CHAPTER 1

INTRODUCTION
1.1 What is nanotechnology?

"Nanotechnology" has become the modern day buzzword in new technological development. It describes many types of research in which the characteristic dimensions of the materials of interest are less than about a micron, or 1,000 nanometers (nm). A nanometer is one billionth of a meter (0.000,000,000 m). Nanotechnology, therefore, involves nanoparticles and nanostructures. Nanoparticles may be individual sub-micron particles of a metal, a metal oxide or an organic complex of a metal. Colloidal-size metal and semiconductor materials in the 1 nm to 20 nm range have been an intriguing area of materials research because they represent a transition range between molecular and bulk properties. In this size range, unique physical, optical and electronic properties are said to be exhibited that are not present in the bulk phase. This phenomenon opens up a completely new perspective for materials design that benefits from the introduction of not only particle size but also particle morphology as new powerful parameters. Challenging innovations in the field of nanomaterials can give rise to revolutionary development like a drastic reduction in the necessary amount of traditional materials and subsequently of the cost.

Scientific interest in highly dispersed small metal particles could be traced back to the age of Faraday [1], who prepared gold colloids having beautiful color. Currently, small and highly dispersed metal or alloy particles with narrow size distribution are called metal or alloy nanoclusters. The properties of metal or alloy depend upon the type of motion of its electrons, which is confined by the space of the materials. According to quantum mechanical rules, electrons in nanoparticles behave like a “particle in a box” and hence will have quantum size effects on their physical properties. Therefore, there is a specific length scale, usually in the low edge region of nanodimension for metallic materials [2-4], below which the properties become sensitive to the physical size, giving birth to a number of novel and unique properties of the nanosized metal compared to their corresponding bulk materials.
1.2 Size and shape dependent properties of metal nanoparticles

The physical and chemical properties of metal nanoparticles depend upon several factors such as

(a) The particle size and particle dispersity,
(b) Structure of the particles
(c) The surface of the particles
(d) The shape of the particles
(e) The organization of the particles and their dispersity

Numerous studies on such size and shape dependent properties have been carried out in the last two decades [5-22]. The size dependent physical and chemical properties have been reviewed extensively by many scientists [23, 24]. These properties highlight many important aspects as follows;

(a) Electronic structure and properties (quantum size effects)
(b) Chemical reactivity
(c) Self-assembly of nanoparticles and
(d) Size dependant structural and thermodynamic properties such as bond length, melting point, and specific heat.

1.3 Electronic properties

When a metal particle with bulk properties is reduced to a size of a few dozen or a few hundred atoms, the density of states in the valence band and the conduction band, respectively decreases to such an extent that electronic properties change dramatically. In a metal, electrons are highly delocalized over a large space (i.e. least confined). This is a result of the fact that the separation between the valence and conduction bands vanishes rendering the metal its conducting properties [25]. Whereas, when the separation between the valence and the conduction band becomes comparable to or larger than kT, the metal becomes a semiconductor. When this confinement further increases the energy separation the metal becomes an 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. This results from the coherent oscillation of the free electrons from one surface of the particle to the other, and is called the surface plasmon absorption.
1.4 Optical properties

Silver nanoparticles are responsible for the yellowish color in stained glass windows. Gold particles are typically red. The spectroscopy of noble metal particles is dominated by the surface plasmon resonance, which is collective oscillation of the conduction electrons. The position and width of the plasmon band depend on a variety of factors, such as the size and shape of the particles, and their dielectric environment [26].

1.4.1 Mie theory

Light absorption by small metal particles is best described by Mie's theory [5]. The absorption spectrum of particles in a given solvent can be calculated from the optical constants of the bulk metal, although the absorption of the particles is often vastly different from that of the bulk metal itself [5]. The simplest case is when the particles are spherical and their size is small compared to the wavelength of light, and the particles are well separated in solution. Within the particle size of about 3-20 nm, the absorbance spectrum does not depend strongly on the particle size. This is because the particles are below the size at which higher order terms in the Mie formula for the absorption constant become significant.

\[
\alpha = \frac{16 \pi 10^6 M n_0^3}{\ln 10 \lambda \rho (\epsilon_1 + 2 n_0^2) + \epsilon_2}
\]

