Chapter 1
Introduction
The progress of technology is closely interlinked with the better living of mankind. The need for advancement in technology is driven by continuous pursuit of further miniaturization and increased functionality with lower power consumption, greater efficiency and cost benefits. The technology in the field including material science, engineering and industry is necessary for developing such miniaturized and functionalized nanomaterials. The term ‘nano’ comes from Greek word meaning dwarf. Nanoscience is the study of the properties, consequent phenomena and manipulation of material at nanoscale ($\sim 10^{-9}$ m). This provides better understanding of the behavior as well as phenomena of materials at nanoscale. Nanotechnology deals with the design, control and integration of atoms and molecules to form materials, structures, components, devices, products and systems at the nanoscale. The inspiration for ever growing interest in the field of nanoscience and nanotechnology was revived by Richard Feynman in his public lecture entitled, “There’s plenty of room at the bottom” [1] on the occasion of American Physical Society Annual Meeting at California Institute of Technology in 1959. The term ‘nanotechnology’ was first used by Norio Taniguchi in 1974 [2] and was popularized by A. Dexler who envisioned a nanorobot that assembles single molecules with atomic precision in order to produce themselves or other objects in his published book entitled, ‘Engines of creation’ in 1980s. Nanotechnology covers a broad indisciplinary field and requires expertise in fields such as physics, chemistry, material science, biology, medicine, engineering, etc. It is the intermediate of atoms and molecules, and macro world where the properties are governed by the fundamental behavior of collection of atoms. Moreover, it offers a great challenge to mankind in which the control of materials at atomic scale is desirable.

Nanomaterial is defined as a material with at least one of its dimensions measured in nanometer ($10^{-9}$ m). Nanomaterials have been used in art and culture of ancient times and more evidently in nature since billions of years, much before the term ‘nano’ came into being. Nature never ceases to amaze us and is capable of making sophisticated materials, captures energy, self healing and storing information with incredible efficiency. A remarkable example of the role of nanostructures in daily life is photosynthesis. The process of photosynthesis is due to the presence of large number of chloroplasts in the leaves. Chloroplasts in a leaf contains disks called thylakoids which
are the sacs containing light sensitive pigments of nanoscale dimensions responsible for absorption of photons from sunlight and subsequent production of sugar and oxygen. Another biological example of molecular machinery is ribosome which is a remarkable nanoscale assembler by combining amino acids to produce proteins. The self-cleaning of lotus leaf is another example of nature’s nanotechnology. The crystals of nanodimensions present in the lotus leaf help water droplets to carry dust and dirt off the surface, keeping the leaf clean at all times. Tiny hair-like projections on the feet of the lizard (Gecko) contain nano-sized structures that act as a dry adhesive and give the lizard the ability to walk on walls and ceilings. Other examples of nature’s nanostructures are abalone, a marine mollusk having shell made up of nanocomposite of calcium carbonate and protein and spiderweb which is nanocrystalline reinforcements embedded in a polymer matrix.

There are evidences for use of material of nanoscale dimension in decoration, art and culture of ancient times even though there was no scientific understanding of these phenomena or any deliberate attempts to produce the nanoparticles. In ancient India, the therapeutic value of finely ground metals and mineral has been known in Rasa Shastra, better known as Ayurvedic pharmaceutics. The fine particles of metal on consumption get absorbed and assimilated into the biological system as Adya Rasa Datu, primary physiological fluids essential for human survival. It is believed that use of these fine metal particles cure ailments, their prolonged use provide strength and immunity which delay the ageing process. One such preparation is Swarna Bhasma, fine particles of gold considered as best rejuvenator and also prescribed for ailments like tuberculosis, cough, anaemia and muscular dystrophy. Swarna Bhasma is also known to have medicinal effect for longevity and prevention of ageing. From ancient times, kajal which is carbon soot has immense medicinal values. The ruby colored stain glass windows from medieval era were due to presence of nanoscale metallic particles within the glass. The interesting phenomenon of producing colors is due to the presence of embedded metal nanoparticles in glass. Another example is fourth century Roman era Lycurgus cup which has nanosized gold and silver particles embedded in the glass. The remarkable characteristic of this goblet is that it appears green under normal lightings but appears red when lighted from within. Tin glazed pottery and copper
glazed lusterware of medieval and Renaissance age are some of the examples of manmade nanoparticles even before the word ‘nano’ was coined.

1.1. Nanomaterials and their classifications

Nanomaterials are categorized mainly into three kinds depending upon the number of confinement of physical dimension in the nanoscale range namely, zero-dimensional (0-D), one-dimensional (1-D) and two-dimensional (2-D) nanomaterials:

(a) Zero-dimensional (0-D) nanomaterials

Systems wherein all dimensions lie within the nanoscale are zero-dimensional (0-D) nanosystems as shown in fig. 1.1(a) wherein the atoms may be arranged randomly (forming amorphous) or nanocrystalline. In case of nanocrystalline arrangement, each nanoparticle is either a single crystal or a large number of single crystals. The latter may have single crystals with different orientations. There are varieties of shapes of nanoparticles such as spherical, needle shaped, platelet, etc.

