Chapter 1

Introduction to nanostructured materials
1.1. Introduction

Nanotechnology is the expected future manufacturing technology that will make most products lighter, stronger, cleaner, less expensive and more precise. Nanoscale materials can be defined as those whose characteristic length scale lies within the nanometric range, i.e. in the range between one and several hundreds of nanometers. Encompassing nanoscale science, engineering and technology, nanotechnology involves imaging, measuring, modelling and manipulating matter at this length scale. Unusual physical, chemical and biological properties can emerge in materials at the nanoscale. These properties may differ in important ways from the properties of bulk materials and single atoms or molecules. Even more popular than "Nanoscience" has become the term "Nanotechnology" which relates to the ability to build functional devices based on the controlled assembly of nanoscale objects for specific technological applications. The importance of both nanoscience and nanotechnology has been confirmed by a number of national and international initiatives to promote their study. Funding agencies in the USA, Europe, Australia and Japan are spending a significant part of their funds for the development of nanoscience and nanotechnology.

Nanotechnology can be defined as the synthesis and engineering at the molecular level for the possible device applications. Nanoscience deals with the investigations of phenomena and properties exhibited by materials at the nano level. A nanostructure is an object of intermediate size between
Introduction to nanostructured materials

molecular and microscopic (micrometer-sized) structures. Nanoparticles made of semiconducting material may also be labeled as quantum dots if they are small enough (typically < 10nm) that quantization of electronic energy levels occurs. Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the case. Size-dependent properties are observed such as quantum confinement in semiconductor particles, surface plasmon resonance in some metal particles and super paramagnetism in magnetic materials. Nanostructured materials have gathered great interest worldwide due to their unique size-dependent properties for chemical, electronic, structural, medical and consumer applications.

Nanoscience and nanotechnology is the science and technology of ultrafine particles. The trend in device oriented manufacturing towards smaller and smaller dimensions has led to the development of nano fabrication techniques as well as understanding the physics of nanometer scale materials [1]. Materials when reduced to nano scale shows entirely different chemical, physical, electrical and optical properties as compared to what they exhibit on the macro scale. At these dimensions the surface to volume ratio becomes very large which determines the properties of the material in the nanoregime. The percentage of atoms at the surface of a material becomes significant as the size of that material approaches the nano scale. Suspensions of nanoparticles are possible because the interaction of
the particle surface with the solvent is strong enough to overcome differences in density, which usually result in a material either sinking or floating in a liquid. Nanoparticles often have unexpected visible properties because they are small enough to scatter visible light rather than absorbing it. For example gold nanoparticles appear deep red to black in solution.

The ultimate motive of nanotechnology is to manipulate and control the individual atoms and such a definition may be extended to the organization of objects having nano dimension. The properties of materials change as their size approaches the nanoscale. Nanoparticles behave quite differently due to the high surface to volume ratio. The more loosely bound surface atoms constitute a significant fraction of the sample whose properties influence the sample’s behaviour. For example, the bending of bulk copper (wire, ribbon, etc.) occurs with movement of copper atoms/clusters at about the 50 nm scale. Copper nanoparticles smaller than 50 nm are considered super hard materials that do not exhibit the same malleability and ductility as bulk copper. The melting point of gold is dramatically reduced when the particle diameter drops below 5nm, it changes its state from solid to liquid at room temperature. Optical properties are modified because of the quantum size effect on the band structure. Optical energy band gap is blue shifted for ultrafine materials. Nano sized copper is blue in colour, this gives scope to a variety of applications in the semiconductor industry.

Two main approaches are used in nanotechnology: one is a "bottom-up" approach where materials and devices are built up atom by atom, the
other a "top-down" approach where they are synthesized or constructed by removing existing material from larger entities. A unique aspect of nanotechnology is the vastly increased surface area to volume ratio present in many nanoscale materials, which opens new possibilities in surface-based science, such as catalysis. This catalytic activity also opens potential risks in their interaction with biomaterials.

In describing nanostructures, it is necessary to differentiate between the number of dimensions on the nanoscale. Nanotextured surfaces have one dimension on the nanoscale, i.e., only the thickness of the surface of an object is between 0.1 and 100 nm. Nanotubes have two dimensions on the nanoscale, i.e., the diameter of the tube is between 0.1 and 100 nm. Finally, spherical nanoparticles have three dimensions on the nanoscale, i.e., the particle is between 0.1 and 100 nm in each spatial dimension. The dimensionality [2D-0D] refers to the number of directions in which the carriers of the material can act as the free carriers. In the case of a bulk material, the electronic carriers are free to move in all the three directions [2]. The nanoparticles discussed in this thesis work belong to two major categories; (i). Semiconductor nanoparticles and (ii). Metal nanoparticles.

