chemotherapy

Cancer is caused by uncontrolled growth and spreading of abnormal cells. Cancer can seriously threaten human health and it leads to death. Although the mechanisms of formation and spreading of cancer are still not well understood, both external factors (e.g., tobacco smoking, chemicals, radiation, and infections) and internal factors (e.g., inherited metabolism mutations, hormones, and immune conditions) are believed to be relevant. These factors may act together or sequentially to initiate and promote carcinogenesis. It may take more than 10 years from the initiation of cell mutation to the formation of detectable cancer. There is a lack of thorough cure for cancers. A worthy goal at present is to develop novel methods of treatment that produces remission and/or palliation for the cancer. Effective
treatments include surgery, radiotherapy, chemotherapy, hormone therapy, photodynamic cancer therapy and immunotherapy. Each of these treatment modalities has advantages and disadvantages, and their combination is usually needed to produce the most effective results. Early detection, complete surgical removal and effective radiotherapy, chemotherapy, and other treatments are critical factors in determining the patient’s prognosis. Among these, early and precise detection is the most important factor, and regular screening examinations play an important role in cancer prevention and treatment. Clinical impressions suggest that the larger the tumor at the time of excision, the greater is the probability that the patient will die of metastatic cancer that was not detectable at the time of surgery (Schabel 1977, Weiss and DeVita 1979). Multimodal therapy that utilizes radiotherapy, chemotherapy, immunotherapy, and other forms of treatments to follow surgery provide a better chance to kill the metastatic cancer cells or, at least, to keep them in the remission state. When surgery and chemotherapy were combined, however, the rate of cure was about 57%. Surgery is not feasible for undetectable cancer, metastatic cancer, or cancer that is not concerned in a solid tumor (e.g. blood leukemia). Chemotherapy, radiotherapy, and immunotherapy, or their combinations become the main treatment procedures in these situations. New methods and techniques are under development and have been a focus in modern medicine, science and technology (Calabresi and Schein 1993, Cavalli et al 1997, Morris et al 1998, Pazdur 1995). In the literature, chemotherapy sometimes is defined as the use of any medicine for treatment of any disease. Chemotherapy for cancer, however, is understood in a narrower sense of using chemotherapeutical agents directed at killing or controlling the cancer cells, and the cancer chemotherapeutic agents are often toxic or even life-threatening in combination with other treatments, a means to cure some types of cancers or, at least, to lengthen the life expectancy of patients. There have been so far hundreds of anticancer agents available for clinical use; some are synthetic chemicals and some are natural extracts.
Combination of chemotherapy with other treatments has become the primary and standard treatments for cancers, as well as for other diseases caused by uncontrolled cell growth and invasion of foreign cells or viruses. Hence scientists are trying to focus nanotechnology to solve the above problem in cancer chemotherapy.

1.5.1.2 Problems in chemotherapy

Chemotherapy is a complicated procedure in which many factors are involved in determining its success or failure. It carries a high risk due to drug toxicity, and the more effective drugs tend to be more toxic. Problems still exist even for successful chemotherapy, and patients have to tolerate severe side effects and sacrifice their quality of life. The effectiveness of chemotherapy depends on many factors, including the drug(s) used, the condition of the patient, the dosage and its form and schedule, etc. With this view in mind, research turned to find out a new and novel technology for the remission of cancer.

The ideal goal for chemotherapy is to deliver the drug(s) with high efficacy at the right time to the desired location with a concentration high enough over a sufficiently long period. It would be ideal if the chemotherapeutic drugs could exert their actions only on the cancerous cells and leave normal cells less affected or even untouched. This is the motivation for controlled and targeted delivery of anticancer drugs. Hence, nanotechnology provides a new route and novel technology for the remission of cancer through earlier detection, controlled and targeting delivery of drugs.
1.5.1.3 Nanoparticle technology for chemotherapy

There has been intensive research in the past few decades in the development of nanoparticles of biodegradable polymers as an effective drug delivery system for medical practice, especially for cancer chemotherapy, gene therapy of cancer and other diseases.