Thus, one has to regard only the dipole term, which depends only on the total metal concentration in the solution and not on the particle size. The absorption coefficient in mol⁻¹Lcm⁻¹ is calculated from the relation [5] where \( \lambda \) is the wavelength of light in nanometers, \( M \) and \( \rho \) are the molecular weight and density of the metal, \( n_0 \) is the refractive index of the solvent and \( \epsilon_1 \) and \( \epsilon_2 \) are the real and imaginary parts of the dielectric constant of the metal. When the size of the particles becomes smaller than the mean free path of the electrons, the absorption bands are broadened; this is accounted for by using size-corrected values of \( \epsilon \) [5].
\[ \varepsilon_1 = \varepsilon_{1\text{bulk}} + \left( \frac{\omega_p^2}{\omega^2} \right) \left( \frac{v_f}{R} \right) \]

where \( \omega \) is the light frequency, \( \omega_p \) the plasmon frequency, \( v \), the electron velocity at the Fermi level and \( R \) the particle radius (\( R/v_f \), mean time of the free movement of the electrons). Resonance with the incident light is reached at the wavelength, where the negative value of \( \varepsilon_1 \) of the metal is equal to twice the dielectric constant of the medium.

### 1.5 Magnetic properties

Nanoscale magnetic materials show novel properties that are markedly different from those of the bulk due to their very small size and fundamental change in the coordination, symmetry, and confinement [27]. For magnetic nanoparticles, the intrinsic magnetic properties are strongly influenced by the particle size, meanwhile they exhibit specific properties such as superparamagnetism and quantum tunneling of magnetization, [28, 29], which are regarded as unique features of magnetic nanoparticles. When reducing the size of magnetic nanoparticles, a transition from polydomain to single domain system takes place. If the particles of ferro or ferrimagnetic materials are smaller than the dimensions of a single domain (for Fe and Co is ca. 20 nm), thermal fluctuations will supersede the Weiss anisotropy above the blocking temperature. Such particles are called superparamagnetic [30]. Magnetic particles smaller than 10 nm are usually superparamagnetic and they do not aggregate because each particle is a single magnetic domain. Bimetallic nanoparticles in particular have raised a wide range of scientific interests because they may exhibit unique, synergistic properties or combinations of properties, which go beyond single components. Formation of alloy nanoparticles containing ferromagnetic \( 3d \) and noble metal elements of the platinum group becomes active with respect to the magnetic behavior of large magnetic moments and high magnetocrystalline anisotropy (i.e. Fe-Pt: \( K_a \approx 6.6 \times 10^6 \text{ erg/cm}^3 \)) of these particles [31].

### 1.6 Self-assembly of metal nanoparticles and formation of superlattices

The spontaneous organization of monolayer protected metal nanoparticles in periodic two-dimensional arrays is archetype of their approach which many of these
arrays demonstrating novel optical and electronic properties. The precise control of the primary structures of metal nanoparticles, such as size, shape, or composition enables one to fabricate secondary structures of nanoparticles which means the regularly ordered metal nanoparticles with well defined 1D, 2D or 3D spatial configuration. Since such ordered metal nanoparticles so-called superlattices are expected to show the novel properties that are not present in the isolated nanoparticles. Chemical self-assembly likely will become an important tool for the realization of integrated nanoscale electronics. In this respect, metal nanoparticles are potentially powerful minimum device components because their surfaces can be modified using a number of well-developed and relatively routine chemical attachment strategies.

The arrays of particles can be critically affected by their shape and size. The uniformity of arrays is determined largely by the size and shape and dispersity [32] as well as the degree of order within the close-packed domains. It should be noted that low size dispersity (5-10% relative standard deviation from the mean) is an important factor in the preparation of sterically stabilized colloidal nanoparticles. Moreover, the type of interaction between the nanoparticles in the self-assembly is also important. Atomic bonding occurs between outer shell (valence) electrons to form ionic, covalent, or metallic bonds, or mixtures of these. In most cases, the interatomic distance is fixed, while the bonding between nanoparticles is generated by a passivating surfactant whose length is variable: thus, the ratio of particle size to interparticle distance is adjustable. This is a parameter likely to determine the 3-D packing of the nanoparticles. The tunable interparticle spacing permits control over interparticle interactions, giving rise to novel tunable structural, optical, and transport properties. In the recent years, molecular recognition strategy has been used for the self-assembly of metal nanoparticles [33-35]. Self-assembly of metal nanoparticles can lead to formation of different types of superlattices. Figure 1.1 shows a schematic diagram explaining the different types of superlattices.

