CHAPTER 1
INTRODUCTION

Materials Science has been witnessing a nanoscale revolution in the past three decades paving way for the development of an entirely new but all pervasive area of chemistry and physics and with immense implications in many disciplines including biology and medicine. This revolution has also led to a more fundamental understanding of the structure-property relations in materials, chemically engineered methods for the synthesis of nanoscale materials, development of faster and smarter computers (which also helped to solve many puzzles of materials chemistry by facilitating intense computing), development of novel tools for imaging, particularly imaging techniques using electrons (such as transmission electron microscopy, scanning electron microscopy, etc.) and also several innovative methods for the utilization of these materials in diverse areas such as optics, imaging, medicine, biomedical engineering, lasers, sensing, industrial catalysis, etc.\textsuperscript{1-21} The reason for this importance is that these materials exhibit novel size- and shape-dependent properties, which are intermediate between molecules and bulk, and often totally new and tunable. Their high surface area enables them to incorporate a wide range of elemental and material composites and smart molecular sensor units.\textsuperscript{4,5}

As the name implies, nanosized materials are those which have at least one of the dimensions in the 1-100 nm range. One nanometer, the billionth of a meter, is about the size of six Carbon atoms in a row. In fact, nature is abundant of such materials. Biology is full of such self-assembled nanostructured bundles in the form of molecular systems such as DNA, lipid bilayers, micellar assemblies etc. which play important, structure-dependent functional activities. Conventional chemistry and physics of materials evolved mostly around molecules and the bulk. On the other
hand, the nanoscale opened up a wide range of interesting, tunable properties and functionalities causing most of the recent advances in Biology, Physics and Chemistry.

The term Nanotechnology was originally coined by Prof. Norio Taniguchi to describe the manipulation or fabrication of devices in the submicron size range. In fact, with the evolution of the area, many definitions for Nanotechnology were suggested by various researchers and out of these, the one suggested by the NASA scientists give arguably the best description of the nano size range. This can be stated as “the creation of functional materials, devices, and systems through the control of matter on the nanometer length scale (1-100nm) and exploitation of novel phenomena and properties (physical, chemical, and biological) at that length scale”.

Nanoporous, particularly mesoporous materials are used for inorganic synthesis and industrial catalysis because of their extremely large surface area. Supported metal oxide catalysts are found to increase the catalytic activity in many reactions. Carbon nanotubes (CNTs) are used for the storage of Hydrogen and other gases. The most important application of nanomaterials (NMs) is in nanodevices and nanoelectronics. Examples are the demonstration of single electron memory, quantum effects, scanning probe tips and sensors. CNTs are used in nanocircuits and nanocomputers. Textile industry utilizes nanotechnology to produce stainless and wrinkleless clothing.

Metal nanoparticles (MNPs) constitute an important class of NMs. The ability of MNPs to manipulate light has been very much applied in chemical and biological sensing, therapeutics and solar cells. This is because of the small dimension of these materials, matching with that of biological systems (for example, proteins are 1-20nm in size, diameter of DNA is ~2.5nm etc). It is also reported that quantum
dots with their size dependent fluorescent properties have been used for biological and cell imaging.\textsuperscript{10,11(a)} Noble MNPs such as Au, Ag, and Cu are proved to have many biomedical applications. El-Sayed \textit{et al.} used Au nanospheres of \textasciitilde{} 40nm size to differentiate between cancerous and non-cancerous cells by dark field light scattering imaging and absorption spectroscopy.\textsuperscript{12} Colloidal Au NPs conjugated with suitable antibiotics are used for biological labelling. It is also reported that certain antibiotic coated Au NPs shows enhanced ability against bacteria.\textsuperscript{13} Colloidal Au is used for such medicinal applications because of its generally non-toxic nature. At the same time, Silver is popular from pre-historic time for the treatment of wounds. It is found to be capable of destroying a broad spectrum of bacteria towards mammalian cells.\textsuperscript{14} The high antimicrobial property of Ag NPs is still a main research interest because of its applications in medicine and a large number of reports can be found in literature.\textsuperscript{15-21}

\subsection*{1.1. Historic aspects}

Noble MNPs have been used in pottery and medicine since ancient times. During 2500 BC Chinese used Gold NPs as drug. The famous “Lycurgus Cup,” kept in British Museum, contains 70 nm sized NPs of Gold-Silver alloy. The cup made from glass appears red in transmitted light and green in reflected light. Similarly, churches of middle ages used gold in colloidal state trapped within the matrix of glass to make aesthetically pleasant ruby coloured glasses of different shades (due to the formation of NPs of different sizes). In 16\textsuperscript{th} century Europe, an aqueous form of colloidal gold called “Aurum Potabile (drinkable gold)” was thought to have curative properties against many diseases.

The advances achieved in various areas of day-today life by nanotechnologists owe their origin to the early scientific research conducted by Michael Faraday, Irving
Langmuir and Albert Einstein. In 1857, Michael Faraday described methods for the synthesis of stable aqueous dispersions of gold NP. He explained how metal particle give characteristic colours.\textsuperscript{22a} Einstein (1905) explained the existence of colloids. He suggested that the colloids behave as big atoms and explained their movement in terms of Brownian motion.\textsuperscript{22b} This theory was confirmed by Jean-Baptiste Perrin, for which he was awarded Nobel prize in Physics in 1926.\textsuperscript{22c}

It was Gustav Mie (1908) who first provided a satisfactory explanation of the dependence of the colour on size and kind of MNPs.\textsuperscript{23} This was modified by Gans\textsuperscript{24} later. However the credit for realising the enormous potential of NPs and their possible implications in different fields is often attributed to Richard P. Feynman. In 1958, he presented his visionary lecture, “There is plenty of room at the Bottom”, detailing the scope of probing into the small particle kingdom.

In early 70’s structural features of MNPs such as magic numbers were discovered using Mass Spectroscopic studies of Sodium metal beam. Groups at Bell Laboratories and IBM fabricated the first 2D quantum wells, and this was the beginning of the development of the zero-dimensional quantum dot. In 1981, Gerd Binning and Henrich Robrer invented the STM at IBM. This microscope allows atomic scale 3D profiles of the surfaces to be imaged. They were awarded Nobel Prize in 1986. With the invention of STM, the interest for new materials with tunable properties progressed a lot.

Late 80s and 90s witnessed the synthesis of a large number of different kinds of nanoscale materials. Richard Smalley, Robert Curl and Harold Kroto synthesized Fullerenes (C\textsubscript{60}) for which they were awarded the Nobel Prize in 1996\textsuperscript{25}. Ijima made CNTs, the first single walled nanotubes.\textsuperscript{26} The study of self-assembly of molecules to metal surface was intensified along with the discovery of these CNTs. Murray, Morris and Bawendi (1993) synthesized the first quality quantum dots of CdS,
CdSe, and CdTe. Using CNTs, a number of experiments were illustrated in various areas like sensing during the years followed. Nanohorns (irregularly shaped nanotubes) were fabricated for use in MeOH based fuel cells. They assemble together creating a high surface area ideal for catalysis. Prototype nano-solar cells have been made by Nanosolar Inc. in California.