1.2. Semiconductor nanoparticles

Nanomaterials can be of various shapes and therefore their properties may change according to their size and/or shape. These materials may be metals, semiconductors, metal oxides, organic materials or biomaterials. Thus there is a tremendous scope to design new materials with
unusual properties. Amongst the various types of nanomaterials, semiconductor nanoparticles have been widely investigated. Semiconductor nanoparticles constitute a bigger sector of the nanotechnology due to their wide range of applications in optics including nonlinear optical device fabrications, luminescent display technology as well as biological applications. Semiconductors have been useful in making electronic as well as optical devices. The drive towards miniaturization of electronic components and integration to accommodate huge number of them in small volume has been there for decades. This has enabled the evolution of very compact digital watches, calculators, computers, laptops etc. Electronic structure of nanomaterials may be different as compared to corresponding bulk material. This has led to interesting devices like single electron transistors, tunnel junctions, magnetic spin valves etc. which do not have bulk counterparts [3].

Besides this, at nano scale, semiconductor materials like silicon that are not optoelectronic materials due to indirect band gap have showed strong luminescence in visible range [4]. Moreover they exhibit emission which is size dependent luminescence. Some groups have showed [5, 6], for II-VI and III-V semiconductors, the change in band gap with particle size. Doped semiconductors such as CdSe, CdS has been used over a long term due to their good luminescent nature. But these quantum dots are found to be quite poisonous in nature so we are in survey of quantum dots which are non poisonous and highly trustworthy. This leads to the choice of ZnO and ZnS as the new nanostructured materials for the biological applications.
1.2.1. Quantum dot

Quantum dots are a non-traditional type of semiconductor with limitless applications as an enabling material across many industries. A quantum dot is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes or excitons (pairs of conduction band electrons and valence band holes) in all three spatial directions.

A quantum dot has a discrete quantized energy spectrum [7]. The corresponding wave functions are spatially localized within the quantum dot, but extend over many periods of the crystal lattice. Larger quantum dots have more energy levels which are more closely spaced. This allows the quantum dot to absorb photons containing less energy, i.e. those closer to the red end of the spectrum. Larger dots have more closely spaced energy levels in which the electron-hole pair can be trapped. Therefore, electron-hole pairs in larger dots live longer causing larger dots to show a longer lifetime. A quantum dot contains a small finite number (of the order of 1-100) of conduction band electrons, valence band holes, or excitons, i.e., a finite number of elementary electric charges. Small quantum dots, such as colloidal semiconductor nanocrystals, can be as small as 2 to 10 nanometers, corresponding to 10 to 50 atoms in diameter and a total of 100 to 100,000 atoms within the quantum dot volume.

One of the optical features of small excitonic quantum dots immediately noticeable to the unaided eye is coloration. While the material which makes up a quantum dot defines its intrinsic energy signature, more
significant in terms of coloration is the size. The larger the dot, the redder (the more towards the red end of the spectrum) the florescence. The smaller the dot, the bluer (the more towards the blue end) it is. The coloration is directly related to the energy levels of the quantum dot. Quantitatively speaking, the band gap energy that determines the energy (and hence color) of the fluoresced light is inversely proportional to the square of the size of the quantum dot. Recent articles in nanotechnology and other journals have begun to suggest that the shape of the quantum dot may also be a factor in the colorization, but as yet not enough information has become available. Furthermore, it was shown [8] that the life time of fluorescence is determined by the size of the quantum dot.

Quantum dots found application as light emitting diodes in sign displays, cell staining for life science observation, even as inks that can aid in spotting counterfeits. Another security application that could soon be realized is luminescent dust, which could be used to track trespassers in restricted areas. Much like fiber optics, quantum dots may also be used to transmit data. Some estimates suggest that data transfer using quantum dots could be a million-fold efficient over standard ethernet connections. While these are some of the cutting edge applications, there are also more mundane ones as well. Quantum dots could be used as a light source in buildings, or even as illumination for computer screens.

1.2.2. Quantum well

A quantum well is a thin layer which can confine quasiparticles (typically electrons or holes) in the dimension perpendicular to the layer
surface, whereas the movement in the other dimensions is not restricted. That means it is a potential well that confines particles, which were originally free to move in three dimensions in to two dimensions, forcing them to occupy a planar region. The confinement is a quantum effect. The effects of quantum confinement take place when the quantum well thickness becomes comparable to the de-Broglie wavelength of the carriers (generally electrons and holes), leading to energy levels called "energy sub bands", i.e., the carriers can only have discrete energy values [8, 9]. It has profound effects on the density of states for the confined particles. For a quantum well with a rectangular profile, the density of states is constant within certain energy intervals.

A quantum well is often realized with a thin layer of a semiconductor medium, embedded between other semiconductor layers of wider band gap (examples: GaAs quantum well embedded in AlGaAs [10], or InGaAs in GaAs [11]). The thickness of such a quantum well is typically < 5–20\text{nm}. Such thin layers can be fabricated with molecular beam epitaxy (MBE) or metal–organic chemical vapor deposition (MOCVD). In optically pumped semiconductor lasers, most pump radiation may be absorbed in the layers around the quantum wells, and the generated carriers are captured by the quantum wells thereafter.