a) One dimensional (1D) superlattices: Ordering of metal nanoparticles for fabrication of 1D superlattices is one of the most challenging tasks since it is difficult to arrange metal nanoparticles into lower symmetry structures. Hence there have been rather few reports on 1D self assembly of nanoparticles. In general, template methods have been used for arranging metal nanoparticles in 1D configuration [36-40]. When
metal nanoparticles are arranged in a 1D configuration, they show a tunneling behavior, which can be useful in the building up of nanodevices such as single electron transistor and single electron memory.

b) Two-dimensional (2D) superlattices: As compared to 1D self-assemblies, 2D self-assemblies are more common and have been studied extensively. Perfect 2D superlattices can be built by the precise control of particle size and shape [41-46]. One of the most common strategies used for the formation of superlattices has been the use of thiols as protecting agents for the metal nanoparticles. The ligand length i.e. the thiol chain length can be varied for tuning the interparticle spacing between the metal nanoparticles in such superlattices. The control of the interparticle spacing is crucial for optimum utilization of these superlattices in optical, electronic and magnetic applications.

![Figure 1.1: Schematic diagram showing different types of self assembly](image)

The Langmuir-Blodgett technique has been effective in this regard. This technique has been effectively used for the large scale formation of metal nanoparticles having assembly areas expanding up to a few hundred square centimeters [47, 48].
Three dimensional (3D) superlattices: Three dimensional (3D) superlattices of metal nanoparticles consist of nanometer to micrometer sized structure made up of close packed metal nanoparticles. Multiple layer deposition has so far been the most commonly used technique for the fabrication of such 3D superlattices [49-52].

1.7 Applications

Metal nanoparticles hold great promise for advanced materials with new electronic magnetic and thermal properties as well as new catalytic properties. Recent and novel applications have been reported such as building electronic devices [53, 54], chemical sensors [55] nascent probes [56, 57], drug delivery [58] and diagnostics [59] and in high density magnetic nanodevices [60]. The noble metal nanoparticles present new opportunities for catalysis for as much as they can act as a bridge between homogenous and heterogeneous catalysts [61a]. For instance the colloidal metal particles of one to ten nanometer mean diameter with narrow size distribution showed enhanced activity and selectivity for the hydrogenation of olefins to dienes [61b-64]. Further more colloidal Pd nanoparticles serve as a good catalyst for Suzuki, Heck, Stille-type coupling reactions for C-C bond formation [65-68]. Platinum and gold nanoparticles catalyze the oxidation of L-Sorbose and CO respectively [69-71]. Apart from catalytic activity of Ag, poly(sodium acrylate) protected Ag nanoparticles show high activity in catalyzing the oxidation of ethylene to ethylene oxide. Ag nanoparticles play an important role in photographic processes [72-74] and in substrate for surface enhanced Raman spectroscopy [75, 76]. In addition, due to their large effective scattering cross-section and their non-bleaching properties Ag nanoparticles hold great promise in the field of single molecule labeling based biological assays [77] and as output enhancers in near field optical microscopy applications [78]. Noble metal particles have also found applications in protein colloid conjugates when they are used as markers and tracers in optical and electron microscopy [79, 80].

1.8 Synthesis of metal nanoparticles

A short review of some of the methods for obtaining nanometer sized metal nanoparticles is described here. Although metal nanoparticles can be produced easily in
any phase (solid, liquid or gaseous) they are often spherical in nature. However for many applications it is desirable to produce nanoparticles with high shape anisotropies.