![Fig. 1.1: Nanosystems (nm size) depicting (a) zero-dimensional (b) one-dimensional and (c) two-dimensional nanomaterials.](image)

(b) One-dimensional (1-D) nanomaterials

1-D nanomaterials as shown in fig. 1.1(b) have one of the dimensions greater than 100 nm whereas other two dimensions are within nanometer range. Such nanostructures
include nanotubes, nanorods and nanowires. 1-D nanostructures may be either amorphous or crystalline. They may exist as standalone or embedded within a matrix.

(c) Two-dimensional (2-D) nanomaterials

2-D nanomaterials are nanostructures for which two of the dimensions are not confined to the nanometer scale. Examples are nanofilms, nanolayers and nanocoating. Similar to 0-D and 1-D nanostructures, they can either be amorphous or crystalline.

1.2. Nanomaterials versus bulk material

When a material is reduced to nanoscale, they display physical attributes different from those of either isolated atoms or their bulk. These account for the unique behavior of nanostructures as compared to the bulk materials.

(a) Surface area to volume ratio

One of the most fundamental difference between nanomaterials and bulk materials is that nano-systems has large ratio of surface area to volume. For the bulk material the properties of large scale materials are predominantly determined by volume and a little contribution from the surface area. However, in nanomaterials the large surface area to volume ratio plays major role in determining the properties of nanomaterials. Each shape of nanostructures has distinct surface area to volume ratio resulting in different properties for different shapes of nanostructures. Hence shape of nanostructures is of significance in nanometer regime. Furthermore, the large proportion of atoms at the surface results in reduction of nearest neighboring atoms of the material. This in turn gives rise to increase in surface energy and decrease in binding energy as compared to that of bulk. This difference may lead to different properties such as structural and chemical properties.

(b) Electronic band structure

The energies of the electronic states as well as spacing between successive energy levels depend inversely on square of the dimension of the system. In bulk the electronic energy levels spread out into energy bands. The reduction of size of material to nanometer scale directly influences the energy band structure leading to quantum
confinement of electrons. Furthermore, the allowed energy bands become farther apart in some cases whereas in other cases the allowed bands are narrower than that of bulk solid. Let us discuss this in terms of electronic confinement by considering the reduced dimensional nano-systems: 0-D, 1-D and 2-D. For 0-D nanostructures, an electron is confined in 3-D space. In case of 1-D nanostructures, electron confinement occurs in 2-D space and delocalization along the axis of nanotube, nanowire etc. whereas in 2-D nanostructures, electron confinement occurs in 1-D space across the thickness but delocalized in the plane of the sheet. Thus, different electron confinements and delocalization states exist for 0-D, 1-D and 2-D nanosystems. Under these conditions of confinement, the normal collective (i.e. delocalized) electronic properties become different than those of bulk and the electrons behave more like ‘a particle in a confined space of 3-dimension, 2-dimension and 1-dimension’. Subsequently, the effect of confinement on the energy state of 0-D, 1-D and 2-D nanosystems can be described respectively as

$$E_n = \left[ \frac{\pi^2 h^2}{2m} \left( \frac{n_x^2}{l_1^2} + \frac{n_y^2}{l_2^2} + \frac{n_z^2}{l_3^2} \right) \right]$$  (0-D)

$$E_n = \left[ \frac{\pi^2 h^2}{2m} \left( \frac{n_x^2}{l_1^2} + \frac{n_y^2}{l_2^2} \right) \right]$$  (1-D)

$$E_n = \left[ \frac{\pi^2 h^2}{2m} \frac{n_z^2}{l_1^2} \right]$$  (2-D)

where h is Planck’s constant, m is the mass of electron, l_1, l_2 and l_3 are the width of confinement along x, y and z directions respectively, and n_x, n_y, n_z are the principal quantum numbers along x, y and z directions respectively. From these above equations, lesser the dimension of the nanostructures, wider is the separations between the energy levels leading to discrete energy levels. As energy is inversely proportional to the dimension of the system, the number of electrons lying between a narrow energy range i.e. density of state (DOS) is also dependent on dimensionality of the structure. Therefore, density of states as a function of energy of electrons shown in fig. 1.2 will be different for 0-D, 1-D and 2-D nanostructures. All these have important implications on the chemical reactivity as well as physical properties such as thermal, electrical, optical
and magnetic characteristics as these characteristics depend on the arrangement of the outermost electronic energy level. Metallic systems may undergo metal-insulator transitions as the system dimension is reduced due to formation of energy band gap in metal. We shall discuss briefly about the change in structural, mechanical, thermal, chemical, magnetic, electronic and optical properties for nanostructures in the following section.

Fig. 1.2: A plot of density of state function for nanosystems such as: (a) zero-dimensional (b) one-dimensional and (c) two-dimensional.