Nanotechnology provides a new way for human beings to visualize and conceptualize the outside world as well as the human body. The size can make dramatic differences in medical treatments. The 20th century might be called the micro era, and the new 21st century is the nano era. As mentioned above, one of the main challenges in chemotherapy is the dosage form for most effective anticancer drugs which relies on the use of toxic adjuvants. Nanoparticles of biodegradable polymers, which have a size small enough to allow intracapillary or transcapillary passage and appropriate surface coating to escape from macrophage uptake, may provide an ideal solution. Nanoparticles can provide a controlled and targeted way to deliver the encapsulated anticancer drugs and thus result in high efficacy and low side effects. A main obstacle for successful chemotherapy is the resistance of cancer cells to effective anticancer drugs and the destructive actions of these drugs to normal cells, tissues and organs. To deliver therapeutic agents to tumor cells in vivo, the drug resistance problem must be solved at the vascular, interstitial and cellular levels.

It has been found that the pore cutoff size of several tumor models lies in the range between 380 nm and 780 nm (Hobbs et al 1998, Yuan et al 1995). Nanoparticles, with their small size and appropriate surface coating, may have the ability to overcome the drug resistance problem and thus greatly improve the efficacy of chemotherapy. Nanoparticles for cancer chemotherapy have been intensively investigated recently. A number of US
FDA-approved biodegradable polymers have been employed to make nanoparticles for controlled delivery of various effective anticancer agents to avoid the using of toxic adjuvants, to realize the desired pharmacokinetics, and to enhance their uptake by cancer cells. Another new material called, as “nanoshells” is a unique, noninvasive way to detect and obliterate cancer cells. Gold plated nanoshells with attached antibodies, when injected into the body, the antibodies attach themselves onto the cancer cells, which are essential for the need of nanocarrier.

1.5.1.4 Need of nanocarrier

Nanotechnology is a novel area of science that provides, with a new hope, the tools and technology to work at atomic, molecular and supramolecular levels leading to creation of devices and delivery systems with fundamentally new properties and functions. Nanocarriers offer a number of advantages making it an ideal drug delivery vehicle.

- Nanocarriers can better deliver the drugs to tiny areas within the body, which are smaller than 100 nanometers.
- Sophisticated techniques and tools have enabled the better characterization and manipulation of materials at the nanoscale level to elucidate nanoscale phenomenon leading to the generation of new era of nanostructure-mediated drug delivery.
- It involves overlap of biotech, nanotech, and information technology, resulting in many important applications in life sciences including areas of gene therapy, drug delivery, imaging, biomarkers, biosensors and novel drug discovery techniques.
Nanocarriers aid efficient drug delivery to improve the aqueous solubility of poorly soluble drugs that enhance bioavailability for timed release of drug molecules, and precise drug targeting.

The surface properties of nanocarriers can be modified for targeted drug delivery e.g. small molecules, proteins, peptides, and nucleic acids loaded nanoparticles are efficiently targeted to particular tissue types.

TARGETED nano drug carriers reduce drug toxicity and provide more efficient drug distribution.

Nanocarriers hold promise to deliver biotech drugs over various anatomic extremities of body such as blood brain barrier, branching pathways of the pulmonary system, and the tight epithelial junctions of the skin etc.

Nanocarriers penetrate tumors easily due to their leaky constitution, containing pores ranging from 100-1000 nm in diameter.

Limitations

Nanocarriers exhibit difficulty in handling, storage, and administration because of susceptibility to aggregation.

It has unsuitability for less potent drugs.