If a quantum well is subject to strain, as can be caused by a slight lattice mismatch (e.g., for InGaAs quantum wells in GaAs), the electronic states are further modified, which can even be useful in laser diodes. Because of their quasi-two dimensional nature, electrons in quantum wells
have a sharper density of states than bulk materials. Therefore semiconductor quantum wells are often used in the active regions of laser diodes [12], where they are sandwiched between two wider layers with higher band gap energy. These cladding layers function as a waveguide, while electrons and holes are efficiently captured by the quantum well, if the difference in band gap energies is sufficiently large.

Quantum wells are also used as absorbers in semiconductor saturable absorber mirrors (SESAMs) and in electro absorption modulators. They are also used to make High Electron Mobility Transistors (HEMTs) [13], which are used in low-noise electronics. Quantum well infrared photo detectors [14] are also based on quantum wells and are used for infrared imaging. If a large amount of optical gain or absorption is required, multiple quantum wells (MQWs) can be used, with a spacing typically chosen large enough to avoid overlap of the corresponding wave functions.

1.2.3. Quantum wire

A quantum wire is an electrically conducting wire, in which quantum effects are affecting transport properties. Due to the confinement of conduction electrons in the transverse direction of the wire, their transverse energy is quantized into a series of discrete values $E_0$, "ground state" energy, with lower value), $E_1$, $E_2$ etc (like particle in a box, quantum harmonic oscillator). An exact calculation of the transverse energies of the confined electrons has to be performed to calculate the wire resistance. Following from the quantization of electron energy, the resistance is also found to be quantized. The importance of the quantization is inversely
proportional to the diameter of the nanowire for a given material. From material to material, it is dependent on the electronic properties, especially on the effective mass of the electrons. In simple words, it means that it will depend on how conduction electrons interact with the atoms within a given material. In practice, semiconductors show clear conductance quantization for large wire transverse dimensions (100 nm) because the electronic modes due to confinement are spatially extended. As a result, their fermi wavelengths are large and thus they have low energy separations. This means that they can only be resolved at cryogenic temperature (few Kelvins) where the thermal excitation energy is lower than the inter-mode energy separation.

The electron transport properties in quantum wires were investigated and a quantum wire resonant tunnelling transistor, which works as a kind of multi channel rotational switch, was proposed in an earlier report [15]. Also there are reports on the ZnO nanowires based gas sensors for ethanol-sensing [16]. The quantum wire based dye sensitised solar cells [17] are now widely used in photovoltaics. It is possible to make quantum wires out of metallic carbon nanotubes [18], at least in limited quantities. The advantages of making wires from carbon nanotubes include their high electrical conductivity (due to a high mobility), light weight, small diameter, low chemical reactivity and high tensile strength. The major drawback of carbon nanotube based quantum wires is the high cost.

1.2.4. Confinement regimes

In a bulk materials, the carriers can exist in nearly continuous band, but in quantum dot structures due to the confinement of charges in all the
three directions, the carriers are restricted to a specific set of completely quantised energy states. The effect of confinement on the resulting energy state of the system can be obtained by solving for the eigen energies of the Schrodinger wave equation for the carriers in a confined space [19].

Different energy state equation can be obtained depending upon the confinement regimes. Depending upon the ratio between the nanocrystal radius $a$, and the bulk exciton radius $a_B$, three different confinement regimes can occur [20].

1. Strong confinement regime
2. Weak confinement regime
3. Intermediate stage

The strong and weak states are determined by the degree of coupling between the electron and hole in the exciton.

(a). Strong confinement regime:

When the quantum dot radius $a_0$ is smaller than the excitonic bohr radius $a_B$, it corresponds to the strong confinement state.

$$a_0 \ll a_B,$$

which means that as the degree of confinement is increased in a smaller dot, the exciton can no longer exist and therefore an electron and a hole can be treated as independent particles [2]. In this situation the coulomb effects are small compared with the quantization of the kinetic energy of the carriers (confinement energies). When these conditions are present, the carriers are said to be strongly confined and the electron and hole wave functions are uncorrelated. Therefore the approach of solving the energy states in a strong confinement regime is similar to that in a weak confinement regime; but the only exception is that in the case of strong
Introduction to nanostructured materials

Confinement, the electron and hole have independent Bessel function and therefore the resulting energy shift expression can be written as,

\[ E = E_g + \frac{\hbar^2 \pi^2}{2eR^2 \mu^*} - \frac{1.786e}{4\pi\varepsilon_0 e_FR} - 0.248E_{ex} \]  

(1.1)

where \( E \) is the band gap of the dots, \( E_g \) is the band gap of the bulk material, \( R \) is the dot size, \( \mu^* \) gives the effective reduced mass as \( \frac{1}{\mu^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*} \) and the last term represents the correlation energy which can be expressed in terms of the excitonic binding energy \( E_{ex} \). \( m_e^* \) and \( m_h^* \) are the individual electron and hole masses respectively.