1.3. Properties at nanoscale

The above mentioned physical attributes of nanoscale objects are responsible for novel and significantly improved physical and chemical properties as compared to their bulk. These novel properties have stimulated the tremendous progress in nanoscience and nanotechnology. We will now discuss some salient changes in different properties at nanoscale with respect to bulk.

1.3.1. Structural properties

Nanostructures have significant proportion of atoms on the surface as compared to interior. The increase in overall surface area of nanostructured material leads to increase in total free surface energy and hence materials in nanoscale dimensions are thermodynamically unstable. The increase in surface energy has often resulted in compressive strain in the nanoparticles which leads to decrease in inter-atomic spacing
in nanostructures of metal [3]. Conversely, increase in inter-atomic spacing has also been observed with decreasing particle size of metal oxide and semiconductors [4]. Hence, the surface energy plays an important role in determining the structure of the nanomaterials. When the size of nanoparticles is \(~1\) nm or less, they possess reduced lattice parameters. The reduced lattice constant is as a result of change in the surface energy and elastic energy to minimize free energy. Larger nanomaterials than \(1\) nm possess structure which is characteristics of the bulk with similar lattice parameters. For most nanoparticles, the size is larger than \(1\) nm, thus most of their properties resemble those of bulk material [5]. When the size of the particle is reduced to nanoscale, the number of atoms/molecules forming the nanoparticle has great influence on its structure. For instance, aluminium is known to exist in face-centered cubic (fcc) structure in its bulk form but it has hexagonal closed pack (hcp) structure in addition to fcc structure in nanoscale dimension.

### 1.3.2. Mechanical properties

Mechanical properties also depend on atomic and structural arrangement of atoms in the material. Nanostructures which have atomic arrangement different from their bulk will show very different mechanical properties. For instance, carbon nanotubes are found to possess high mechanical strengths and high elastic limits leading to high mechanical flexibility and reversible deformation [6]. The ease of formation or support of defects highly influences mechanical properties such as hardness. In nanomaterials, the ability to support defects in a material is reduced leading to greater hardness. Hardness (\(H\)) can be expressed as a function of size: \(H \sim C/d^{1/2}\) where \(C\) is a constant and \(d\) is the grain size. With decrease in the grain size, hardness is increased. This increase in the hardness can be explained to be due to the fact that the grain boundary acts as obstacles to dislocation motion due to disorderness and non-coplanar with its neighbour. Hardening by nanodispersion has been known to be the oldest application of controlled nanoscale structuring. For instance, the alloy of aluminium and copper has been hardened by nanodispersing the copper of nanoscale dimension. Reducing the copper particle size to about \(5\) nm, hardness increases by a factor of about \(10\) [7]. Moreover, the large ratio of surface area to volume of nanostructured materials can also enhance the mechanical properties such as plasticity, ductility and strain which are interface dependent. Metal
nanostructures and ceramic are able to undergo extensive deformation without causing necking or fracture which is referred to as superplastic property. This is possibly due to grain boundary diffusion and sliding which are significantly higher in a nanostructured material.

1.3.3. Thermal properties

Thermal properties such as melting point of a material are correlated with the bond strength. In bulk materials, the surface to volume ratio is small and the curvature of the surface is negligible. As a result, the surface effects of a bulk solid does not influence melting point. In case of nanomaterials due to large ratio of surface to volume, the nano-system may be regarded as containing surface phases with different free energies. In addition, the curvature of the surface for 0-D, 1-D and 2-D nanomaterials is very pronounced. As a result, the melting temperature for nanomaterials is different from its bulk. Moreover, the large increase in surface energy and change in the interatomic spacing with decreasing size of nanoparticles have significant effects on their thermal properties such as melting point, thermal conductivity. For instance, the melting point of gold nanoparticles is observed to decrease rapidly as the nanoparticle size is reduced beyond 10 nm [5]. Opposite behavior is observed for metallic nanocrystals embedded in aluminium matrix [8]. In addition to the melting temperature, the size reduction to nanoscale affects the heat transport mechanism viz. phonon scattering and electrons. In bulk material, the phonon wavelength is much smaller than the length scale of the microstructures. However, in nanomaterials the dimension of nanostructure is of same order as phonon wavelength. This leads to quantum confinement of phonons. The phonon confinement is similar to that of electron confinement. For instance, quantum confinement of phonons occurs in three dimensions in 0-D nanomaterials. In 1-D nanomaterials, phonon confinement is in two dimensions whereas in 2-D nanomaterials, quantum confinement of phonon is in one dimension.

1.3.4. Chemical properties

The change in the electronic band structure has influenced the ionization potential as it tends to get higher for small atomic clusters than that of corresponding bulk material.
Furthermore, nano-systems such as nanoparticles and nanolayers have large ratio of surface area to volume. This has profound effect on reactions that occur at the surface such as catalytic reactions, detection reactions and reactions that require physical absorption of certain species at material surface. Moreover, nanostructures have high surface to volume ratio and different crystal structures which leads to alteration of the chemical reactivity from that of their bulk counterparts. Catalysis using nanostructures can enhance the rate, selectivity and efficiency of chemical reactions. Nanomaterials such as gold nanoparticles adopt new crystal structure i.e. icosahedral structure instead of face centered cubic arrangement. This structural change can lead to increase in the catalytic activity even though bulk gold is not a good catalyst. Furthermore, nanostructures often show new chemical properties different from their bulk counterparts. For instance, medicine having nanostructured particles can get dissolved easily in water even though micro-dimensional particles are insoluble in water.