1.5.1.5 Quantum dots

Quantum dots are nanoparticles and are smaller than the wavelength of visible light. They can impart new properties while remaining
invisible themselves. The quantum dots luminesce under ultraviolet light, with size of the dots controlling its color. For example, 2 nm quantum dots luminesce bright green, while 5 nm quantum dots luminesce red. Nanoparticles of cadmium selenide (quantum dots) glow when exposed to ultraviolet light. When injected, they seep into cancerous tumours. The surgeon can see the glowing tumor, and use it as a guide for more accurate tumor removal. They fluoresce or stay much longer than dyes conventionally used for tagging cells. Dots are tagged to proteins and their glow enables the identification of specific proteins or DNA making it possible to diagnose various diseases.

When DNA in a test sample binds with a specific DNA on a quantum dot probe, the sample fluoresces under UV radiation and this signal can then be analyzed. This technique can be designed to detect genes of harmful pathogens ranging from staphylococcus to anthrax. The development of new and novel nano-sized sensors is underway that can detect and diagnose cancer in the early stages, when there are only a few thousand-cancer cells in the body. A few drops of the patient's blood is placed on the sensor test chip. The chip contains thousands of nanowires that can detect proteins and other biomarkers left behind by cancer cells.

1.5.2 Catalytic Applications of Metal Colloids

Metal nanoparticles are known for its potent activity in the area of catalysis. These novel materials have a very large specific surface area, consequently a large percentage of catalyst’s metal atoms are available to the substrates leading to higher reactivity and selectivity. Numerous investigations had been performed to probe the metal nanoparticle as catalysts in various organic reactions. Nanosized Pd colloids generated in-situ by reduction of Pd(II) to Pd(0) are involved in the catalysis of phosphine-free
Heck and Suzuki reactions. Coordinating polymers such as poly(vinyl-2-pyrrolidone) have shown to protect nanostructured metal particles that have an average diameter of ca.1-3 nm and a narrow size distribution. The resulting materials are effective catalysts for olefin hydrogenation, nitrile hydration, photoinduced electron transfer and Suzuki reactions. Au/Pd and Pd/Au systems on a TiO\textsubscript{2} support have been used in stabilized and nonstabilized forms as heterogeneous catalysts for the hydrogenation of hex-2-yne to cis-hex-2-ene. A new class of heterogeneous catalyst has emerged with the incorporation of mono and bimetallic nanocolloids in the mesopores of MCM-41 or via the entrapment of pre-prepared colloidal metal in sol-gel materials. They were found to be active catalyst in the hydrogenation of cyclic olefins such as cyclohexene, cyclooctene, cyclododecene, and norbornene.

1.5.3 Fuel Cell Catalysts

‘Fuel cell technology’ allows the direct conversion of chemical energy into electric energy. The fuel cell is an electrochemical reactor where the catalyst systems are an important component. Nanostructured metal colloids are very promising precursors for manufacturing multimetallic fuel cell catalysts that are truly nanosized (i.e. < 3 nm) and have high metal loadings (30 wt-% of metal) with less amount of catalysts. The decreasing of the amount of catalysts can be achieved mainly by decreasing the size of particles. This leads to a better use of catalysts, as it is clear that only metallic atoms present on the surface can be involved in the different adsorption steps, which are always part of the electrocatalytic process. Hydrogen fuel cell catalysts rely on pure Pt, whereas Pt-alloy electrocatalysts are applied for the conversion of reformer gas or methanol into electricity. Colloidal Pt/Ru catalysts are currently under widespread investigation for low temperature (80°C) polymer membrane fuel cells.
1.5.4 Sensor Applications

Sensors can be classified as chemical and biosensors, which depend upon the nature of electro-active material (catalyst) used for the sensor applications. The materials used for the detection of organic or inorganic substrate are known as sensor materials. The materials used may be non-biological or biological substrate. If non-biological substrates such as metal electrodes, polymer stabilized metal nanoparticle electrodes etc., are used as sensor materials, then they are known as chemical sensors. If biological materials such as glucose oxidase (GOx), other enzymes etc., are used then they are known as biosensors.