Nanoelectronic CO$_2$ sensors were developed by Star et al. in 2004. The same group demonstrated the use of CNTs as biosensors. O’Neal et al. (2004) showed that tumors in mice can be eradicated by photothermal ablation using near IR- absorbing NPs without affecting the healthy tissues. Ajayan et al. developed multifunctional filters using CNTs. These filters could filter bacteria and viruses from water and separate petroleum into its molecular components. Chung et al. developed a new type of magnetic sensor for detecting biomolecules. This involves measuring the Brownian relaxation of magnetic NPs bound to the target biomolecules.
1.2. Properties of Nanomaterials (NMs)

As stated earlier, NMs are characterized by their small dimension. They are larger than molecules, but smaller than bulk. Generally, for most of the materials including conductors, semiconductors, and insulators, there is a critical size of ~100nm below which they exhibit unique physical and chemical properties. NMs, whose dimensionalities fall in this regime have a significant portion of atoms on their surfaces. This is because of the reduction in particle size which results in a decrease in the number of shells and an exposure of more number of atoms when compared to the bulk. It is observed in many cases that 85 – 90% atoms are on the surface. For example, if we consider the packing of atoms in hcp or ccp structure, we can see that there is a sharp decline in the percentage of surface atoms with increasing size.

![Figure 1.1. Pictorial representation of hexagonal close packed full-shell ‘magic number’ clusters. It can be seen that as the number of atoms increases, the percentage of surface atoms decreases. (adapted from Chem. Soc. Rev. 2006, 35, 1162 - 1194.)](image)

<table>
<thead>
<tr>
<th>No. of atoms</th>
<th>13</th>
<th>55</th>
<th>147</th>
<th>309</th>
<th>561</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage of surface atoms</td>
<td>92%</td>
<td>76%</td>
<td>63%</td>
<td>52%</td>
<td>45%</td>
</tr>
</tbody>
</table>

Also, as the size decreases, the collective surface area and surface area to volume ratio increases. The enormous increase in surface area to volume ratio with decrease in size is shown below taking the example of a cube.
Length of one side | 20μm | 10μm | 2μm | 100nm
---|---|---|---|---
Total surface area (HxWxNumber of sides x Number of cubes ) | 2400μm² | 4800μm² | 24,000μm² | 4,80,00μm²
Total Volume | 8000μm³ | 8000μm³ | 8000μm³ | 8000μm³
Surface area to volume ratio | 0.3 | 0.6 | 3.0 | 60

**Figure 1.2:** Schematic diagram showing the increase in surface area as size decreases

In addition, the surface area also depends on particle shape. Cubes, spheres, cylinders, spheroids etc. are some of the common shapes that NMs achieve. Among the different shapes a material can achieve, sphere is the lowest energy configuration.

**1.2.1. Quantum confinement:** According to the definition, NMs have at least one of the dimensions in the nanoscale regime. When particle dimension is reduced, energy levels start to become discrete rather than the continuum in the bulk. This increase in the energy level spacing with decrease in dimension of a material is referred to as quantum confinement effect.
In such a situation, properties of NMs cannot be understood using Classical Mechanics, but can be explained only on the basis of Quantum Mechanics. According to Quantum Mechanics each particle is characterized by function $\Psi$ and the fundamental equation of matter is the Schrödinger equation. Using this equation, average value of angular momentum, position, and energy can be solved with the help of mathematical operators.

### 1.2.2. Density of States

Density of States (DOS) is an important physical property of a material (quantum mechanical system) which helps to understand various spectroscopic and transport properties of materials. DOS is defined as the number of states per unit energy range. The electronic energy levels and DOS determine the optical, electronic and other properties of a material.

**Figure 1.3.** Schematic diagram showing the quantum confinement. Energy levels become discrete as size decreases.
The DOS changes significantly with decreasing size. DOS of 0D (Quantum Dot), 1D (Quantum wire), 2D (Quantum well), and 3D (bulk semi conductor) materials are illustrated in Figure 1.4.

\[ \text{Density of states: Top Left to Bottom Right (a-d) illustrates the change in DOS with change in size of a nanostructure. DOS becomes discrete in the case of a quantum dot (d) and it becomes continuous in the case of a bulk semi conductor (a). In the case of a 2D system DOS assumes a staircase shape (b) and in the case of a 1D system it is almost discrete with some continuity (c).} \]

The properties of 0D, 1D, and 2D materials are briefly described below.

1.2.2.1. Zero Dimensional Materials (0D)

These materials exhibit quantum confinement in all the three spatial dimensions. Therefore the motion of electrons and holes in all the three dimensions is restricted. Spherical NPs, clusters, etc. are examples of 0D materials. Small nanostructures
with diameters 1-10 nm (amorphous or semi crystalline) are generally called nanoclusters. On the other hand, agglomerated amorphous nanostructures are referred to as nanopowder.

(a) Quantum Dots (QDs): These are special cases of semiconducting nanocrystals with dimensions in 1-30nm range. In bulk semiconductors, the band gap is a few eV. If the applied voltage is higher than this value, the electron jumps from conduction band to valence band, leading to the creation of electron-hole pairs known as excitons. The separation between electron and hole is called Bohr- exciton radius. The interesting properties of QDs are due to their extremely small size leading to quantum confinement and results in an increase in the band gap as shown below.

**Figure 1.5.** Schematic diagram showing increase in band gap as size diminishes: Energy levels become discrete from left end (bulk semiconductor) to right end (atoms)

In the case of bulk semiconductors, the band gap is considered as fixed. On the other hand, the energy levels in quantum dots become discrete as the size decreases and at this stage, Bohr exciton radius ($r_B$) value significantly changes by the addition or
subtraction of even a single atom. In bulk semiconductors, since \( r_B \) is much smaller than the size of the crystal, the exciton is free to move throughout the lattice. But in quantum dots, \( r_B \) is of the same order of magnitude as the diameter of the crystal (D). Empirically, maximum quantum confinement is when \( D < 2 \ r_B \). Thus a QD can be described as a material whose dimensions are comparable to Bohr- exciton radius.

\[ \text{Fig 1.6: Illustration of Bohr exciton radius. The distance between the electron in the conduction band and the hole created in the valence band is the Bohr exciton radius.} \]

Efros (1980) explained the size-dependent properties of quantum dots using the following equation.

The band gap, \( E_n = E_g + \frac{\hbar^2 \pi^2}{2 m R^2} \),

where \( E_g \) is the band gap of bulk semiconductor, \( \hbar \) is the Planck’s constant, \( R \) is the radius of the quantum dot, and \( m \) is the mass of the exciton given by
\[ m = \frac{m_e m_h}{(m_e + m_h)} \], where \( m_e \) and \( m_h \) are the masses of the electron and hole respectively.

Brus et al. modified the equation by considering the Coulombic interaction factor. Then the form of the equation becomes

\[ E_n = E_g + \frac{\hbar^2 \Pi^2}{2m R^2} - \frac{1.786 e^2}{\varepsilon R} + 0.284 E_R; \]

where \( E_R \) is the Rydberg constant (special correlation energy) of the bulk semiconductor given by

\[ E_R = \frac{m e^4}{2 \varepsilon \varepsilon_0 \hbar^2} = 13.56 \frac{m}{\varepsilon m_e}; \]

where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon \) is the dielectric constant of the bulk semiconductor, and \( m_e \) is the mass of electron.

(b) Clusters: A group of atoms held together by weak van der Waal’s force of attraction (as in the case of inert gas clusters), or covalent bonds (in the case of semiconductor clusters) or metallic bonds (as in the case of metals) is called a cluster. The percentage of surface atoms in a cluster depends on the number of atoms from which it is formed. A NP of 10nm size will have ~ 10% atoms on the surface whereas a NP of size 1nm will have almost 100% atoms on the surface. It is possible to produce clusters of any materials. Among them clusters of noble metal atoms occupy significant position since they show unique optical, electronic, magnetic, and other properties. This in turn is due to their electronic band structures which differ from that of semiconductor NMs. There is no band gap between valence band and conduction band which is analogous to that of bulk metal.
Figure 1.7. Schematic diagram showing the density of states of bulk metal and small clusters: Left:-band structure of bulk metal. Middle:- As the size decreases the continuum of the bulk metal transforms to discrete levels especially at the band edges. Right:- discrete energy levels in the case of molecules. The approximate diameter, nuclearity and Kubo gap are indicated. (adapted from *Chem. Soc. Rev.* **2000**, *29*, 27-35.)