1.8.1. Chemical reduction method

Chemical reduction method is one of the most common and facile methods for obtaining metal nanoparticles of desired size and shape. Non-spherical particles have been synthesized by chemical reduction method using surfactants or polymers that influence the thermodynamics and kinetics of crystal growth along a certain direction [81-83]. A number of chemical reducing agents are used. Some of the most commonly used reducing agents are sodium borohydride [84], hydrazine hydrate [85], hydrogen (H₂) [86], N, N’dimethylformamide [87], formaldehyde [88] etc. The control of the particle size is done by changing the ratio of nucleation rate to particle growth. Some solvents such as methanol, ethanol and iso-propanol can act as both a solvent as well as a reducing agent [89]. The refluxing of alcohols in the presence of stabilizers yields well-dispersed metal nanoparticles.

1.8.2 Electrochemical method

The pioneering work on electrochemical reduction method to produce metal nanoparticles was developed by Reetz et al [90]. The electrochemical reduction method offers a large-scale synthesis of metal nanoparticles. The size of the nanoparticles can be controlled by using a suitable stabilizer and by varying the current density. Metal nanoparticles can be easily prepared in organic solvents by this method.

1.8.3 Chemical vapor deposition technique

Chemical vapor deposition (CVD) precursor development is a method that is traditionally used in the synthesis of ceramics but recently the concept of CVD has been used in the synthesis of metal nanoparticles by using organometallic precursors instead of metal alkyls and alkoxides. This method uses precursors, such as coinage-metal mesityl complexes which lack halide contaminants. These precursors are heated up until the point of vaporization and then cooled with reactive gas that makes the metal atoms zero valent. As the mixture cools the metal atoms condense to form nanoparticles. Their size is controlled by the rate of cooling [91, 92].

1.8.4 Sonochemical method

High intensity ultrasound is a powerful tool for preparation of metal nanoparticles. The ultrasonic irradiation causes acoustic cavitations, which leads to the
formation growth and impulsive collapse of bubbles in a liquid. This leads to an increase in temperature and pressure in the bubbles.

There are three different reduction pathways under sonication

(a) Reduction by H atoms.
(b) Reduction by secondary reducing radicals formed by hydrogen abstraction from organic additives with OH radicals and H atoms.
(c) Reduction by radicals formed from the pyrolysis of the additives has been identified at the interfacial region between cavitation bubbles and the bulk solution.

Metal nanoparticles of Au [93], Ag [94] and Pt [95] have been successfully synthesized by the sonochemical reduction technique.

1.8.5 Microwave irradiation method

Recently the microwave irradiation technique has been used for the generation of noble metal nanoparticles [96, 97]. In principle, the microwave irradiation technique is a high temperature synthesis method. The generation of metal nanoparticles originates from the heating effect rather than the energy of the quantum of a microwave. Polar molecules can be heated quickly under the microwave irradiation. In comparison with conventional heating, more uniform nucleation and a shorter crystallization time will be achieved for the formation of colloids.

1.8.6 γ-Irradiation technique

Metal aggregates were first prepared by the radiolytic reduction method by Fujita in 1962 [98]. Twenty years later, the Belloni group and the Henglein group successfully synthesized metal particles by radiation induced reduction [99-103]. From then, this method has been well developed for synthesis of metal nanoparticles. Henglein et al have made a large contribution in this field of research. Noble metal nanoparticles of Ag [104], Au [105], Pd [106], Pt [107] etc and bimetallic alloys such as Ag-Au [108], Pd-Pt [109], Ag-Pt [110] etc. have been synthesized by this method. Other transition metals such as Fe, Co [111], Cu [112] and Ni [113] that have a very low reduction potential have been successfully synthesized by this method. In the recent years the radiolytic reduction technique has further advanced and is being used in combination with other techniques such as thermal, ultrasonic irradiation technique etc. to obtain desirable properties in a nanomaterial. γ-irradiation is a convenient way to
polymerize monomers without the use of any cross-linking agents. Metal particles embedded into such polymer matrices have received increased attention. Thus, this route has also been extended to synthesis of Ag/polyacrylamide [114], Ag/ poly(butylacrylate-co-styrene) [115], Ag/polyacrylonitrile [116] and Cu/polyacrylamide [117]. Combining \(\gamma\)-irradiation with the liquid crystal template method has lead to the synthesis of Pt metal in hexagonal liquid crystals [118]. Ever since the importance for obtaining non spherical or shape controlled synthesis has increased, a number of scientists have tried using \(\gamma\)-irradiation technique for the preparation of metal nanoparticles of different shapes. However there has been relatively less number of reports on this kind of work. While the preparation of intended nanomaterials can be achieved by a simple technique of \(\gamma\)-irradiation, understanding of reaction mechanism is important. Hence the pulse radiolysis technique was invented and used for the investigation of mechanism of formation of metal nanoparticles. The mechanism of formation and growth of Ag clusters [119], Au clusters, [120], have been studied by pulse radiolysis technique.