1.3.5. Magnetic properties

Bulk ferromagnetic materials usually form multiple magnetic domains. The large proportion of surface atoms in nanomaterials have enhanced magnetic coupling leading to magnetic properties different from their bulk. Nanostructures of magnetic materials have more dominant exchange forces due to strong coupling resulting in alignment of all spins in the neighboring atoms. This gives rise to a critical grain size below which the material will be in a single magnetic domain. The critical diameter $D_c$ for a spherical grain [9] is given by

$$D_c = \frac{9\gamma_b}{\mu_0 M_s^2}$$

where, $\gamma_b = 4(AK_1)^{1/2}$ is the domain wall energy which is related to the exchange energy and anisotropy energy of magnetic domain in a ferromagnetic material, $A$ is the exchange constant (or exchange stiffness) which arises due to exchange coupling between neighboring magnetic domains and is dependent on the material and temperature, $K_1$ is the anisotropic constant, $\mu_0$ is the magnetic permeability of free space and $M_s$ is the saturation magnetization. If the grain size is significantly smaller than the critical diameter, the overall magnetic coercivity is lowered. In addition, magnetization
of the particles which are otherwise distributed randomly due to thermal fluctuations, become aligned on application of a magnetic field. These nanoparticles of magnetic material are known to exhibit a phenomenon called superparamagnetism in which the material exhibits a single magnetic domain. This phenomenon is similar to paramagnetism although it occurs at a temperature below Curie temperature of the ferromagnetic material and there is no remnant magnetization on removing the applied magnetic field. Additionally, bulk magnetic metal is found to exhibit magnetoresistance in which the electric resistance increases on application of strong magnetic field. However, nanoscale multilayers consisting of strong ferromagnet and non-ferromagnetic material exhibit much greater magnetoresistance effect, a phenomenon characterized by high resistance on application of magnetic field.

1.3.6. Electronic properties

In case of bulk material, conduction of the electrons is delocalized. When these electrons move, they get scattered by phonons, impurities and interfaces. The nanoscale effects in the electronic properties is the electron confinement which results in discreet energy states in place of energy bands in solids and the reduction of scattering centers. Moreover, the discrete nature of energy states becomes more apparent when the dimension of nanoscale objects is comparable to the de Broglie wavelength of the electron. In some cases, a conductor can behave like a semiconductor or insulator and vice versa.

In case of 2-D nanostructures, the confinement of electrons occurs along the thickness while the carrier motion is along the plane of the sheet. The electrons are trapped in a potential well of width equal to the thickness of nanoscale objects. The total energy thus consists of two components; one term pertaining to confinement along the thickness and another for the unrestricted motion along other two dimensions. Due to confinement, scattering by phonons and impurities is restricted along the plane. However, large amount of grain boundary area provides an additional in-plane scattering. Smaller the size of the grain, the lower is its conductivity. In case of 1-D nanostructures such as nanotube, nanowire or nanorods, quantum confinement occurs along two dimensions whereas electrons are delocalized along their axis. Consequently,
the energy depends on two quantum numbers resulting in sub-bands instead of a single band. In addition, the confinement results in restriction of scattering by phonons and impurities along the axis of the nanotube, nanorods or nanowire even though boundary scattering is more due to large surface area. This results in ballistic electron transport along the axis particularly at low temperature. In case of 0-D nanoscale objects, the motion of electrons is totally confined along the three dimensions. This implies that the energy states are discreet and localization of electrons takes place in all the three directions. In such case, metallic system can behave as semiconductors or insulators due to the formation of energy gap which is not possible in bulk material. Additionally electron tunneling occurs between adjacent nanostructures when voltage is applied between the nanostructures causing the alignment of discrete energy levels in the density of states. The resonance is characterized by sudden increase in the tunneling current. Conduction in highly confined structures such as nanodots is sensitive to the presence of carrier and hence the charge state in the dot. This effect results in conduction which may involve a single electron which will require a small amount of energy to operate a switch, transistor or memory element. All these phenomena arising out of quantum confinement in nanostructures can be applied to produce radically different type of components for electronic, optoelectronic and photonic devices.