The specific physical properties (magnetic, optical, thermal etc.,) of very small particles have opened a completely new field of applications for bioelectronics. The changes in the functionality of spherical nanoparticles by modifying the surface made them extremely interesting. A controlled interaction of biomolecules with the particle surface plays a crucial role in their ultimate utility. Hence, a controlled interaction of biomolecules with various nanoparticles is the most important for modern bioelectronics and life sciences. This includes processes using surface-activated magnetic nanoparticles for magnetic biosensing, imaging, and hyperthermia treatment. Another class of applications is found in particle plasmon behavior. Small gold particles show a change in plasmonic absorption and/or a shift in wavelength when affinity reactions take place at their functionalized surface when treated with biomolecules. These affinity reactions indeed provoke a change in dielectric constant and as such can be used to monitor the interactions by light in a transmission plasmonic biosensor.
Transmission plasmon biosensor is based on transparent sensing substrates coated with metal nanoparticles (e.g. gold or silver). The detection principle is based on the difference in absorption of light when antigens bind to the antibody-coated surface or not. This novel nanoparticle-based biosensing principle can be seen as an easy and cost-effective alternative for conventional biosensing techniques, using less reagents, no carcinogenic agents, enabling shorter assay times and detailed monitoring of antibody immobilization. Hence, the system is optimized and tuned towards different applications such as the detection of DNA, food contaminants (i.e. antibiotic residues) and screening of cancer markers (i.e. prostate specific antigen).

1.6 CARBON NANOTUBES

Perhaps the most interesting nanostructures widely investigated with huge applications are the carbon nanotubes. A nanotube may consist of one tube of graphite (a single-walled nanotube, SWNT) or a number of concentric tubes, called as multiwalled nanotubes (MWNTs). Although carbon nanotubes are not actually made by rolling graphite sheets, it is possible to explain the different structures by considering the way graphite sheets might be rolled into tubes as shown in Figure 1.6. The structure of the nanotube influences its properties, including conductance, density and lattice structure. It is known that some nanotubes are conductors, while some are semiconductors. There are a variety of structures of carbon nanotubes, and these various structures have different properties.
Figure 1.6  Shows different schematic representation of SWCNTs and MWCNTs

1.6.1  Fabrication and Properties of Carbon Nanotubes

Carbon nanotubes can be made by laser evaporation, carbon arc methods and chemical vapor deposition. Carbon nanotubes have the most interesting property that they are metallic or semiconducting, depending on the diameter and chirality of the tube. In the metallic state, the conductivity of the nanotubes is very high. One reason for the high conductivity of the carbon nanotubes is that they have very few defects to scatter electrons and thus have very low resistance. High currents do not heat the carbon tubes the same way as copper wires. Nanotubes also have a very high thermal conductivity,
almost a factor of 2 more than that of diamond. This means that they are also very good conductors of heat. Carbon nanotubes are very strong and its carbon-carbon bonds are sp$^2$ hybridized. The tensile strength of carbon nanotubes is about 45 billion pascals. High-strength steel alloys break at about 2 billion pascals. The carbon nanotubes are about 20 times stronger than steel.

1.6.2 Applications of Carbon Nanotubes

The unusual and attractive properties of carbon nanotubes make its possible applications in wide areas of technology ranging from battery electrodes, electronic devices, reinforcing fibres for advanced composites and computer hardwares as interconnects to carry large currents without heating since carbon nanotubes with diameters of 2 nm have extremely low resistance. They can also serve as heat sinks, allowing heat to be rapidly transferred away from the chip due to high thermal conductivity.

1.6.2.1 Biomedical applications

Single walled carbon nanotubes can be cut into smaller sections using sonication in a mixture of concentrated sulfuric acid and nitric acid. This process makes the tubes opened. Once opened, tubes can be filled with a variety of materials, for example, enzymes, protein and DNA. This type of research is expected to pave an avenue in drug delivery system to cure infected organs. A suitable drug can be inserted into the hollow space of the nanotubes, when injected into the body, the drug will start operating slowly at the infected sites.