The \(\gamma\)-irradiation method has some advantages such as:

(a) The reaction proceeds at room temperature and ambient pressure

(b) Unlike chemical reduction method, no impurities or unwanted reaction products are obtained.

(c) As there is an instantaneous distribution of the reducing radicals in the solution particle size and size distribution can be easily controlled and

(d) The particle size can also be controlled by the amount of dose observed by the precursor solution.

1.8.7 Photochemical Technique

The photochemical reduction method involves the use of UV irradiation for the reduction of metal ions to metal nanoparticles. Some of the earliest work done using UV irradiation for the synthesis of metal nanoparticles has been carried out in aqueous solution [121-125]. In the recent years new strategies have been applied to the synthesis of metal nanoparticles by this method. Ever since the importance of shapes and size-controlled synthesis has increased, the photochemical method has proved to be one of the most facile and simple technique for obtaining metal nanoparticles in various shapes such as nanoplates, nanorods, nanowires etc. The UV reduction has been used to obtain long Au nanorods [126], beautiful Ag dendrites [127] and large thin Au nanoplates with
triangular or hexagonal shapes [128]. UV irradiation has been carried out in reverse microemulsions in the presence of surfactants or polymers to yield metal nanoparticles of Au, Ag and Pt [129-131]. Esumi, et al. have successfully prepared Au nanoparticles stabilized by block copolymers, polyelectrolytes and dendrimers [132]. Some of the strategies employed in UV photolysis method are as follows:

(a) The use of photosensitizers
(b) Seed method for generation of larger particles
(c) Change of reaction parameters for size control
(d) Light induced transformation to different shapes

Among the various techniques discussed we have chosen to use the γ-irradiation method and the photochemical reduction technique.

1.9 Bimetallic nanoparticles

Bimetallic nanoparticles posses new properties, which arise due to synergy between two metals which form the particles. Hence, bimetallic nanoparticles have better properties as compared to their monometallic counterparts. Table 1.1 shows a list of bimetallic metal nanoparticle systems, which have been successfully prepared by γ-irradiation and photochemical reduction technique.

Table 1.1 List of bimetallic metal nanoparticle systems prepared by γ-irradiation and photochemical reduction technique.

<table>
<thead>
<tr>
<th>Noble metal</th>
<th>Synthesis technique</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Au(core)Ag(shell)</td>
<td>γ-irradiation</td>
<td>[133]</td>
</tr>
<tr>
<td>Au(core)Ag(shell)</td>
<td>UV-irradiation</td>
<td>[134]</td>
</tr>
<tr>
<td>Au(core)Pt(shell)</td>
<td>γ-irradiation</td>
<td>[135]</td>
</tr>
<tr>
<td>Pt(core)Au(shell)</td>
<td>γ-irradiation</td>
<td>[136]</td>
</tr>
<tr>
<td>Ag/Pt alloy</td>
<td>UV-irradiation</td>
<td>[137]</td>
</tr>
<tr>
<td>Ag/Pt alloy</td>
<td>γ-irradiation</td>
<td>[138]</td>
</tr>
<tr>
<td>Ag/Pd alloy</td>
<td>UV-irradiation</td>
<td>[139]</td>
</tr>
<tr>
<td>Au/Pt alloy</td>
<td>γ-irradiation</td>
<td>[140]</td>
</tr>
</tbody>
</table>

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1.10 Stabilization of metal nanoparticles

Metal nanoparticles can be stabilized by various stabilizers, which can be divided into four types:

(a) Polymers
(b) Ligands and surfactants
(c) Solvent or anions
(d) Solid supports

A short review of the stabilizers listed above is described in the following section. Their mechanism of stabilization and the literature survey of the use of these stabilizers in the γ-irradiation and photochemical reduction technique have been discussed.