(b). Weak confinement regime:

When the quantum dot radius, \( a_0 \) is few times greater than the excitonic bohr radius, \( a_B \); the confinement corresponds to the weak confinement regime.

\[ \text{ie}; \quad a_0 \gg a_B \]

which means that coulomb interaction energy is on the order of the electron and hole sublevel separations and it has to be taken into account. Here the electron and hole motions are strongly correlated via coulomb interaction and the nanocrystal energy spectra are determined by the quantization of the motion of the exciton center of mass [2]. Expression for energy quantization in a spherical 0D structure is,

\[ E = \frac{\hbar^2 \pi^2}{2em \cdot R^2} + E_g - E_{ex} \]  

(1.2)
where $m'$ is the translational mass of the exciton which is the algebraic sum of the electron and hole masses (effective exciton mass: $m' = m_e^* + m_h^*$) and $R$ is the mean dot size. The eqn. (1.2) gives the shift in energy that occurs when a bulk solid exciton is confined in 3D in the range of 3-10 times the exciton bohr radius. i.e; a blue shift in energy results as the size of the crystal decreases.

(c). Intermediate stage

In the intermediate stage, the energy structures of nanocrystals are determined by a complex interplay between quantum confinement and the coulomb electron-hole interaction. Due to the relatively large exciton bohr radius II-IV nanocrystals are convenient systems for the studies of the strong, weak and intermediate regimes [20]. The coulomb interaction scales with the nanocrystal radius as $a^{-1}$ where as the confinement energies are proportional to $a^{-2}$. Therefore in the strong confinement regime the coulomb term in the Hamiltonian can be ignored which leads to a problem of independent quantization of electron and hole energies. Effective mass approximation (EMA) has proven to be a powerful tool for describing energy structures in semiconductors, but it fails in the limit of very small nanocrystals [20].

1.2.5. Particles at the nano level

Semiconductor nanocrystallites are known to exhibit unique size dependent optical properties, which render them attractive from the view point of integrated photonic devices. Quantum confinement effects are
particularly important, if the crystalline dimension is less than a critical size known as the exciton bohr radius of the material.

Controlled variation of nanocrystalline size results in remarkable changes in the properties from molecular to bulk. Blue shift in the optical absorption spectrum, size dependent luminescence, enhanced oscillator strength and nonlinear optical effects are some examples of the interesting properties exhibited by these nanocrystals.

Due to the small size of the nanocrystals and hence their relatively large surface to volume ratio, the effect of nanocrystal surface on the charge carriers cannot be neglected [20]. In practice the surface properties must be modified in some way in order to control nanocrystal growth and reduce or prevent the charge carriers interacting with the surface, thus realizing effective quantum confinement. Surface passivation with various organic ligands or epitaxial over coating with a wide band gap semiconductor can be used to enable efficient radiative recombination of charge carriers.

1.2.6. Physical concepts of nanocrystals

Electronic states and probabilities of optical transitions in molecules and crystals are determined by the properties of the atom and their spatial arrangement. An electron in an atom possesses a discrete set of states, resulting in a corresponding set of narrow absorption and emission lines [19]. In semiconductors, broad bands of the allowed electron and hole states separated by a forbidden gap give rise to characteristic absorption and emission features completely dissimilar to atomic spectra. The evolution of
the properties of the matter from an atom to a crystal can be described in terms of the two steps,

(i) From the atom to cluster

(ii) From cluster to crystal

As the particle size grows, the properties can be described in terms of the particle size and shape. When the particle size becomes comparable to the de-Broglie wavelength of the elementary excitations, they are often called “Quantum crystallites”, “Quantum dots” or “Quasi zero dimensional structures”. As the size of these crystallites ranges from one to tens of nanometers, the word “Nanocrystals” is widely used [19].

From the viewpoint of the solid state physics, nanocrystals are just a kind of a low dimensional structure complementary to quantum well (two dimensional structure) and quantum wire (one dimensional structure). Quantum wires and quantum wells possess translational symmetry in one or two dimensions and statistically a large number of electronic excitations can be created. In nanocrystals translational symmetry is totally broken, and only a finite number of electrons and holes can be created within the same nanocrystal. Therefore the concepts of electron-hole gas and quasi momentum are not applicable to nanocrystals [19]. Additionally a finite number of atoms in nanocrystal promotes a variety of photo induced phenomena like persistent and permanent photo physical and photo chemical phenomena that are known in atomic and molecular physics but do not occur in solids.
From the view point of molecular physics, a nanocrystal can be considered as a kind of large molecule. Every nanocrystal ensemble has inhomogeneously broadened absorption and emission spectra due to their distribution of sizes, defect concentration, shape fluctuation, environmental inhomogeneities and other features.