Controlled and targeted drug delivery represents one of the frontier areas of science. Drugs can be encapsulated in a variety of carriers. The carrier can be carbon nanotubes, a nanotube made of something other than
carbon, a structure like a silicon wafer with antibodies or some other molecules that will bind to the drug. Nanoparticles can enter the damaged cells and release enzymes that initiate the cells auto destruct sequence, known as ‘apoptosis’. Alternatively they can also release enzymes to repair the infected cells and return it to normal functioning. Drugs in nanocrystalline form can be administered in smaller doses because they can be delivered directly to the tissue and in controlled doses according to the patient’s requirements.

1.6.2.2 Fuel cells

Carbon nanotubes have applications in battery technology. Lithium, which is a charge carrier in batteries, can be stored inside nanotubes. It is estimated that one lithium atom can be stored for every six carbons of the carbon nanotubes. Storing hydrogen in nanotubes is another interesting application and is related to the development of fuel cells as sources of electrical energy for future automobiles. A fuel cell consists of two electrodes separated by a special electrolyte that allows hydrogen ions, but not electrons, to pass through it. Hydrogen is sent to the anode, where it is ionized. The free electrons travel through an external circuit to the cathode. The hydrogen ions diffuse through the electrolyte to the cathode, where electrons, hydrogen and oxygen combine to form water. The system needs a source of hydrogen, which can be obtained from the stored hydrogen inside the carbon nanotubes. It is estimated that the carbon nanotubes can store 5% -10% of hydrogen in it (Dillon et al 1997).

1.6.2.3 Catalysis

A catalyst is a material, typically a metal or alloy that enhances the rate of a reaction between chemical reactants. Nanotubes serve as catalysts for
some chemical reactions. For example, nanotubes with ruthenium metal bonded to the surface have been demonstrated to have a strong catalytic effect in the hydrogenation reaction of cinnamaldehyde in the liquid phase compared with the effect when the same metal Ru is attached to other carbon substrates. Chemical reactions have also been carried out inside nanotubes, such as the reduction of nickel oxide NiO to the base metal Ni. Cadmium sulfide crystals have been formed inside nanotubes by reacting cadmium oxide (CdO) crystals with hydrogen sulfide gas at 400°C.

1.6.3 Literature review

Literature review related to the synthesis and characterization of various metal nanoparticles including their electrocatalytic and biomedical applications were reviewed and were incorporated at an appropriate places in the thesis.

1.7 IMPORTANCE OF THE PRESENT INVESTIGATION

Nanoparticles and nanoparticle based materials have many unique properties that can be exploited in many areas of science and technology. The world of colloid and cluster has risen to this challenge and is beginning to find ways to organize nanometer sized particles on the micron and submicron scale. Nanoparticles, which display unique functions, can be fashioned from many materials and have a wide functional diversity very different from their bulk counterparts, with much of their electronic, optical and catalytic properties originating from their quantum scale dimensions. Though nanotechnology finds its application in a variety of areas, research focused on fuel cells and drug deliveries, especially for non operable diseases like cancer are one of the frontier areas of nanomaterials currently investigated.
Targeted nano drug carriers reduce drug toxicity and provide more efficient drug distribution. Nanocarriers hold the promise to deliver biotech drugs over various anatomic extremities of body such as blood brain barrier, branching pathways of the pulmonary system, and the tight epithelial junctions of the skin etc. Nanocarriers better penetrate tumors due to their leaky constitution, containing pores ranging from 100-1000 nm in diameter.

New and novel nano-sized sensors are underway that can detect and diagnose cancer in the early stages, when there are only a few thousand cancer cells in the body. Nanotechnology is improving the capability of biochips, devices that when implanted in the body, could offer ways of treating life-threatening conditions, including cancer and heart disease.