1.10.1 Polymers

A polymer consists of a non-polar chain and a polar head group. γ-radiolysis method has proved to be an excellent technique by which metal nanoparticles could be well dispersed into a polymer matrix. Metal nanoparticles embedded into a polymer matrix could be synthesized in-situ by using γ-rays for the radiation reduction of silver ions and the radiation polymerization of the monomer simultaneously [141]. Changing the polymer/metal ratio can yield shape control over the metal nanoparticles. An organic monomer taken into a solution self organizes into micelle like aggregates with an inner hydrophilic region and an outer hydrophobic part or chain. Such micelle like aggregates can polymerize to polymer spheres with an inner hydrophilic region under γ-irradiation. This preorganized polymer matrix can act as a template or nanoreactor for the stabilization of metal nanoparticles into them. In this approach γ-irradiation offers an ideal means by which polymerization and formation of metal nanoparticles in the polymer matrix takes place in-situ at room temperature.

1.10.2 Ligands and surfactants

Surfactants have a characteristic molecular structure consisting of a lyophobic group (hydrocarbon chain) and a lyophilic group (functional group). This amphiphilic nature of a surfactant causes the concentration of the surfactant at the surface thereby reducing the surface tension of the solvent. It leads to orientation of the molecule at the surface with its lyophilic group in the solvent medium and its lyophobic group oriented away from it [142, 143].
1.10.3 Solvents or anions

Bare or “unprotected” metal nanoparticles are prepared in the absence of any protecting agent, they are however not really unprotected but are stabilized by the solvent molecules or simple anions that are adsorbed over their surface. These metal nanoparticles are “resoluble” in many other organic solvents. Anions such as $\text{OH}^-$, $\text{SO}_4^{2-}$, $\text{H}_2\text{PO}_4^-$, and $\text{CO}_3^{2-}$ are known to stabilize gold nanoparticles efficiently [144, 145]. Large anions such as heteropolyanions (i.e. polyoxometalates) are also known to be efficient stabilizers for many noble metal nanoparticles.

1.10.3.1 Polyoxometalates (POM)

Polyoxometalates (POMs) are discrete, nanoscale (0.6-2.5 nm) molecular oxygen-metal clusters containing early transition metal cations $M = (\text{V, Nb, Ta, Mo, or W})$ in an oxygen-coordinated octahedra, $\text{MO}_6$. By sharing edges and corners, these octahedra usually form a highly symmetrical structure of general formula $X_mM_yO_z^-$, where $X = (\text{B, Si, Ge, P(V), As(V)},$ and some other elements) are the so-called heteroatoms. POMs adsorbed on metal surfaces have many promising technological applications. These include, among others, new heterogeneous catalysts for industrial oxidation of hydrocarbons, new electrocatalysts for hydrogen production and oxygen reduction in fuel cell applications, new electron transfer mediators for chemical sensors, and new corrosion inhibitors for replacing the still widely-used yet toxic chromate inhibitors.

The unique primary structures of POM result in many “value-adding” properties advantageous to processing that distinguish POMs from metallic oxides and conventional compounds [146, 147]. These include diverse molecular composition and aesthetically appealing geometric shape, redox reversibility and tunable redox potentials, strong acidity, high solubility, and good structural and thermal stability. Thus, POM stabilized metal nanoparticles can be of fundamental importance for its current and future practical applications that spread over diverse fields such as catalysis, chemical/biological sensing, corrosion inhibition, geochemistry, and environmental chemistry as well as clinical chemistry.