Also, as the size of crystallites and their concentration grow, the heterogeneous medium "matrix-crystallites" becomes a subject of the optics of ultra disperse media, thus introducing additional aspects to the optical properties of nanocrystal ensembles [20]. The matrices coloured with semiconductor nanocrystal have been known for centuries as stained glasses. Because of these features, studies of the optical properties of the nanocrystals form a new field of bordering solid state physics, optics, molecular physics and chemistry.

1.2.7. Electron states in crystal

A nanocrystal can be considered as a three dimensional potential box in which photon absorption and emission result either in creation or in annihilation of some elementary excitation in an electron sub system. These excitations are described in terms of quasi particles (electron, holes and excitons) known for bulk crystals [19]. Features connected with absorption and emission of light in nanocrystals can be understood in terms of the quantum confinement approach.
(a). Particle in a potential well

In order to consider electrons in a crystal, we start with a particle in a one dimensional potential well. The relevant time-independent Schrödinger equation is given as,

$$\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + U(x) \psi(x) = E \psi(x) \quad (1.3)$$

where $m$ is the particle size and $E$ is the particle energy. The potential $U(x)$ is considered as a rectangular well with infinite walls and is given as,

$$U(x) = \begin{cases} 0 \text{ for } |x| \leq \frac{a}{2} \\ \infty \text{ for } |x| \geq \frac{a}{2} \end{cases} \quad (1.4)$$

where $a$ denotes the well width.

From elementary quantum mechanics, it is known that the Schrödinger equation stated above has the solutions of both even and odd types and is given as,

$$\psi^{(-)}(x) = \sqrt{\frac{2}{a}} \frac{\cos}{\sqrt{2mE}} \quad \text{for } n=1, 3, 5 \ldots \ldots \quad (1.5)$$

$$\psi^{(+)}(x) = \sqrt{\frac{2}{a}} \frac{\sin}{\sqrt{2mE}} \quad \text{for } n=2, 4, 6 \ldots \ldots \quad (1.6)$$

The most important result of the problem is a discrete set of energy values given by,

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2} \quad (1.7)$$
where \( n \) takes values 1, 2, 3, etc. This equation gives values of kinetic energy. The minimum energy a particle can have (for \( n=1 \)) is given by,

\[
E_n = \frac{\hbar^2 \pi^2}{2ma^2}
\]  

(1.8)

This energy is called the particle’s zero point energy.

(b). Electron in a coulomb potential

The coulomb potential is given by the following eqn,

\[
U(r) = -\frac{e^2}{r}
\]  

(1.9)

The equation for the radial part of the wave function can be written as,

\[
\left[ \frac{d^2}{d\rho^2} + \varepsilon + \frac{2}{\rho} - \frac{l(l+1)}{\rho} \right] U(\rho) = 0
\]  

(1.10)

The dimensionless argument \( \rho = \frac{r}{a^0} \) and energy, \( \varepsilon = \frac{E}{E^0} \) are expressed in terms of the so called atomic length unit \( a^0 \) and atomic energy unit \( E^0 \) as given by,

\[
E^0 = \frac{e^2}{2a^0} \approx 13.6eV
\]  

(1.11)

where \( a^0 = \frac{\hbar^2}{m_0e^2} \approx 5.292 \times 10^{-10} \text{ nm} \) with \( m_0 \) being the electron mass.

As a solution for the radial part of the wave function, the energy levels obey a series, \( \varepsilon = -\frac{1}{(n_r + l + 1)^2} = -\frac{1}{n^2} \), where the number \( n = (n_r + l + 1) \) is called the “principal quantum number”. Here \( n_r \)
determines the quantity of nodes of the corresponding wave function and is called the “radial quantum number”.

For every \( n \) value, exactly \( n \) states exist differing in \( l \), which varies from 0 to \( (n-1) \) and additionally for every \( l \) value, \( (2l + 1) \) degeneracy occurs with respect to \( m = 0, \pm 1, \pm 2 \ldots \). 

Therefore the total degeneracy is 
\[
\sum_{l=0}^{n-1} (2l + 1) = n^2
\]

For \( n=1, l=0 \) (1s state), the wave function obeys a spherical symmetry with radius \( a^0 \) corresponding to the most probable distance where an electron can be found [19]. The relevant term \( a^0 \) in real atom like structures is called “Bohr radius”. The problem of a particle in a spherical potential well is used to model an electron and a hole in a nanocrystal and the hydrogen atom model is essential to model for excitons in a bulk crystal and in nanocrystals.