Researchers have come up with a unique method of detecting cancer in which gold nanoparticles were bound to a specific antibody displayed a 600 percent greater affinity for cancer cells than for noncancerous cells. The change in the absorption spectrum of the gold nanoparticles allows the differentiation between cancer cells and noncancerous cells. Many cancer cells have a protein, known as epidermal growth factor receptor (EFGR), all over their surface, while healthy cells typically do not express the protein as strongly. By conjugating, or binding, the gold nanoparticles to an antibody for EFGR, suitably named anti-EFGR, the researchers were able to get the nanoparticles to attach themselves to the cancer cells and in a living cell to make cancer detection easier. Hence, the gold particles are useful for cancer detection and remission of cancer. Gold nanoparticles have demonstrated remarkable properties, displaying non-toxicity to human cells and biocompatible.

Another important objective is to develop novel electrodes for fuel cell constructions since it is the most essential for modern life of
industrialized nations to obtain alternatives energy in order to fulfill their requirements. Due to environmental and economic concerns associated with fossil fuels, the world needs a clean, abundant, and economically attractive alternative source of energy. Hence, scientists are currently trying to find out ways to reduce the amount of precious metals needed for fuel cells.

1.8 SCOPE OF THE PRESENT INVESTIGATION

In the current investigation, work is mainly focused on the synthesis of nanoparticles and nanocomposites with a special emphasis on the role of nanomaterials in fuel cells and biomedical applications.

Objectives of the present investigation

The objectives of the present investigations are detailed below:

1. To investigate the role of metal nanoparticles towards electrocatalytic oxidation of simple organic molecules. The following attempts were made to use two different conductive polymers namely polypyrrole (PPy) and polythiophene (PTh) as catalysts support for fuel cell applications.
   o Synthesis of citrate ion stabilized Pt(0) and Pt-Pd(0) bimetallic nanoparticles using trisodium citrate salt as reducing agent.
   o Fabrication of monometallic and bimetallic nanoparticles decorated conductive polymer electrodes utilizing previously synthesized Pt(0) and Pt-Pd(0) nanoparticles.
   o Probing the oxidation of industrially potent fuels like methanol, ethylene glycol, formaldehyde and formic acid
utilizing the fabricated electrodes [nanoparticles decorated polymers].

2. To study the efficiency of carbon nanotubes (CNTs) and carbon nanotubes-polymer composites as catalyst support for the nanoparticles towards the electrocatalytic oxidation of organic compounds like methanol, ethylene glycol, formaldehyde and formic acid. The following attempts were made for fuel cell applications using carbon nanotubes and carbon nanotubes-polymer composites as catalysts support.

- Synthesis of metal nanoparticles like Pt, Pt-Pd and Pt-Ru decorated carbon nanotubes (Pt/CNT; Pt-Pd/CNT and Pt-Ru/CNT) and Pt nanoparticles decorated carbon (Pt/C) for comparative studies using glycerol as reducing agent.

- Synthesis of conductive polymers and carbon nanotubes-conductive polymer (polypyrrole and polythiophene) composites as supporting materials (PPy/CNT and PTh/CNT) using ammonium persulphate and ferric chloride as oxidizing agent for pyrrole and thiophene respectively at 0°C under sonication.

- Decoration of metal nanoparticles like Pt, Pt-Pd and Pt-Ru on carbon nanotubes-polymer composites (Pt/PPy-CNT; Pt-Pd/PPy-CNT; Pt-Ru/PPy-CNT and Pt/PTh-CNT; Pt-Pd/PTh-CNT; Pt-Ru/PTh-CNT) and Pt nanoparticles decorated polymer (for comparative studies) using formaldehyde as a reducing agent.

3. To synthesize amine functionalized POSS, POSS stabilized metal (Pt(0)/POSS, Au(0)/POSS and Ag(0)/POSS) nanoparticles by wet chemical techniques and to study their role in the oxidation of glucose as well as their antimicrobial activity.
4. To synthesize the natural drugs and their derivatives such as turbomycin, p-methyl turbomycin and p-methoxy turbomycin and to study their effect of interaction with Au(0) nanoparticles. Further, the microbial activity of in vitro antibacterial drugs capped nanoparticles against various strains of gram-positive and gram-negative organisms like *Micrococcus luteus*, *Staphylococcus aureus* and *E. coli* is investigated.