1.3.7. Optical properties

In nanostructures, the reduced size has profound impact on highest occupied orbital i.e. valence band (VB) and lowest unoccupied orbital i.e. conduction band (CB). Thus processes such as optical emission and absorption involving transitions between these bands will be altered. The absorption energy of nanostructures is influenced by quantized density of states of valence and conduction bands and the excitonic levels. As we approach 0-D from 2-D nanostructures, the quantum confinement becomes stronger and density of states are more quantized resulting in blue shift of optical band gap [10]. The absorption peak associated with the formation of exciton shifts to lower wavelength with decreasing size of the nanostructure. In weak confinement regime, i.e. when the dimensions of nanostructures are few times larger than the exciton Bohr radius, the Coulomb interaction between electron and hole leads to an increase in the exciton binding energy (energy difference with the lowest exciton state and the
conduction edge) causing the shift of the exciton peak to higher energy. However, in strong confinement regime i.e. when the dimension of the nanostructure is sufficiently smaller than the exciton Bohr radius, motion of electrons and holes are independent because their wave functions are uncorrelated. Consequently, nanostructures exhibit change in their optical properties mainly shift in optical band gap (shown in fig. 1.3) as a result of quantum confinement in semiconductor nanostructures. The excitonic peaks of bulk semiconductor are observed in the absorption spectra at low temperature and are too weak to be seen at room temperature. However, strong excitonic states may appear in the absorption spectra for nanostructure at room temperature. This is because the enhanced confinement in nanomaterials increases the exciton binding energy and reduces the possibility for exciton ionization at higher temperatures. Optical emissions may also occur when there is recombination of an electron and a hole which causes the generation of a photon. If the photon energy is in the visible range then the phenomenon is known as luminescence. For nanomaterials, the emission peak shifts towards the shorter wavelength due to quantum confinement as size of the nanostructure decreases.

![Fig. 1.3: Schematic of band structure (a) Bulk and (b) Nanostructure.](image)

The optical properties of metals are affected by nanoscale. Metallic nanoparticles have fascinated for their colorful properties for over thousands of years. Moreover, the synthesis of nanoparticles of metals had been established long before the concept ‘nano’ came into being. Roman Lycurgus cup of the 4th century and stain glass of the 17th
century have unique optical properties due to surface plasmon resonance (SPR) of gold and silver nanoparticles. This phenomenon was not known until Faraday proposed that metal of reduced size is capable of strong interaction with light [11]. The next significant contribution in the study of optical properties of metal nanoparticles was made by Mie in 1908 who published a seminal work [12] on extinction properties of metal sphere on interaction with photons. It is now well known that the interaction of light with free electrons in nanoparticles of noble metal such as gold and silver can give rise to collective oscillations commonly known as surface plasmons. We shall discuss about surface plasmon resonance of metal nanoparticles in section 1.4 and the applications of metal nanoparticles on account of surface plasmon resonance in section 1.5.

1.4. Surface plasmon resonance in metal nanoparticles

Many metals such as gold, silver, copper, aluminium, etc. can be treated as free electron systems whose electronic and optical properties are described by the conduction electrons only. Bulk metals show plasmonic behavior that describes collective oscillation of conduction electrons. The frequency with which the electron density oscillates relative to the lattice of positive ions is called plasma frequency, \( \omega_p \). For a bulk metal with infinite sizes in three dimensions, \( \omega_p \) can be expressed as

\[
\omega_p = \left( \frac{Ne^2}{\varepsilon_0 m_e} \right)^{1/2}
\]

where \( N \) is the number density of electrons, \( \varepsilon_0 \) is the dielectric constant of vacuum, \( e \) is the charge of electron and \( m_e \) is the mass of electron. The quantized plasma oscillation in metal is known as plasmons. The plasma frequency for metal lies in far UV regions. Plasmons in bulk metal cannot be excited optically. For metal nanostructures, the surface plasmons can be excited by light. When light is incident on a metal nanoparticle, free electrons are driven by the electric field to collectively oscillate relative to the positive lattice ions. The schematic of the interaction of incident light with the surface electrons of a metal nanoparticle is shown in fig. 1.4. The displacement of the negative charges due to the electric field gives rise to polarization charges at the surface resulting in a restoring force. The physical origin of the light absorption by
metallic nanoparticles is the collective oscillation of free electrons in resonance with the incident electromagnetic radiation which is known as surface plasmon resonance.

Fig. 1.4: Schematic of interaction of surface electrons of a metal nanoparticle with incident light.

For metal nanoparticles having size much smaller than the wavelength (λ) of light i.e. radius, \( r << \lambda \), the contribution to the extinction cross section (absorption + scattering) can be considered to be from dipoles [12] only. In this regime, the electric field of the electromagnetic radiation can be considered as a constant (quasi-static regime).