(c). Electron in a periodic potential

Consider a particle in a potential of type \( U(x) = U(x+a) \) which shows the translation invariance. Then the Schrödinger equation takes the form,

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi(x+a) + U(x)\psi(x+a) = E\psi(x+a)
\]

ie; the wave functions \( \psi(x) \) and \( \psi(x+a) \) satisfy the same Schrödinger equation with the same eigen value \( E \).

ie; \( |\psi(x+a)|^2 = |\psi(x)|^2 \)
Wave function that satisfy the Schrödinger equation with a periodic potential can be written as, \( \psi(x) = e^{ikx} u_k(x) \) where,

\[ u_k(x) = u_k(x + a) \]

which means that the eigen functions of the Hamiltonian with a periodic potential is a plane wave modulated with the same period as the potential. This statement is known as the “Bloch's theorem”. The wave numbers \( k_1 \) and \( k_2 \) differ by a value \( k_1 - k_2 = \frac{2\pi n}{a} \), where \( n = \pm 1, \pm 2, \pm 3, \ldots \). Each of these intervals contains the full set of non-equivalent \( k \) values and is called the “Brillouin zone”. The dispersion curve has discontinuities at points \( k_n = \frac{m_n}{a} \) for every \( k_n \) value. The value \( P = \hbar k \) is called “quasi-momentum”. It differs from the momentum by a specific conservation law. Although the \( E(k) \) relation in the case under consideration differs noticeably from that for a free particle, it can be expressed as,

\[ E(k) = \frac{\hbar^2 k^2}{2m^*(k)} \]

where \( m^*(k) \) is a function referred to as “effective mass”. For every periodic potential there exist extrema in the band structure and energy expression can be of the form,

\[ E(k) = E_0 + (k - k_0) \left( \frac{dE}{dk} \right)_{k=k_0} + \frac{1}{2} (k - k_0)^2 \left( \frac{d^2E}{dk^2} \right)_{k=k_0} + \ldots \ldots \ldots \]

(1.14)
Neglecting the contributions from terms higher than $k^2$ we get the simplified expression analogous to above energy value expression. Therefore the effective mass $m^*$ is given by the relation,

$$ m^* = \frac{1}{\frac{d^2E}{dk^2}} = \text{constant} \quad (1.15) $$

where as for a free particle $m^* = m$.

To summarize the properties of a particle in a periodic potential, we can conclude with the following results

(i) A particle is described with a plane wave modulated with a period of the potential.

(ii) The particle state is characterized by the quasi momentum.

(iii) The energy spectrum consists of a wide continuous bands separated from each other by forbidden gaps.

As a plane wave, a particle in a periodic potential exhibits quasi free motion without acceleration. With respect to the external force the particle behaviour is described in terms of the effective mass.

1.2.8. Concept of quasi particles: Electron, Hole and Exciton

Electrons in the conduction band of a crystal can be described as particles with charge $-e$, spin $\frac{1}{2}$, mass $m_e^*$ and quasi momentum $\hbar k$ with respect to the conservation law. From the above mentioned parameters only the charge and the spin remain the same for an electron in a vacuum and in a crystal.

Quasi particles are described as the elementary excitations of the system consisting of a number of real particles. Under this consideration an
electron in the conduction band is the primary elementary excitation of the electron subsystem of a crystal. The further elementary excitation is a hole, which is a quasi particle relevant to an ensemble of electrons in the valence band from which one electron is removed. This excitation is characterized by the positive charge $+e$, spin $\frac{1}{2}$, effective mass $m_h^*$ and a proper quasi momentum.

If a photon of energy comparable to the band gap energy is incident on a semiconductor, then they can be absorbed by the electrons forming atomic bonds between neighboring and so provide them with enough energy to break free and move around in the body of the crystal. Within the band theory of solids this would be described as “exciting an electron from the valence band across the band gap into the conduction band”. If the energy of the photon is larger than the band gap, a free electron is created and an empty state is left within the valence band. This empty space behaves very much like an air bubble in a liquid and rises to the top of the lower energy state. This hole behaves as though it was positively charged and hence forms a bond with the conduction band electrons. The attractive potential leads to the reduction in potential energy of the electron and hole. This bound electron-hole pair is known as exciton.

1.2.9. ZnO: An outlook

ZnO is a versatile material and has been used considerably for its catalytic, electrical, optical and photochemical properties [21]. Due to its wide band gap of 3.37eV and large exciton binding energy of 60meV at room temperature, ZnO is recognized as a promising optoelectronic
material in the blue-ultraviolet (UV) region and as an excellent candidate for dye sensitized oxide semiconductor solar cell, gas sensors or field emitter. ZnO is a direct II-IV semiconductor that crystallizes in the wurtzite structure at 300K with lattice constants of \( a = 3.25 \text{Å} \) and \( c = 5.21 \text{Å} \). The energy gap at room temperature is \( E_g = 3.37 \text{eV} \) and the free exciton binding energy equals 60meV [7, 21].