For nanoclusters of small dimension, the spacing between the energy levels (known as “Kubogap”) becomes comparable to kT (the thermal energy), which results in a marked change in the conducting properties of the cluster. According to Band theory, the breadth of a band is proportional to the strength of interaction between neighboring molecules. In the case of small molecules, this interaction is weak (Figure: Right end). However, somewhat stronger interactions will occur in the case of small metallic clusters. Additional energy states will be formed at the band edges resulting in greater DOS near Fermi energy (E\(_F\)). In such a state, small metal clusters lose their ability to conduct electrons due to the existence of clearly defined highest
occupied cluster orbitals (HOCO) and lowest unoccupied cluster orbitals (LUCO). These metal clusters show insulating behavior.

Since quantum confinement starts at the band edges than at the centre of the band, metals are less affected by quantum confinement in comparison with semiconductors or insulators. Another feature is that metal nano clusters (MNCs) are comparatively more sensitive to shape than size in contrast to semiconducting or insulating NMs. This is also because of the electronic band structure of metals by which MNCs exhibit quantum confinement at very small sizes. Larger clusters behave more or less classically. For metallic clusters with size > 2nm, another phenomenon called Surface Plasmon resonance (SPR), proposed by Mie, is valid. This is discussed in the optical properties of metal clusters.

1.2.2.2. One Dimensional (1D) and Two Dimensional (2D) Materials

One-dimensional materials are the second class of nanoscale structures in which the crystallite size is restricted to nanoscale in two directions but is not restricted in the third direction. Here the electron-hole motion is confined in two directions, while free movement is possible in the third direction. These are also called quantum wires where the two dimensions are comparable to Bohr-Exciton radius. CNTs are examples of 1D nanostructure.

Quantum wires are electrically conducting or partially conducting and their transport properties can be explained using Quantum Mechanics. Due to the confinement in two dimensions, the energy states are quantized into a series of
discrete values. The result is that the resistance of quantum wire cannot be deduced using the formula

\[ \Omega = \rho \frac{l}{a} \]

where \( \rho \) is the resistivity, \( l \) and \( a \) are length and cross sectional area. For such a quantum wire, the exact solution is obtained with the help of Quantum Mechanics, since \( \Omega \) is quantized.

Two-dimensional materials are another class of nanoscale structures in which the crystallite size is on the nanoscale in one direction but is not restricted in the other two directions. Here the electron-hole motion is confined only in one spatial direction. These are also called quantum wells. Here one dimension is comparable to Bohr-Exciton radius. Thin films are examples of 2D materials.

**1.2.3. Variation in Fundamental Properties:** NMs exhibit variation in fundamental properties because of their size, shape, composition, and assembly. These include optical, electrical, magnetic, thermal, and mechanical properties.

**1.2.3.1. Optical properties of MNPs**

It is well established that clusters of Au, Ag, and Cu show interesting optical properties. Au shows its characteristic \( \lambda_{\text{max}} \) in the electronic spectra around 520nm, Ag around 400nm, and Cu around 560nm. Colours exhibited by these MNPs are the result of a phenomenon called Surface Plasmon Resonance (SPR) absorption, the frequency at which conduction electrons oscillate in response to the alternating electric field of incident radiation. The free conduction electrons on the surface of a metal are considered as free electron cloud or gas around positively charged nuclei. When an oscillating electric field interacts with the conduction electrons of a metal,
the electron cloud gets disturbed. It is considered that all electrons see the same field at a given temperature and a displacement of electron cloud takes place, leading to surface charge polarization.

**Figure 1.8** Plasmon oscillations for a sphere, showing the displacement of the electron cloud relative to the nuclei under the influence of electric field (adapted from reference 41)

This charge polarization is temporary, since the Coulombic attraction from the positively charged nuclei will pull the electron cloud to the initial position. Such a situation leads to the collective oscillation of the electron cloud called plasmon polaritons, which is contrary to the free plasmon present in bulk metals. Shopper proposed the term ‘Plasmons’. He suggested that the dipolar repartition imposes a new restoring force on the electron cloud which conflicts with the external electric field. When light couples in phase with the natural frequency of the plasmon oscillation, a resonant condition is achieved and this leads to the absorption of electromagnetic radiation and finally the excitation of the electron cloud to conduction band.

Generally, SPR can be of two types: SPP (Surface plasmon polaritons) and LSPR (Localized surface plasmon resonance). SPP originates from the propagating waves along a metal surface. LSPR originates from very small particles; smaller than the wave length of light (or the condition is that radius should of the order of 1/100 of wave length of light). The NPs experiences a field that is spatially constant, but with
a time-dependent phase, which is called quasi-static limit. The result is that only the
dipolar resonance of the plasmon contributes to optical resonance. SPP is influenced
by the type of metal, refractive index of the environment and the surface of the
material. Roughened and edged surfaces show enhancement in EF. Contrary to SPP,
LSPR can generate a local field enhancement of 100 – 1000 times greater than the
incident light. This is due to the confinement of the surface plasmon to a small
volume which results in an oscillating electromagnetic field very close to the surface
which is known as the dipolar plasmon resonance. As a result, the extinction
coefficient reaches a maximum value at the resonance frequency giving rise to a
single, sharp absorption band. For larger particles quadrupole or higher resonance
can occur which may lead to multiple absorption bands. These higher order
resonances will have lower intensity than dipolar plasmon resonances. In such a
case, the particle only absorbs energy and the absorption cross section can be
calculated using Mie equation. The study of interaction of light with NMs is called
Nano Optics. Since this field involves Plasmons it is also called
Nanoplasmonics. 33-38

Mie (1908) provided an exact solution for the
strong color changes displayed by spherical
particles provided that the dielectric constant
of the particle and environment are known.
He neglected the interaction between the
particles and applied Maxwell’s equation to
spherical particles with a bulk dielectric
function $\varepsilon_\omega$.

The Mie theory can be explained as follows:
When an electromagnetic radiation of intensity $I_0$ and wavelength $\lambda$ passes through a medium having dielectric constant $\varepsilon_0$, the transmitted intensity is given by

$$I = I_0 e^{-\mu l},$$

where $\mu$ is the extinction coefficient, a function of the total number of particles $N$ and volume of colloidal particles $V$.