1.10.4 Solid supports

Supported nanoparticles too have been prepared by gamma irradiation. In such studies meal nanoparticles are either synthesized ex-situ and then they are loaded over
the solid support or irradiation of the metal precursors in-situ after adsorbing them over the supporting material. Ag clusters supported on zeolites have been successfully studied by this method [148]. The ionizing radiation can easily penetrate into the pores of the zeolite and homogenous reduction of metal ions even in the smallest of pores is possible. Irradiation of H$_2$PtCl$_6$ solution present in mesoporous materials lead to the formation of uniform Pt nanowires [149]. Ag nanoclusters have been prepared inside NaY zeolite and their formation has been studied by optical absorption spectroscopy and ESR. Kapoor et al have demonstrated the formation of small Pt nanoparticles in side the pores of NaA zeolite and their activity towards oxidation of cyclohexane [150].

1.1.0.4.1 Zeolites

Zeolites form an extraordinary, diverse and interesting class of inorganic polymers. They have continued to fascinate scientists for decades due to the immense opportunities they offer for research. They have benefited the chemical industry equally, in numerous ways. Recently, their range of application has widened considerably, more noticeably as heterogeneous catalysts, catalyzing a number of organic reactions. Zeolites are crystalline hydrated alumino-silicates, possessing a rigid framework based on an infinitely extending three-dimensional network of Si$_4$O$_{12}$ and AIO$_4$ tetrahedra, linked through oxygen atoms. Within this framework are present well-defined channels and cavities of specific dimensions rendering them microporous. The negative charge on the AIO$_4$ tetrahedron is compensated by cations, resulting in an electrically neutral framework. The crystallographic unit cell of a zeolite may be represented as M$_{2x/n}$[(Al$_2$O$_3$)$_x$(SiO$_2$)$_4$].zH$_2$O where ‘M’ represents exchangeable cation of ‘n’ valency generally from group I or II, rare earth ions or an organic species and ‘z’ gives number of water molecules [151, 152]. Among the large number of natural and synthetic variants of zeolites, Faujasite (Y zeolite) is the single largest type of zeolite industrially used.

The structure of Y zeolite consists of a negatively charged, three dimensional framework of SiO$_4$ and AIO$_4$ tetrahedra, joined to form an array of truncated octahedral (β-cages/sodalite cages), which in turn are joined at the octahedral faces by hexagonal prisms resulting in tetrahedral stacking, creating α-cages or supercages with a diameter of 13Å. These supercages are connected through 12-membered rings (7.4 Å diameter) to form the large pore system of the zeolite. Besides the structure also comprises of a
small pore system made up of sodalite cages and the connecting hexagonal prisms. Figure 1.2 shows the schematic diagram representing the structure of faujasite (Y).

![Figure 1.2: Cage like structure of Faujasite Y](image)

### 1.11 Scope of the thesis

The brief literature survey presented here fairly describes the importance of metal nanoparticles and provides opportunities in this area for innovative research and development. We feel it is possible to contribute in the mechanistic aspect of metal nanoparticle formation, their stability, properties and applications. In the scope of this work we have covered Ru, Pt, Ag and Au metal nanoparticles. We have used γ-radiolysis, UV photolysis, pulse radiolysis and chemical reduction methods for the preparation of stabilized metal nanoparticles. Overall the motivation has been to use γ-irradiation and UV irradiation to reduce metal ions to metal atoms without the use of additional reducing agents.

A brief literature survey presented in the beginning fairly describes the importance of metal nanoparticles, their preparation, characterization and the size dependent physical and chemical properties and shows the opportunities in this area for innovative research and development. In the scope of this work we have considered synthesis, structure, stability and morphology of Ru, Pt, Ag and Au metal nanoparticles.
Chapter 1

We have used γ-radiolysis, UV photolysis, pulse radiolysis and chemical reduction methods for the preparation using i) polymers, ii) solid supports like zeolites, iii) surfactants or co-ordination ligands and iv) solvents or anions as stabilizers. The work has been described in different chapters.

The basic principles in synthesis and characterization techniques have been explained. The radiolysis, photolysis and chemical reduction methods have been described. The systems have been carefully chosen to include i) polymers, ii) solid supports like zeolites, iii) surfactants or co-ordination ligands and iv) solvents or anions and also their modified forms as stabilizers. Different chapters have been organized based on the nature of these stabilizers. The nanomaterials were characterized by UV-vis, XRD, TEM, SEM, XPS, TPR, and FTIR spectroscopy techniques.
Chapter 1

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Ph.D. Thesis
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Chapter I

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