The Zn atoms are tetrahedrally coordinated to four O atoms and the Zn d-electrons hybridize with O p-electrons. The crystal structure of ZnO can be rock salt, zinc blende and wurtzite. From the calculations of ground state total energy of ZnO for different crystal structures by using a first principle periodic Hartree-Fock linear combination of atomic orbital theory, the wurtzite structure appears to be the most thermodynamically stable phase. Wurtzite zinc oxide has a hexagonal structure (space group \( \text{C6}m\bar{\text{c}} \)) with lattice parameters \( a = 0.3296 \) and \( c = 0.52065 \text{ nm} \). The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated \( \text{O}^2^- \) and \( \text{Zn}^{2+} \) ions, stacked alternately along the c-axis (figure 1.1).
The solution phase method at moderate temperature was recently reported to produce flower like ZnO nanocone and nanowire arrays on a Zn foil [21]. While most research to date has focused on vapour deposition, solution methods offer advantages of low temperature processing, large area uniformity, benign chemistry and potentially inexpensive manufacturing. Photoluminescence and cathodo luminescence spectra of the solution-grown ZnO nanorods were actively studied earlier [23].

In nanocrystals, the quantum confinement effect becomes a predominant investigation field which gives rise to many interesting optical and electronic properties [24]. The phenomenon concerning the quantum confinement effect in ZnO nanocrystals were rarely studied due to large electron effective mass caused by the large band gap (3.37eV) of this material. The large exciton binding energy of this material makes it an attractive candidate for room temperature lasing application. Additionally, the Coulomb interaction of electron and hole has reduced the exciton confinement energy partly due to the small dielectric constant in this system, which is also related to large band gap. Thus, the ZnO binary semiconductor material will have a small quantum confinement effect in quantum dot and quantum well structures.

The structural, morphological and luminescence properties of ZnO nanostructured films are usually influenced by the preparation techniques. Different types of ZnO nanostructures such as nanowires [24], nanorods [25], nanobelts [26], nanonails [27] and nanowalls [28] are reported in the literature. Among the various hierarchical structures, ZnO nanowires and
nanorods are widely studied on account of their suitability for various device applications. Usually one-dimensional nanorods are synthesized using thermal evaporation, chemical vapour deposition and molecular beam epitaxy techniques which are high temperature processes requiring costly equipment.

In recent years, the preparation of ZnO nanostructures through wet chemical methods has attracted a great deal of interest. The solution approach to the synthesis of ZnO nanorods is a viable low temperature simple process. Vayssieres et al developed a low temperature wet chemical process to produce arrays of ZnO nanorods [29] on various substrates. Wang et al synthesized arrays of obelisk-like ZnO nanorods [30] using an aqueous solution deposition method. Lee et al studied the fabrication of ZnO nanorod arrays on Si and Zn foil [31] using a low temperature aqueous solution method. Even though several methods are available for ZnO nanorod synthesis, systematic studies on the effect of precursor concentrations and deposition parameters on the growth of ZnO nanorods are only rarely reported in the literature.

The tetrahedral coordination in ZnO results in noncentro symmetric structure and consequently piezoelectricity [32] and pyroelectricity [33]. Here in our work we demonstrate the wet chemical route method for the synthesis of ZnO nanoparticles. This bottom up approach is motivated due to the considerable interest in the fabrication of optoelectronic devices.
1.2.10. Nanophosphors: An overview

Luminescence or ‘weak glow’ [34] is the radiation emitted by a material excessive in comparison to thermal radiation. It results from the transition of an excited electronic state to a ground state or another state lower in energy, the duration of which is much longer than the period of light vibrations ($10^{-10}$ sec). The competing radiationless transitions result from interactions with the lattice or a transfer of energy to other ions. Luminescence, depending on the mode of excitation, is reflected in expressions such as photo-, electro-, chemi-, thermo-, sono-, or tribo luminescence. In practice, most often the excitation is via X-rays, cathode rays or UV emission of a gas discharge. The position of the band in the luminescence spectrum is independent of the method of excitation and is determined only by the inter-level spacing. Two other terms quite often used to classify luminescent materials are fluorescence ($\tau < 10$ ms) and phosphorescence ($\tau > 100$ms). As the mechanism of luminescence is associated with the duration of glow, the decay law of luminescence is exponential in fluorescence and hyperbolic or still more complicated for phosphorescence. The luminescent emission from the mineral “barite” on exposure to sunlight was identified as ‘photoluminescence’ (PL) first by Vincenzo Cascariolo. A material photoluminesces when excited by monochromatic light or by UV radiation with a spectrum broad enough to overlap the ion absorption bands. The phenomenon is pictorially illustrated using either a one-dimensional diagram of energy levels (in the form of
straight lines) or a bidimensional pattern (energy versus interionic distance) of the same levels in the form of configuration curves [35].

The three elementary processes between ion's states are: excitation, emission and radiationless transitions. If the interaction between the ion and the lattice is weak, the wavelength of the emission band matches that of the absorption band. For example, the f electrons in trivalent rare-earth (RE$^{3+}$) ions are shielded from the interactions with the lattice. If the interaction is fairly strong, as in transition metal ions, the emission band shifts towards longer wavelength with respect to the absorption band — a relation known as the empirical Stoke's law [36].