$$\mu = \frac{N}{V} C_{\text{ext}};$$

where $N$ is the number of particles in a medium, $V$ is the volume of colloidal particles and $C_{\text{ext}}$ is the extinction cross section of a particle. For larger particles,

$$C_{\text{ext}} = C_{\text{abs}} + C_{\text{scat}}.$$

The total extinction coefficient $C_{\text{ext}}$ for $N$ particles of volume $V$ is composed of a series of absorption and scattering modes. $C_{\text{abs}}$ and $C_{\text{scat}}$ can be obtained by solving Maxwell’s equations. Mie predicted that for very small particles extinction is mainly due to absorption. He derived the expression for the extinction coefficient $C_{\text{ext}}$ for small particles of radius $R$ surrounded by an insulating homogeneous medium (dielectric constant $\varepsilon_m$) is given by

$$C_{\text{ext}} = \frac{24 \pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \left\{ \left( \varepsilon_\omega' - 2 \varepsilon_m' \right) + \left( \varepsilon_\omega'' + \varepsilon_m'' \right) \right\};$$

and

$$\varepsilon_\omega = \varepsilon_\omega' + i \varepsilon_\omega''$$

where $\lambda$ is the wavelength of the electromagnetic radiation and $\varepsilon_\omega$ is the dielectric constant of the particles. From this equation, the position and line shape of the plasmon absorption of spherical MNPs can be deduced. The factor ‘2’ in the denominator indicates spherical shapes. The extinction cross section will be maximized when the denominator of the equation is minimized or when $\varepsilon_\omega' = -2 \varepsilon_m'$ becomes the condition for resonance. It becomes clear that LSPR peak
strongly depends on the dielectric constant of the environment. The dielectric
constants of metals $\varepsilon'$ and $\varepsilon''$ are strongly frequency dependent and contain both real
and imaginary components. Thus the absorption shown by the metal NPs can be
predicted when the condition $\varepsilon' = -2\varepsilon_m$ is fulfilled. As a result, the long wave-
length absorption by the bulk metal condenses into a single surface plasmon band. It
is also clear from the equation that the magnitude of absorption is proportional to $R^3$.
So, for small particles, LSPR is dominated by absorption. As the size of the particle
increases, scattering becomes dominant. Mie proved that LSPR wavelength of Au
nanospheres can be tuned over 60 nm by varying the size between 10 and 100 nm.
He also found that there is noticeable variation in linewidth with particle size, due to
combination of interband transitions and higher order (non-dipole) plasmon modes.
If the particle size becomes comparable to or smaller than the mean free path of
electrons the collision of the particles with the surface becomes prominent. Thus the
effective mean free path is greater than that in bulk, resulting in broadening and blue
shift in $\lambda_{\text{max}}$.

Although Mie theory agrees well with the experimental spectra of spherical particles
in the size regime $>20$ nm, it failed to describe spectra of non-spherical particles like
elongated nano rods. Gans (1912) modified Mie equation for rod shaped particles by
predicting that the SPR band of such particles split into two modes due to different
orientation of the rod with respect to the electric field of the incident light.

The modified expression is given by
$$C_{ext} = \frac{8\pi^2 R^3 \epsilon_{m}^{3/2}}{3A} \sum \left( \frac{1}{P_j^2} \epsilon' \right)^{\cdot} \left( \epsilon' + \frac{1-P_j}{P_j} \epsilon_m \right)^{\cdot} r^2$$; where $P_j$ represents the depolarization factors for the nano rod axes ($a > b = c$), which are defined as

$$P_a = \frac{1-r^2}{r^2} \left[ \frac{1}{2r} \ln \left( \frac{1+r}{1-r} \right) - 1 \right]$$, and

$$P_b = P_c = \frac{1-P_c}{2};$$ where $r$ is a parameter given by $\sqrt{1-(b/a)^2}$.

The plasmon resonance for nanorods splits into two bands. As the aspect ratio increases, the energy separation between the resonance frequencies of the two plasmon bands also increases. The high energy band corresponds to the oscillation of the electrons perpendicular to the major axis of the rods and is referred to as the transverse plasmon absorption. The other absorption band which is red-shifted to lower energies is caused by the oscillation of the electrons along the major axis of the nanorods and is known as longitudinal surface plasmon absorption. The transverse plasmon absorption has a linear dependence on the aspect ratio and the dielectric constant of the medium.

These equations are used to calculate the extinction spectra of Au nanorods of any aspect ratio.

Drude model (1900) describes spectra of very small MNPs taking the dielectric constant also into account.\textsuperscript{39} This model considers the conduction electrons as ‘plasma’.

\textbf{Figure 1.9.} Schematic representation of Plasmon resonances in metal nanoparticles. Fig. eg. A) Au NPs; (B) Au Nanorod; (c) Hollow Au NPS; (D) Aggregate (adapted from J. Phys. Chem. C, 2008, 112, 10323–10337.)
The positively charged ions are surrounded by the electrons and the metal as a whole becomes electrically neutral. When electromagnetic radiation interacts with metal, the loosely bound plasma oscillates coherently with a resonant frequency given by

$$\omega_p^2 = \frac{4\pi N e^2}{m^*},$$

where \( N \) is the number of electrons in plasma, \( e \) is the charge of electron and \( m^* \) is the effective mass of electrons. Since these oscillations are quantized they are called plasmons. Also, since the penetration depth of electromagnetic radiation (UV to IR) falling on metals is ~50 nm, the properties of surface electrons becomes as important as compared to bulk electrons. Drude model also predicts that if conduction electrons have a higher possibility to polarize, it is easier for SPR to occur with a lower frequency and sharp bandwidth than that in the bulk. Hence SPR of MNPs especially that of Au, Ag, and Cu falls in the visible part of the EM spectrum.

For NPs of other shapes, the induced EF is not evenly distributed around the surface. Hence SPR is different from that of spherical NPs. Different numerical approaches viz. Discrete Dipole Approximation (DDA)\textsuperscript{40,41}, Finite Difference Time Domain (FDTD)\textsuperscript{42,43}, and Finite element method (FEM) are used to evaluate the spectra of such non-spherical nanosystems.

The effect of shape on SPR has been studied by many theoretical groups and it is established that there is a general relationship between SPR and shape or morphology.\textsuperscript{44,45} SPR is also affected by substrate, particle-particle interaction, etc. It is found that SPR shifts if the dielectric properties of the surrounding media are changed. Similarly, the width and frequency of SPR depends on the interaction between particles.
When the optical properties of alloy systems are considered, the dielectric function of the alloy NP is to be taken into account. It is calculated in terms of the dielectric functions $\varepsilon_A$ and $\varepsilon_B$ for NPs of same size, but made of pure metals A and B, which constitute the alloy.

$$\varepsilon = \alpha \varepsilon_A + (1 - \alpha) \varepsilon_B;$$

where $\alpha$ is the relative volume concentration of the metal A.

The dielectric functions $\varepsilon_A$ and $\varepsilon_B$ are calculated in the same way as for single MNPs. Another important aspect of alloy NPs is their extinction maximum. The Drude form of extinction value for an alloy system is given by

$$C_{\text{ext, alloy}} = \frac{4\pi n^3 c \gamma_{\text{alloy}}}{\lambda_{\text{alloy}}^2} \frac{1}{\lambda_{\text{alloy}}^2 + \gamma_{\text{alloy}}^2} r^2;$$

where $\gamma$ is the electron relaxation time, $\lambda_{\text{alloy}}$ is the $\lambda_{\text{max}}$ of the alloy system.

Many physicists and chemists have attempted to give a clear description of the surface plasmon band. Liz-Marzan et al. reviewed on Mie theory and effective Medium Theory in 2004. Kreibig and Volmer gave a broad overview of the existing plasmon band theories. Optical properties of NPs with arbitrary shape were explained by Schatz et al. using Maxwell equation. In the case of semiconductors, the reduction in the particle size results in an increase in the band gap which in turn results in a shift of the light absorption towards the high energy region (blue shift).