For the quasistatic regime \((r << \lambda)\), the extinction cross section is dominated by absorption only and is expressed as

\[
\sigma_{\text{ext}} = \frac{24\pi^2 R^3 \varepsilon_m^{3/2}}{\lambda} \frac{\varepsilon_2(\omega)}{|\varepsilon_1(\omega) + 2\varepsilon_m|^2 + \varepsilon_2(\omega)^2} \tag{1.1}
\]

where \( \varepsilon_m \) is the dielectric constant of the surrounding matrix, \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) are real and imaginary parts of complex dielectric function \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \). The extinction cross section has a resonance when the denominator of equation 1 is minimum,

i.e. \(|\varepsilon_1 + 2\varepsilon_m|^2 + |\varepsilon_2|^2 = \text{minimum.} \)

Therefore, the condition for resonance to occur is

\[
\varepsilon_1 = -2\varepsilon_m \tag{1.2}
\]
provided that the imaginary part of dielectric function $\varepsilon_2 \ll 1$ or weakly dependent on frequency [13]. For the condition to be satisfied, $\varepsilon_1$ should be negative which is possible only for some metals in the optical region. At the frequency, $\omega_{sp}$ (or wavelength, $\lambda_{sp}$) at which the condition is satisfied, the collective oscillation of free electrons is in resonance with the electromagnetic radiation. The plasmon resonance frequency (or wavelength) lies in the visible range for nanoparticles of metals such as gold, silver and copper.

Metal nanoparticles exhibit unique and tunable optical properties on account of SPR in visible region which is not seen in its atomic or bulk form. The SPR results in strong enhancement of absorption and scattering and is the origin of intense color and other interesting properties [12,14]. The resonance wavelength is dependent on size and shape of the nanoparticles [13,15-18], dielectric properties of the surrounding matrix [17,19], composition of metals [17] and interparticle distances [13,20]. The optical properties can be tuned through out the visible and near infra red region by changing the factors mentioned above. We shall discuss briefly about the dependence of resonance wavelength on the above mentioned factors.

### 1.4.1. Dependence on size, shape, dielectric properties and particle-particle interaction

The resonance wavelength of surface plasmon oscillation depends on the nanoparticle size [13,15-18]. Size dependence of plasmon absorption in the quasi-static regime comes from the dielectric function $\varepsilon(\omega, r)$. For intrinsic size regime ($r << \lambda$), the surface plasmon wavelength cannot be explained only by size effects [13]. However, for larger nanoparticles ($r < \lambda$) i.e. in extrinsic size regime, the resonance peak redshifts increase in size of the nanoparticle [21]. The plasmon resonance bandwidth increases with decrease in size [22] for $r << \lambda$ regime. However, in large nanoparticles ($r < \lambda$) the plasmon bandwidth increases with increasing size [13]. The broadening of the resonance band is attributed to retardation effects as a result of excitation of different multipole modes [22].
Metal nanostructures having different shapes such as spherical [23], triangular [24], rods [25], prisms [26], cubes [27] etc. have been reported. The shape of metal nanostructures has great influence on the surface plasmon absorption peak [13,15-18]. The surface plasmon oscillation in metal nanostructures arises due to the restoring force in response to the polarization induced by a displacement of the electron cloud with respect to the positive metallic lattice in the presence of the electric field. The magnitude of restoring force depends on shape of the electron cloud [13] and the polarization of the light. A nanostructure with a sharp surface curvature (e.g. nanotriangles or nanorods) along the polarization direction has weaker Coulombic restoring force on the electron cloud as compared to a sphere. This results in redshift of wavelength of surface plasmon resonance. For any shape, the polarizability can be expressed in terms of depolarization factor L [21] as:

\[
\alpha = \frac{4\pi\varepsilon_0 R^3}{L} \left[ \frac{\varepsilon_0 - \varepsilon_m}{\varepsilon + \left( \frac{1-L}{L} \right) \varepsilon_m} \right] 
\]

(1.3)

For spherical nanoparticle which is isotropic in all three directions, L=1/3, the equation (4) becomes

\[
\alpha = 4\pi\varepsilon_0 R^3 \frac{\varepsilon_0 - \varepsilon_m}{\varepsilon + 2\varepsilon_m} 
\]

(1.4)

Gold nanorods have two plasmon resonance peaks corresponding to the oscillation of free electrons along and perpendicular to the long axis of the rods [28] while gold nanodots has a single plasmon resonance peak. The transverse mode coincides with the plasmon resonance wavelength of the spherical nanoparticles whereas the resonance wavelength of longitudinal mode lies in the longer wavelength as compared to that of transverse mode and is strongly dependent on the nanorods aspect ratio (~ length/width) [29]. However if gold nanorods of varying aspect ratio are made to align parallel to each other inside an optically transparent aluminium oxide
membrane, they exhibit only one plasmon resonance [30]. The plasmon resonance peak also depends on the complex dielectric function of the composite material (metal nanoparticles and aluminium oxide) which was calculated by Maxwell-Garnett theory if the dielectric data of the metal and host matrix are known [13].

The plasmon resonance wavelength is sensitive to the dielectric properties of the substrate matrix surrounding the metal nanoparticles [16-17]. The resonance wavelength shifts to longer wavelength with increase in the dielectric constant of the surrounding matrix [31] due to decrease in Coulombic restoring force on the displaced electron cloud. The presence of substrate changes dielectric constant in the vicinity of metal nanoparticles which induces charge distribution on the substrate. This affects charge distribution of the nanoparticles resulting in the resonance wavelength shift.