5. To investigate the antileukemic drugs (namely 6-mercaptopurine, 6-thioguanine and 5-fluorouracil) capped nanoparticles towards in vitro antibacterial and antifungal behaviour against various strains of gram-positive, gram-negative and fungal organisms like *Micrococcus luteus*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *E. coli*, *Aspergillus fumigatus* and *Aspergillus niger*.

6. To study the antileukemic activity of Au nanoparticles capped antileukemic drugs for practical application (Cell line-In vitro studies).

The thesis is divided into eight chapters. A brief summary of the chapters has been discussed in the following paragraphs. Chapter one reviews the introduction about the nanomaterials, various methods of synthesis, their importance and applications. This chapter highlights the overall literature survey on different types of synthesis of metal nanoparticles like wet chemical route, sonochemical method and electrochemical synthesis etc., followed by some of the important characterization techniques used for nanoparticles. Further, the imperative applications of metal nanoparticles in various disciplines like electrocatalysis, targeted drug delivery, sensors etc., have also been included in this chapter, besides the scope of the present investigation.
Chapter two presents the various chemicals, materials and instruments used in the present work. The experimental procedures adopted to synthesize organic materials, metal nanoparticles and fabrication procedure of electrodes for electrochemical oxidation are included in addition to the details of utilization of metal nanoparticles for antimicrobial and anticancer studies.

In Chapter three and four, the role of metal nanoparticles in electrocatalytic reactions towards fuel cell applications has been elucidated. A special emphasis is given on the role of catalyst supports in the electrocatalytic reactions. In this regard, various supports have been used viz. conductive polymers (polypyrrole, polythiophene), carbon nanotubes (SWCNT & MWCNT) and polymers-CNT composite materials. Development of novel materials in fuel cells is one of the intrigued areas of research and in this regard, we have utilized these materials in the oxidation of industrially imperative fuels.

Chapter three describes the electrocatalytic applications of conductive polymers supported metal nanoparticles for fuel cell applications. Two different conductive polymers were used in the present work viz. polypyrrole and polythiophene as a supporting matrix for the nanoparticles fabricated on Indium doped Tin Oxide electrodes (ITO/PPy or ITO/PTh). The metal nanoparticles supported with polymers were then used as a probe for studying the oxidation of various organic compounds like methanol, ethylene glycol, formic acid and formaldehyde. The particles in nanometer sized domain are electrodeposited during the course of electro-synthesis of polymer which produces a homogeneous and uniform distribution of catalyst particles onto the polymer electrodes. In addition, the use of nanometer-sized particles provides a larger surface area thus improving the catalytic activity and also helps in reducing the quantity of utilization of precious metals. The electrodes
were modified with two different types of nanoparticles catalysts viz. Pt monometallic (Pt(0)) and Pt-Pd bimetallic nanoparticles (Pt-Pd(0)).

Chapter four explains the studies on the role of carbon nanotubes and carbon nanotubes-polymer nanocomposite materials towards fuel cell applications. This study is an extension of work presented in chapter three. In this chapter, two different experiments have been carried out, one involving the role of metal nanoparticles decorated carbon nanotubes and the other, metal nanoparticles decorated conductive polymers/carbon nanotube composites. The present investigation describes a new route for the spontaneous Pt, Pt-Ru and Pt-Pd nanoparticles deposition on surface-oxidized carbon nanotube sidewalls using glycerol as reducing agent by conventional heating method. In view of the good catalytic activity of the conductive polymers as observed from the previous chapter, the work has been extended to study the activity of carbon nanotubes-polymer composite materials towards electrocatalysis reactions. Hence the second part of the investigation involves the chemical synthesis of carbon nanotubes-conductive polymer composites as the supporting material for different oxidation reactions. The decorations of mono and bimetallic nanoparticles (Pt, Pt-Ru and Pt-Pd) on carbon nanotubes-conductive polymer composites were done using formaldehyde as reducing agent. Comparative studies have been carried out using Pt nanoparticles decorated polymers in the absence of carbon nanotubes.