Theoretical explanations regarding the plasmonic properties of bimetallic particles were given by Stern and Ferrel, who showed that an interface plasmon mode can exist at the boundary between two metals. According to them, in a bimetallic system, the two metals have different electron densities and hence two plasmon frequencies. Hence at the bimetallic interface the resonant frequency $\omega$ of the plasmon wave is given by
\[ \omega = \left[ \frac{1}{2} \left( \omega_p^2 + \omega'_p \right) \right]^{1/2} \text{; where } \omega_p \text{ and } \omega'_p \text{ are classical plasma frequency and different plasma frequency based on the dielectric constant at the interface.} \]

Several other groups have also given theoretical explanations about the plasmonic properties of bimetallic particles. Cottancin et al. combined the classical Mie Theory with quantum effects which play an important role at this size regime.\textsuperscript{50} Similarly, Tang et al.\textsuperscript{51(a)} and Pelligrini et al. demonstrated a shift in plasmon resonances in the case of Ag/Pt and Au/Ag systems.\textsuperscript{51(b)}

Optical absorption spectroscopy is the most common technique in explaining the quantum effect in semiconductor NPs. Using this method, the energy gaps can be observed. However, if inhomogeneous broadening exists, the discrete states may not be visible in the spectra. The self-assembly of semiconductor NPs was studied by Skolnick et al.\textsuperscript{52} The hot electron dynamics of quantum wells and dots was examined by Nozik et al.\textsuperscript{53} Magnetic resonance studies on semiconductor NPs have been conducted by many groups.\textsuperscript{54}

1.2.3.2. Electrical and Electronic Properties

The electrical conductivity of solids is determined by its electronic structure or band structure. Generally, in solids, the valence band is completely filled with electrons and separated from the empty conduction band with the energy gap of \( E_g \). For metals \( E_g = 0 \), with an overlap of the valence and conduction bands. In the case of semi conductors, \( E_g \) is small. The electrons can be excited from valence band to conduction band using light or heat, which results in partial conductivity. In insulators, \( E_g \) is high and the electrical conductivity is restricted. The conducting nature of the solids can be affected by various factors like temperature and particle
size. When the particle size is reduced to nanometer range, $E_g$ increases and the conductivity shows a marked difference as described as in 1.2.2.1.

**Figure 1.10.** Difference in band gaps for different materials. Left: Insulator; Middle: Semiconductor; Right: Conductor

Carbon based materials are extensively used in the electronic industry due to their high conductivity and mechanical stability. CNTs and nanowires have recently been exploited as building blocks to fabricate nanoscale electronic devices through self-assembly. The prototype devices that have been demonstrated include Field-Effect Transistors (FETS), p-n junctions, bipolar junction transistors, complementary inverters and resonant tunneling diodes.

Generally, as the critical dimension of an individual device becomes smaller and smaller, the electron transport properties of their components become important. Studies from a number of groups indicate that some metal nanowires undergo transition to become semiconducting as their diameters are reduced below certain values.\textsuperscript{55-57} For instance, studies by Dresselhaus et al., on assays of single crystalline Bi nanowires indicated that these nanowires underwent a metal to
semiconductor transition at a diameter of ~52 nm. Experiments done by Choi et al., on individual single-crystalline Bi nanowires of ~40 nm in diameter showed that these nanowires were semiconductors or insulators.

In addition to the above experiments, the function of Au_{55} clusters as quantum dots in a three dimensional collective has been demonstrated by G. Schmid et al. It was found that due to extreme small size of these particles, discrete energy levels are formed. The electronic conductivity of many clusters in a row results from tunneling processes between them through the ligand shells. Such a cluster wire should therefore conduct electrons without resistance.

1.2.3.3. Thermal Properties

As the nanocrystal size decreases, a decrease in solid-liquid transition temperature has been observed in a wide variety of materials. The surface atoms are unsaturatedly coordinated and therefore the surface energy will be high. In the case of solids, rigid bonding geometries cause stepped surfaces with high energy edge and corner atoms. In a dynamic liquid phase, surface atoms move to minimize the surface area and to an unfavorable surface interaction. The surface energy is always lower in liquid phase as compared to the solid phase. While melting, the total surface energy is reduced. The smaller the size of the nanocrystal, the larger would be the contribution made by the surface energy and results in a sharp lowering in the melting temperature.

It is typical for bulk materials that the surface atoms form negligible part of the total number of atoms. For example, a spherical particle of 50 nm diameter has only about 6% of surface atoms. The melting point of a solid is reached when the order of the lattice is beginning to be destroyed. As the coordination number of surface
atoms becomes smaller, these are more easily rearranged than those in the center of
the particle, and the melting process starts earlier.\textsuperscript{59-61}

1.2.3.4. Mechanical Properties

The size effects exhibited by NMs result in the change of most of the mechanical
properties of these materials. Hardness and elastic modulus, toughness, scratch
resistance, fatigue strength, capillary focus, adhesion etc. are modified when the size
comes to nano-regime.

Much progress has been made in understanding the mechanical properties of single
wall CNTs and Multiwall CNTs. CNTs are very strong through the three-fold
bonding of the curved graphene sheet, which is stronger than in diamond due to their
differences in C-C bond length (0.142 and 0.154nm for graphene and diamond,
respectively).

It is shown that the tensile strength of SWCNTs can be 20 times that of steel. One
important application of CNT is in composite materials, which are reinforced by the
introduction of SWCNTs or MWCNTs. Mechanical properties of CNTs can be
measured by AFM.\textsuperscript{62-64}

1.2.3.5. Magnetic Properties

Magnetic properties of a material are fundamentally determined by its electronic
structure. When the size is reduced, electronic properties change by reducing the
symmetry of the system and by introducing a quantum confinement. The strength of
a magnet is measured in terms of coercivity and saturation magnetization values.
These values increase with a decrease in grain size and an increase in the specific
surface area of the grains.

26
NPs exhibit magnetic properties because of the large surface to volume ratio. The surface energy becomes important when compared to the bulk energy; the energy barrier to overcome the magnetization inversion is $K_{\text{eff}} V$ when $K_{\text{eff}}$ is the magnetic anisotropy constant and $V$, the particle volume. In the case of NPs, the volume is so small, therefore the thermal energy ($k_B T$) is enough to invert the magnetization with relaxation times as low as a few seconds. Thus the materials loose coercivity and remnance, giving rise to the so-called superparamagnetic behavior.

The magnetic anisotropy constant $K_{\text{eff}}$ varies with the average particle size as,

$$K_{\text{eff}} = K_\infty + \frac{6 K_s}{d} \geq d \geq$$

where $K_{\text{eff}}$ is the magnetic anisotropy constant for the bulk material ($5 \times 10^4$ Jm$^{-3}$) and $K_s=3.3\times10^{-1}$ mJm$^{-1}$. An analogous increase in the magnetic anisotropy of NPs was reported by many authors. $^{65-67}$

The magneto-optical properties of various NPs have been well studied. Ordered ensembles of magnetic Fe$_3$O$_4$ and CoFe$_2$O$_4$ NPs were first formed on the surface of the aqueous phase from the corresponding dispersion in organic solvents and then transferred on solid substrates. It was established that the degree of local order of the structures under study depends on the particle size. Pileni et al. reported the self-organization of magnetic Co NPs into 1D chains of 8nm length. $^{66}$ Magnetic measurements show that with reference to partially disordered NP aggregates, the reduced remnant magnetization and coercivity of the ID Co NP chains increased from 0.52 and 0.13T to 0.60 and 0.14T, respectively. These were attributed to the enhanced alignment of their magnetic moments along the direction of the applied magnetic field. Such a high magnetic anisotropy could not be detected for disordered NP aggregates.
1.2.3.6. Chemical Properties

Catalytic activity: The large surface area of NMs provides increased adsorption of reactant molecules on the surface, resulting in higher catalytic activity. Additionally, the increase in the number of surface atoms can create more number of active sites, which also enhances the catalytic activity. It is proven that small MNPs are good catalysts for many reactions. Transition metal clusters exhibit strong variations as a function of size not only in their physical and electronic properties but also in their chemical behavior as catalysts. The ability to accept or donate charge plays a key role. For example, bulk gold is inert and catalytically inactive. However, in early 90s, Haruta et al. reported that small Au particles are catalytically active.68

MNPs supported on porous structures are another important category of NMs. The main features of a porous material are its porosity (macro-, meso-, micro- or combinations), textural and physical properties, surface functionality and surface energy. Such porous materials with defined pore sizes allow specific adsorption sites suitable for catalysis. It is also possible to control the size and shape of NPs by tuning the textural properties of these materials. Many natural substances like clay, biological tissues, and synthetic materials like metal oxides (CeO$_2$, SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_3$O$_4$, etc.), carbonaceous materials like CNTs, polymers like polyvinylpyridine, dendrimers etc. have been used as supports.