The surface plasmon resonance wavelength is highly influenced by interaction of nanoparticles in close proximity [20,32] due to coupling of the plasmon oscillations of individual nanoscale objects. The plasmon oscillation at resonance enhances electric field in the vicinity of the nanoparticle. Nanoparticles in close proximity can thus interact with each other resulting in decrease in the frequency of the surface plasmon oscillation of the system as compared to that of isolated nanoparticles. Consequently, increase in the number of nanoparticles induces a red shift of the surface plasmon wavelength [33]. The shift of plasmon resonance also shows dependence on the polarization. When nanoparticles are aligned along an axis parallel to the polarization of incident light, nanoparticles get polarized in such a way that the induced local field is in the same direction as the electric field of incident light but opposite to the restoring force resulting in decrease in frequency of the plasmon oscillation [34]. When the incident field is perpendicular to the axis of the alignment, it polarizes the nanoparticles induced field against the applied field but in the same direction as the restoring force resulting in increase in frequency of the plasmon oscillation.

Bimetallic nanostructures of two different metals have surface plasmonic properties different from their individual metal nanostructures in terms of tunability and sensitivity [35]. The spectral position of SPR peak of bimetallic nanostructures further
depends on the composition and distribution of the two metallic nanostructures [13] in addition to the above described factors. The interaction between two metal leads to formation of either core-shell type or alloy-type nanostructures [36].

1.5. Applications of metal nanoparticles

The dependence of plasmon resonance wavelength of metal nanoparticles on different factors such as size, shape, dielectric properties and interparticle separation etc. discussed in section 1.4 can be exploited for applications in various fields such as electronics [37], biosensings [38-41], bio-imaging [42], photo-thermal therapy [43-46] drug delivery [47], photonics [48], plasmonics [49,50] and photovoltaic cells [51,52]. In addition, molecules conjugated with metal nanoparticles exhibit enhanced surface enhanced Raman scattering (SERS) effects [53].

The phenomenon of SPR of metal nanoparticles results in enhancement of optical absorption and scattering which make them superior than conventional dyes for biological and biomedical imaging [42]. The sensitivity of the resonance peak to the change in dielectric properties surrounding the nanoparticles has been employed for applications in sensing biomarkers for Alzheimer’s disease [38] and other biomolecules [39,40]. The surface plasmon absorption can be efficiently converted into heat within picoseconds time scale [34]. This rapid photo-thermal conversion leads to localized heating of the medium surrounding the nanoparticles. This plasmonic heating of metal nanoparticles has potential for selective photo-thermal therapy of cancer [43-46]. The enhancement of strong electromagnetic field in the vicinity of a metal nanoparticle on account of surface plasmon resonance can be used in SERS [53,54] technique resulting in strongly enhanced Raman signal from molecule attached with metal nanoparticle and plasmonic device [49,50]. The ultrafine metal particles are found to exhibit high catalytic activity in oxidation of carbon monoxide [55] on accounts of its structural effects [56].

We have discussed the SPR in nanoparticles of metals in individual and bimetal formation, and various factors influencing the spectral position of resonance
wavelength. Hence it is of great significance to explore the possible methods used in earlier studies for fabricating metal nanostructures and bimetallic nanostructures of different sizes and shapes.

1.6. Earlier methods of fabrications of metal nanostructures

Nanofabrication holds key to the development of novel miniaturized materials for devices and functional systems. Fabrication of metal nanostructures has been known for thousands of years. The properties and performance of material are highly influenced by thermodynamics and kinetics of processing and methods of fabrication.

The earliest methods of synthesis of metal nanostructures are mainly chemical based. Chemical methods involve a number of reactions taking place in liquid or gas phase. The formation of atoms/molecules can be accomplished by using chemical reaction(s) under controlled reaction conditions. The resultant atoms/molecules can then undergo elementary nucleation followed by growth processes leading to the formation of nanoparticles. The reduction of metal ions in solution is one of the most common method which dates back to Faraday [11] in 1857 who obtained a ruby aqueous solution of gold by reducing an aqueous gold salt with phosphorus in carbon disulphide. This method has been used for fabrication of metal nanostructures [57,58]. Precursors, reducing agents and stabilizing agents are used to promote or control the reduction reactions for the synthesis of metal nanoparticles. The growth of metal nanoparticles dispersed in solution has advantage of stabilizing the nanoparticles from agglomeration and easy extraction of the nanoparticles from the solvent. Electrochemical deposition method [59] has been explored for the fabrication of nanowires of metals [60], semiconductors [61] and conductive polymers [62]. The advantage of electrochemical deposition method is that it needs few reagents to be added. The main disadvantage of this method is that it is very slow as compared to plasma methods which will be described. In order to speed up the process, high current is passed through the electrodes which results in mossy deposits of the metal affecting adversely the morphology and electrical properties of nanostructures. The presence of chemical contaminants is main concern even if the choice of precursors, reducing agents as well as surfactants is made judiciously. Moreover, fabrication of metal nanostructures on
substrate for application in photonics device is always a challenge by the chemical methods.