The applications of metal nanoparticles in fuels cell reactions viz. the oxidation of industrially important fuels like methanol, ethylene glycol, formic acid and formaldehyde have been studied using nanoparticles like Pt, Pt-Pd and Pt-Ru are dispersed onto various support materials like (a) carbon nanotubes (SWCNTs and MWCNTs), (b) polypyrrole/carbon nanotubes composite (PPy/CNT) and (c) polythiophene/carbon nanotubes composite (PTh/CNT).
With noteworthy developments in the understanding of nanosystems, research efforts are being concentrated on integrating them with biology and medicine. Resistance of bacteria to bactericides and antibiotics is a subject of immense interest due to the development of resistant strains. In view of this, the present work has been extended to study the effect of metal nanoparticles for antimicrobial activity and oxidation of glucose.

Chapter five is devoted in the synthesis of amine functionalized POSS and various metal nanoparticles/POSS composites. In this regard, Ag/POSS, Au/POSS, Pt/POSS nanocomposites are synthesized and their antimicrobial activities have been investigated. In view of their potential activity, simple non-enzymatic biosensors has been constructed using metal nanoparticles-POSS composites (NPs/POSS) modified electrodes and are utilized as a probe for investigating the electrooxidation of biologically important molecule, glucose. The working electrodes namely Ag/POSS/graphite, Au/POSS/graphite and Pt/POSS/graphite have been made by mechanical immobilization on the graphite electrode to form a thin film of the catalyst on the electrode surface. The efficiency of POSS-nanoparticles modified electrodes towards the oxidation of glucose has been studied and reported in this chapter.

Chapter six focuses the applicability of gold nanoparticles in the detection of antibiotics and its microbial activity. In this section, the chemical synthesis and characterization of three different substituted coloured triaryl cation antibiotics have been reported. The complexation of antibiotics has been carried out with citrate stabilized gold nanoparticles. The analytical techniques like UV-visible spectrum, FT-IR, cyclic voltametry and transmission electron microscopic analysis have been used for investigating the effect of interaction of these drugs with gold nanoparticles. Further the antibacterial efficacy of drug coated gold nanoparticles has been studied.
against various strains of gram-positive and gram-negative bacteria and was found that the turbomycin protected gold nanoparticle complexes acted as better antimicrobial agents than turbomycin alone.

Chapter seven illustrates the biological assays of anticancer drugs capped nanoparticles and their role in antimicrobial and anticancer activities. Three different antileukemic drugs namely 6-mercaptopurine, 6-thioguanine, and 5-fluorouracil have been selected for the present study. The binding interactions of these drugs with gold nanoparticles have been studied using various analytical techniques. The antibacterial and antifungal efficacies of drug coated with metal nanoparticles have been studied against various strains of gram-positive, gram-negative bacteria and fungal organisms. The toxicity and anticancer activity behaviour of drugs coated nanoparticles are investigated through in vitro studies (cell line). The studies indicated that drugs coated metal nanoparticles show better antibacterial, antifungal and anticancer activities than pure drugs alone, showing that the gold nanoparticles act as a good drug carrier. The growth inhibition of bacteria and fungi was found to be more in drug-nanoparticle formulation when compared with pure drug moiety. Thus gold nanoparticles with drug formulations has a profound effect on the antibiotic and anticancer activities, increasing the efficacy in drug delivery, which shows that the gold nanoparticles could be used as an effective carrier for these antibiotics and anticancer drugs.

Chapter eight presents the summary and conclusion of the preceding chapters including the extension of the present work in future.