Gold NPs, porous gold materials and supported mesoporous materials are widely used as catalysts. Similar experiments have been carried out with other metals such as Ni, Cu, Pd, etc.69-75 These experiments also reveal that chemical properties can be tuned over a wide range by variation of the cluster size. Noble MNPs supported on various transition metal oxides have been studied by a many research groups for a
series of catalytic reactions including oxidation-reduction, epoxidation of alkenes, hydrogenation, water gas shift reaction, etc.

Such MNPs supported on porous structures are also used as photo catalysts. Oxides like TiO$_2$, RuO$_2$, WO$_3$, SrTiO$_3$, Fe$_2$O$_3$, ZnO and chalcogenides like CdS, CdSe, FeS$_2$ etc. have suitable band gap to be excited by UV or Visible light, and the redox potentials can promote a series of oxidative or reductive reactions. Among semiconductors, TiO$_2$ is used as the most appropriate material for photocatalytic purposes, due to its unique optical and electrical properties, chemical stability, non-toxicity and low cost.

1.2.4. Self-Assembly

Self-assembly is one of the most energetically favored and intelligent method for the creation of structurally organized NP assembles. This is a thermodynamically guided process based on the fundamental interactions such as hydrogen bonding, polar and non-polar interactions, etc. The fascinating functional organizations of the molecules of life are governed by such interactions. Protein folding and aggregation, assembly of living cells during mitosis, pairing of bases in DNA, formation of lipid bilayers etc. are examples of such self-assembly processes found in nature. Taking clue from nature, it is possible to self-assemble NPs based on the spontaneous or synergistic organization of components into hierarchically ordered structures or organization of structures into 1D, 2D, or 3D architectures.

For the synthesis of organized nanoscale assemblies, top-down and bottom-up approaches are being used of which bottom-up type self assembly has been employed more commonly. Various types of self-assembly processes exist. The building blocks organize into ordered macroscopic structures either through direct
interactions (spontaneous assembly) or indirectly using a template or an external field (directed self assembly). The structure of the final product represents a thermodynamic minimum that results from equilibration of these interactions. Self-assembly minimizes defects and is a route to build up structures having high degree of perfection.

Spontaneous assembly is found to be very common among organic materials. Yagai et al. explained the self organization of H-bonded rosette assemblies of Oligo (p-phenyleneethynylene)s attached melamine derivatives leading to the formation of organized structures of nanoscale dimensions. Cell-like vesicular assemblies are also popular because of their potential applications in drug delivery. Shape-defined self assemblies of various NMs, artificial nanocarbon superhydrophobic surfaces, assemblies of Fullerenes and Porphyrins etc. were also illustrated by different groups. 84,85

Generally, the NP thin films and their assemblies are classified into 1D, 2D, and 3D-assemblies and are extensively studied by many research groups.86-88 These methods include solvent evaporation, Langmuir-Blodgett (LB) transfer and layer-by-layer assembly. Compared to 2D- and 3D-assemblies, 1D- NP assemblies are rather rare, due to the difficulties arising during their synthesis. However, one-dimensional nanowires, nanotubes etc. have also been prepared.89-91 There are also reports where bio molecules like DNA and proteins are employed as templates for the synthesis of one dimensional assembly.92-93 Metals such as Au, Ag, Pt, Pd etc. have been organized in this manner. Warner et al. showed that branched or ribbon like Au NPs could be prepared on DNA templates.94

Directed self assembly mostly involves a template or an external environment. Generally templates can be considered as surface modified substrates (in 1D, 2D, or
3D) containing active sites, which can selectively induce NPs deposition. The strategy to modulate directed self assembly involves the control over template concentration, understanding and using of the coordination sites in template molecules, influence of surrounding media etc. It is shown that geometrical control allows the assembly to organize into homodimers, trimers, and tetramers by simply varying the initial concentration of the template molecules. Mirkin et al. and Peng et al. proposed the concept of DNA controlled nanocrystal assembly in 1996.95,96 They showed that Au NPs can be functionalized either by large numbers of DNA strands, leading to network materials, or by discrete number of DNA strands, forming discrete assemblies. Polymer mediated assembly was introduced in 2000, showing that the control of solvent polarity or temperature may trigger the reversible H-bonding between a linear polymer and Au NPs.97

In the self-assembly of NPs, block copolymers are proved to be good templates, since they self assemble into well defined nanostructured arrays over macroscopic distances.98,99 The self-assembly by controlling the pH of the solution is reported by many groups. Various shapes of NMs like spheres, rods etc. have been prepared by pH regulated routes.100-103 Another factor that controls self-assembly is solvent polarity. Formation of a series of 1D structures, nanorods, chain like structures or spherical aggregates have been reported.

Self assembly processes can also be found at interfaces where the nature of the interface directs the self assembly. The assembly is possible either at solid interfaces or liquid interfaces. Here the driving force is the reduction in interfacial energy. Yogev et al. showed that liquid-like colloid Ag films can be obtained at the interface between organic (CH₂Cl₂) and aqueous phases.104 Similar experiments were reported where ordered structures of Au were obtained at liquid – liquid interface. Sathaye et
al. illustrated the formation of ordered layers of NPs at the interface between two immiscible liquids by chemical reduction immediately at the interface.\textsuperscript{105}

1.3. Synthesis of nanosized materials

Synthesis of NPs started a century back when Faraday synthesized Au NPs by wet chemical route. A number of methods have been developed so far to generate differently colored or shaped MNPs. Even now, the synthesis of NPs continues to be an active area, since these materials find immense applications in various areas like medical diagnostics, therapeutics etc.

In bottom-up method, the atoms produced by the reduction of ions are assembled to generate nanostructures and in top-down method, the bulk material is subsequently reduced into NPs by way of physical, chemical, or mechanical processes. In addition to these two approaches, there is also the Hybrid Fabrication Technology, which is a combination of distinct top-down and bottom-up mechanisms that can occur simultaneously.\textsuperscript{106,107}

Among the modern directions in top-down approach, lithographic techniques have attracted much interest. There are numerous energy sources employed in lithographic processes. In photolithography, radiations in the UV-Vis region and X-rays are used. Electron and ion beams have also been applied in lithographic procedures. These are known as Electron beam lithography and Ion beam lithography, respectively. In multiphoton photo lithography, soft materials are used to remove dimensional restrictions.\textsuperscript{108} Other nanolithographic techniques include Nano-imprint method, Shadow evaporation etc. Torkelson et al. demonstrated the generation of nanopatterns on PMMA film supported on a silica substrate using electron beam lithography.\textsuperscript{109}
In top-down method, particles can also be generated from vapor or from liquid phase. In the former case the material is made to evaporate at very high temperatures in a furnace until the vapor is supersaturated and then subjected to cooling whereby the particles are formed by condensation. In laser pyrolysis, high energy laser beam causes vaporization of the material and decomposition into its constituents, which then condense into small particles. Plasmas with temperatures above 10,000°C also are used to break materials into individual atoms, which when removed and cooled agglomerate into particles. Another method is to use highly energetic charged atoms of inert gases like Argon to bombard into a material. This results in an ejection of all atoms from the solid’s surface. This process is known as sputtering.