Ijima’s discovery [63] of carbon nanotubes from graphitic soot, synthesized by arc plasma has brought plasma based methods to the forefront of nanofabrication. Following this discovery, nanostructured materials, nanostructures, nanoparticles etc. of a wide range of materials such as metals, semiconductors, oxides, nitrides have been produced by plasma based methods. Plasma environments have salient features which make them versatile tool for fabrication of nanostructures. Moreover, it circumvents the shortcoming/ limitation of chemical based nanofabrication.

Some of the plasma based fabrication methods are arc discharge, exploding wire, direct current (DC) sputtering, radio frequency (RF) sputtering, magnetron sputtering and pulsed laser deposition. Plasma is generally divided in terms of density and temperature. Density of plasma can be either low, moderate or high while depending upon the species temperature, plasma can be subdivided into two main categories: (i) low temperature (fraction of eV to few tens of eV) plasma and (ii) high temperature (> few hundreds of eV) or hot plasma. Arc discharge is a plasma based method which generates large number of material ions and reactive gas ions. The discharge produces plasma of high density (~ $10^{21}$ m$^{-3}$) and has temperature in the range of few eV to keV. Some of the above methods require a very high vacuum. The formation of arc discharge occurs when a high current-density and low voltage electric current passes between two electrodes placed in vacuum. The main disadvantage of this method is that it needs a large amount of energy to produce arc discharge. The formation of microdroplets of the material is main concern in this method. DC sputtering normally produces neutral atoms due to low degree of ionization and these neutral atoms are difficult to control and direct towards the substrate. Moreover, this process requires high substrate heating and has low deposition rates as compared to some of the other plasma methods. The shortcomings of DC sputtering have been addressed in RF sputtering by applying RF potential to a metal electrode behind the insulator wall of the discharge [64]. The plasma in RF discharge has low density (~ $10^{-10}$-$10^{16}$ m$^{-3}$) and is of low temperature ($T_e$~ 1-5 eV and $T_i=T_n$~ 0.025 eV). It is able to achieve high deposition rate for insulating films [65]. However, heating or biasing of
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the substrate is required to improve the deposition, uniformity and quality of the film. This limits the usage of insulating substrates such as glass, quartz etc. The degree of ionization of DC sputtering is also improved in magnetron sputtering by confining plasma using magnetic field to leak hot electrons [66]. This is done by strengthening the outer ring of the magnets relative to the central one. This plasma will cause higher sputtering rate by accelerating the ions towards the cathode. The process is able to remove the need for substrate biasing by unbalancing the magnetic fields. However, the problem of arcing results in the ejection of droplets from the target surface. There are efforts for improving the conventional magnetron sputtering discharge so as to increase the metal ionization, target utilization, deposition rates and to avoid the target poisoning and reduce arching. Some of the designs are by pulsing the applied voltage [67,68], additional ionization by RF [69], microwave power [70] or by increasing the magnetic confinement [71]. The modification is done to generate highly ionized plasma. The application of secondary discharge to create dense plasma between the target and the substrate forms one of the basis for ionized physical vapor deposition (iPVD) such as inductively coupled [69] or microwave driven discharges [70]. Electron cyclotron resonance (ECR) discharges produce plasma of high densities $\sim 10^{17}$-$10^{18}$ m$^{-3}$. Ionization as well as deposition rate in microwave amplified magnetron sputtering is much higher than the conventional magnetron sputtering. In order to achieve higher plasma densities, magnetron sputtering can be operated at high power applied in pulse. The system is able to produce highly ionized plasma whose density is of the order of $10^{19}$ m$^{-3}$ [72] and is reported to have achieved ionization upto 70 %. This technique has been found to be useful in improving target utilization as well as substrate pretreatment for better adhesion. However, the deposition rate is reduced to 25-35 % of the rates in conventional magnetron sputtering possibly due to lower magnetic confinement in the target-to-substrate region resulting in low conductivity. Pulsed laser ablation and consequent deposition employs a high power laser to ablate material from solid (or liquid) target surface such that the stoichiometry of the material is preserved through the interaction. When a high power laser is focused onto a target material, it induces a rapid heating of the material within the localized interaction volume of the target surface. The growth as well as the quality of the deposited film depends on many factors such as choice of substrate, substrate temperature and kinetic energies of the various
constituents inside the plume. The typical energy with which the ablated material hit the substrate is about 100 eV. The main disadvantage of this technique is macroparticle formation and uniformity which is limited to small area. Moreover, the large kinetic energies of the plume species often causes resputtering and defects in the substrate surface.

1.7. Conclusion

Nanostructures and nanomaterials have played significant role in the daily life of mankind. Nanostructures/ nanomaterials have physical as well as chemical properties different from its bulk material on account of their large surface area to volume ratio. Nanostructures of metal exhibit distinct optical attributes by virtue of their surface plasmon resonance which can have applications from photonics to biosensing. Chemical methods have been one of the earliest methods but presently plasma based methods are more frequently adopted due to their advantage over chemical methods.
References

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