Bottom-up techniques include both gaseous phase and liquid phase methods. Chemical vapor deposition (CVD) and Atomic layer deposition (ALD) are gaseous phase methods.

In the bottom-up chemical strategies, a variety of reaction conditions are employed for suitably architecturing the NMs. These include choice of the reduction technique, kinetics of nucleation and growth, concentration and structure of the capping agent, pH of the medium, temperature, rate of stirring, etc. Nucleation and growth of the particle are important factors for controlling the size of the NPs. This is achieved by the choice of the capping agent. A surfactant or polymer is generally used as a capping material to control the growth of the NPs. Various research groups have successfully prepared NMs using different capping agents and reducing agents. Thiols, citrates, polymers like PVA, PVP, starch etc. are examples of capping agents and sodium citrate, NaBH₄, hydrazine, ascorbic acid, glucose etc. are commonly used as reducing agents.³⁻¹² Other bottom-up techniques include chemical, electrochemical, sonochemical, thermal, and photochemical methods.
NPs of many sizes and shapes have been produced with various metals using various bottom-up techniques. These include spherical NPs, rods, cubes, disks, wires, tubes, shells, cages, stars, multibranches etc. Complex nanocrystal heterostructures like bimetallic and trimetallic structures have also been synthesized by several groups by assembling two or more components together. The bimetallic, trimetallic, and other such hybrids are generally called hybrid NPs. Since the individual components possess different surface properties, crystal lattices, redox potentials, crystal morphologies etc., a successful combination of these materials into a hybrid material of desired property is still a challenge for scientists.

Bimetallic and trimetallic NPs are ideal for sensing, catalysis, photonic devices, gene delivery and electronic devices due to their tunable composition and other plasmonic properties. Synthesis of such hybrid systems can be done in many ways like Deposition-Precipitation method, Galvanic replacement method, co-precipitation, template methods etc.

Core-shell NPs are a kind of bimetallic NPs having well–defined core and a shell both in the nanometer range. These particles have numerous applications in pharmaceuticals, optics, drug delivery, and areas like chemical engineering due to their peculiar structures. Metal–metal oxide core-shell NP system is widely studied among core-shell particles. Liz–Marzan et al. developed a synthetic procedure to prepare silica-coated nanosized clusters like Au, Ag, and CdS. Mayya et al. developed a method for the controlled coating of Au NPs with TiO$_2$. Reverse micelle and sol – gel techniques are also employed in the synthesis of metal–metal oxide core-shell NPs.

A wide variety of synthetic procedures are employed to produce bimetallic and trimetallic NPs. These include co-reduction of metal ions, polyol method,
photochemical method, gamma irradiation, sputter deposition, electroless plating, and microwave synthesis.

Bulk forms of Au and Ag are mutually soluble and generally their nanoforms are also soluble. This is why their SPR peaks can be smoothly extrapolated between those of Au and Ag by changing the composition. The alloy formation can be easily observed by a linear dependence of the plasmon absorption maximum with respect to the composition of alloy NPs.\textsuperscript{134,135} Au/Ag non-alloy or core-shell NPs exhibit two characteristic absorption peaks, in which the absorbance of one peak increases with respect to the other corresponding to the increase in concentration of one of the components. Morris and Collins prepared Au-Ag bimetallic particles for the first time in 1964 which followed numerous synthetic methods for such hybrid NPs.\textsuperscript{136} Papavassiliov demonstrated the preparation of alloy NPs in 1976 by the evaporation of Au/Ag alloys.\textsuperscript{137} Following this, Köhler \textit{et al.}\textsuperscript{138} prepared Au/Ag alloy NPs by a two-step method. Later, by the co-reduction of HAuCl\textsubscript{4} and AgNO\textsubscript{3} by sodium citrate, El-Sayed \textit{et al.} could produce Au/Ag alloy NPs of narrow size distribution.\textsuperscript{139} They demonstrated that with increasing amount of Au in the particles, the plasmon red shifts. It was concluded that the shift is the result of a modification in the band structures for either pure Au or pure Ag. Okazaki \textit{et al.} produced Au/Ag alloy NPs using sputter deposition method.\textsuperscript{140} Similar to isotropic bimetallic NPs, anisotropic plasmonic bimetallic NPs were also prepared. Here the mechanism for controlling the shape is similar to those used for isotropic NPs. A small change in the procedure such as the amount of reactants, reaction time or reduction conditions allows control over the shape of the NPs formed. A variety of Au/Ag nanostructures with controlled geometric shapes and structures have been prepared. Bard and colleagues prepared cube shaped NPs.\textsuperscript{141} Sastri \textit{et al.} fabricated Au/Ag core-shell NPs using
lemongrass as the reducing agent. They showed that Neem leaf broth can also be used to produce bimetallic Au/Ag NPs.\textsuperscript{142} Pentagonal NPs were synthesized by Huang et al.\textsuperscript{143} Murphy \textit{et al.} prepared Au/Ag nanowires by a seed mediated growth method.\textsuperscript{144} Toshima \textit{et al.} developed methods to synthesize trimetallic particles.\textsuperscript{145-146} These experiments proved that bimetallic particles with high aspect ratio exhibit most unique properties since both transverse and longitudinal modes are subjected to modification depending on the composition. A large number of NPs are synthesized using a range of techniques for various applications.\textsuperscript{147-156}

1.3.1. Green Chemistry

Many synthetic methods employed so far by chemists suffered from hazardous chemicals, low material conversion, high energy requirements, and difficulty in purification. Hence new, environmentally responsible, synthetic strategies for were suggested which led to the implementation of Green Chemistry. It is based on a set of principles which reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and application of chemical products. These principles were originally defined by Anastas and Warner.\textsuperscript{157}

This approach aims to design nanoscale materials which can cause least or little hazards to health and environment. Incorporation of green chemistry principles into nanosynthesis\textsuperscript{158-163} also provides design schemes, which assure safer materials. The choice of the reducing agent, capping agent, and the reaction media are issues in nanosynthesis that are gaining scientific attention.\textsuperscript{162,163}
1.4. Applications of Nanomaterials

NMs have immense variety of applications in different areas like catalysis, sensing and imaging, electronics, cosmetics, water purification, medicine and biology, and in fuel cells. Some of these are already discussed.

1.4.1. Catalysis: NMs are found to be efficient catalysts in both homogeneous and heterogeneous catalysis due to their high surface area, higher activity and selectivity, and longer life time. Since smaller particles have larger fraction of atoms on the surface, these are well suited for catalytic activity. Ever since Haruta et al. discovered that small Au NPs have excellent catalytic properties, Au and transition metal clusters have been extensively used as catalysts.\textsuperscript{68}

El-Sayed et al. reported that difference in shape and crystal structure can lead to different catalytic rates. They showed that shapes with more corners and edge atoms have higher activity than similar NPs with fewer corners and edge atoms.\textsuperscript{164} Mesoporous materials are very efficient catalysts due to their high surface area, narrow pore size distribution, and well-defined chemical properties of the surface. A number of reactions have been studied over mesoporous materials which include conversion of synthetic gas, oxidative dehydrogenation of alkanes or benzene, Knoevenagel condensation, Claisen–Schmidt condensation, acylation, synthesis of acetals / ketals, etc.\textsuperscript{165-178} Mesoporous materials like MCM-41, MCM-48, and FSM-16 have been successfully used for such applications for a long time.\textsuperscript{4-9}

1.4.2. Sensing: Just like catalysis, the application of NMs in sensing has been an emerging aspect in nanosciences owing to the highly tunable physical, chemical, thermal, optical, and electrical properties and their high surface areas. Many types of sensors have been successfully fabricated by different groups.\textsuperscript{179-182} MNPs such as
Au, Ag and metal oxide NPs such as Fe₂O₃/Fe₃O₄ have been used in the fabrication of a series of sensors. The research interests towards greener as well as noncytotoxic materials suitable for bioimaging, biolabelling, and biodiagnostics led to the realization of semiconducting nanodots.\textsuperscript{183} Quantum dots of PbS, CdSe, or CdTe cores with epitaxially grown ZnS or CdS shells with <10nm size are found to have very high quantum yields (ca.90%), which can be finely tuned under controlled experimentation. These quantum dots with narrow emission spectra are useful for biomedical imaging.\textsuperscript{184} Nanostructured conducting polymers are used to detect volatile organic compounds and alcohols.\textsuperscript{185} In the recent years, there are plenty of reports where specific NPs have been developed for a wide range of selective sensing applications.\textsuperscript{186-190}

1.4.3. Medicine and Biology: Medicinal applications of NMs have also been on the rise.\textsuperscript{191-204} The interface between biological systems and NMs has recently attracted interest since these materials proved to have potential as intravascular probes for both diagnosis and therapeutics. The discovery and design of nanoscale drugs are making enormous contributions towards controlled and targeted drug release, diagnosis, tissue replacement and in surgical aids. Drugs can be associated with the NPs in entrapped, encapsulated, or attached form. Nanodrugs are being synthesized in various forms such as nanospheres, nanocapsules, nanopores, dendrimers etc. This helps to gain better control over the drug release process.
1.5. Toxicity of nanomaterials

The rapid growth of Nanoscience and Technology in diverse areas has made it so important that it is being applied in all aspects of daily life. The extremely small size and high surface area, the unique physical, chemical as well as electronic properties endow them most useful in specific areas like bio-sensing, targeted drug and gene delivery and in medical imaging. Because of the similar size scales they can interact with biological systems. The ability of NPs to cross cell barriers, enter cells, and interact with subcellular structures is well established. These small particles are also found in a variety of consumer products in the form of cosmetics, sunscreens and in Textile industry. Ag and ZnO NPs are used in food packaging and in washing machines. NPs exist in the atmosphere from both natural and anthropogenic sources. Examples of natural NPs include soil colloids, airborne nanocrystals of sea salts, volcanic eruptions, biogenic magnetic clay, etc. Carbonaceous NMs like metal oxides such as TiO$_2$, ZnO, ZnS semiconductor materials, including quantum dots, zerovalent metals such as Fe, Ag, Au and Cu, Zn, Ni, Pt, Pd and nanopolymers such as dendrimers are examples of anthropogenic NPs.

Recent studies reveal that there is dramatic increase in the NP production over the past few years. Processes ranging from simple combustion to large industrialization processes release NPs into atmosphere. For the past few years, the concern over human and environmental hazards caused by the NMs has been on the rise and this resulted in the emergence of a new field known as Nanotoxicology, which deals with the effects and potential risks of particulate structures of <100nm in size. Toxicologists point out that the interaction of these NMs with biological systems may lead to unexpected and unanticipated consequences. Reports detail the possible risks associated with NPs, including the risks for environment and risks to biological
systems which demonstrate that NMs can affect biological behaviors at the cellular, subcellular, and protein levels.\textsuperscript{205-211} One hypothesis is that these NPs induce oxidative stress as a result of extremely reactive free radical formation. These reactive species once entered into the intracellular compartments, result in the oxidation and damage of lipids, proteins, and DNA.\textsuperscript{209} With the rapid growth in the activities, there are growing environmental concerns and regulations and immense quantum of research for assessing the risk of the nanoparticles to the overall biological health.\textsuperscript{212-220}

1.6. Present study

Noble MNPs, especially Au and Ag, have attracted much attention due to their versatile optical and electrical properties, catalytic behavior, and applications in medical diagnostics and treatments. Their bimetallic alloy NPs, self-assembled three dimensional networks, and other modified architectures are of importance due to their wide range of applications. Biocompatible nanosystems will have added advantage in their applications in biomedical research. The work presented in this thesis is also an attempt in this direction. The chapters are arranged in the following manner.

The second chapter discusses the general instrumental methods for the characterization of NPs and NPs networks. Fundamentals of electron spectroscopy, electron microscopy (TEM and SEM), AFM, surface area measurements, XRD etc. and the utilization of these techniques for the characterization of the nanostructured materials are presented.

Chapter 3 deals with the synthesis and characterization of starch stabilized Au, Ag, and Au-Ag alloy NPs as well as the antibacterial activity studies using these
particles against gram positive and gram negative bacteria such as *Staphylococcus aureus*, *Escherichia coli*, *Acinetobacter* sp. and *Klebsiella* using the conventional disc diffusion method. It is well known that the Ag NPs systems can be used as bactericides for medical applications. On the other hand, the Au NPs above 5 nm size are considered as non-toxic and these particles do not exhibit any antibacterial property. It has been reported over the years that it is possible to prepare alloy NPs of Au and Ag and that their surface plasmon absorptions can be tuned. Herein we synthesize starch-stabilized Au, Ag, and Au-Ag NPs and investigate if it is possible to tune the bactericidal/ biological activity of Ag NPs by alloying with the more benign Au nanoclusters. Particularly, we wanted to investigate if any correlation can be obtained between the $\lambda_{\text{max}}$ of the SPR absorption and the bactericidal property. Since the capping agent and the reducing agents used need to be biologically compatible, we employed the green chemical route for the synthesis of the NPs using starch as the capping agent and $\beta$-D- glucose as the reducing agent, in aqueous media. It is observed that while the starch stabilized Ag NPs are excellent antibacterial agents, the alloys do not show any noticeable activity.

The fourth chapter deals with the networking of Au, Ag, and Au-Ag NPs to form mesoporous gold, thin films, and sponge. Herein, we have tried to mimic the *lotus leaf* effect by modifying the surface of mesoporous sponge by a self assembled layer of decanethiol. We have also synthesized superhydrophobic, mesoporous, Au sponge which can stabilize air around it when placed inside water.

The fifth chapter deals with dealloying of the Au-Ag alloy NPs as well as mesoporous Au-Ag sponge. Dealloying of the NPs is followed by UV-Visible absorption studies. Mesoporous Au-Ag alloy sponge synthesized was also dealloyed
to make catalytically active gold surfaces. Typical catalytic experiments are also carried out.

The sixth chapter deals with the synthesis of mesoporous TiO$_2$ in the anatase phase following a template-free route, plausibly through a control of the molecular speciation of the precursor molecular systems in a dispersion medium. The sample thus synthesized is characterized using various characterization techniques. TiO$_2$ supported Au NPs systems were also synthesized and their catalytic applications are studied.

The seventh chapter presents the conclusions of the results of the investigations described in the previous chapters and presents a future outlook of the work.