Excitation and emission are separated by a time interval i.e., by the life time of the excited state ($\sim 10^8$ sec or more). This time interval is sufficient for the system to adapt itself to the given excited electronic state which includes shifting of the surrounding (ligand) ions to a new equilibrium position, rearranging the interionic distance and transition to the lowermost of the vibrational levels ($\sim 10^{12}$ sec) i.e., to the excited electronic level. If a transition occurs between the levels, say, m (excited electronic state) and n (ground state or state of lower energy), the life time $\tau_m$ is expressed as,

$$\tau_m = \frac{1}{(\Sigma A_{mn} + \Sigma C_{mn})}$$

(1.16)

where, $A_{mn}$ and $C_{mn}$ denote the probability for radiative and nonradiative transitions between the levels. The summation is relevant whenever the transition occurs not over a single but over several sub-
adjacent levels. The fraction of emission transitions with respect to the sum total of emission and radiationless transitions gives the quantum yield \( \eta \),

\[
\eta = \frac{\sum A_{mn}}{(\sum A_{mn} + \sum C_{mn})}
\]

(1.17)

If there are \( N_m \) photons in the excited state initially, the exponential law of luminescence decay states that after a time \( t \),

\[
N(t) = N_m e^{-t/\tau_m}
\]

(1.18)

A direct relation exists between the emission intensity and the probability \( A_{mn} \) of emission transition given by,

\[
I_{em} = N_m h\nu_{mn} A_{mn}
\]

(1.19)

Thus, shorter the life time of the excited state i.e. time for photon emission, more intensive shall be the glow. Conversely, the greater the probability \( C_{mn} \) of radiationless transition, the lesser the intensity of glow and hence the quantum yield. The greater the oscillator strength for a given transition, higher shall be the intensity of the emission, provided radiation fewer transitions are absent. Photoluminescence is divided into two major kinds: intrinsic and extrinsic depending on the nature of electronic transition producing it.

(a). Intrinsic luminescence

The luminescence shown by the pure material itself is called the intrinsic luminescence. There are three kinds of intrinsic luminescence: band-to-band luminescence, exciton luminescence and cross luminescence.
(1). Band-to-band luminescence

The recombination of an electron in the conduction band with a hole in the valance band generates band-to-band luminescence. This kind of luminescence is observed in pure crystals at relatively high temperatures. For example Si, Ge and IIIb-Vb compounds such as GaAs. The light emission from bright light emitting diodes and semiconductor lasers is usually due to band-to-band transition process.

(2). Exciton luminescence

An exciton moves in a crystal conveying energy and produces luminescence owing to the recombination of the electron and the hole. There are two kinds of excitons: Wannier exciton and Frenkel exciton. The Wannier exciton model expresses an exciton as composed of an electron in the conduction band and a hole in the valence band bound together by the Coulomb interaction. The expanse of the wave function of the electron and hole is much larger than the lattice constant. This kind of luminescence is observed in inorganic semiconductors such as IIIb-Vb and IIb-VIb compounds. Wannier excitons are stable only at relatively low temperatures where the binding energies of excitons are higher than the thermal energy. At higher temperatures, excitons are no longer stable and band-to-band luminescence appears instead.

The Frenkel exciton model is used in cases where the expanse of the electron and hole wave function is smaller than the lattice constant. Typical examples are organic molecular crystals and inorganic complex salts. In these materials, the excited state of an isolated molecule or a complex ion
transfers from molecule to molecule or from complex ion to ion usually, owing to dipole-dipole interactions. It is therefore regarded as the exciton state. Luminescence characteristics are similar to those of isolated molecules or complex ions.

(3). Cross luminescence

Cross luminescence is produced by the recombination of an electron in the valance band with a hole created in the outer most core band [37]. This is observed in a number of alkali and alkaline earth halides and double halides. This occurs only when the energy difference between the top of valance band and that of the outermost core band is smaller than the band gap energy. Or else, an auger process occurs selectively. The shape of the spectra reflects the grouping of the molecular orbitals in the clusters involving cations with a hole in the core shell and nearest neighbour halide ions. For crystals with more than one type of cation, the spectrum reveals information about the 'active' cation which contains the core hole and also about the other cations. A notable characteristic of cross luminescence is that the decay time is very fast, of the order of nanoseconds or less, and hence such luminescent systems are used as scintillators [38].

(b). Extrinsic luminescence

Luminescence caused by intentionally incorporated impurities (or activators) is classified as extrinsic luminescence. Most of the observed types of luminescence that have practical applications belong to this category. Extrinsic luminescence in ionic crystals and semiconductors is classified into two types: unlocalized and localized.
(1). Unlocalized type

In the unlocalized type, the electrons and holes of the host lattice, i.e., free electrons in the conduction band and free holes in the valence band, participate in the luminescence process. This includes two kinds of luminescence transitions, namely the transition of a free carrier to a bound carrier and the transition of a bound electron at a donor to a bound hole at an acceptor. These kinds of luminescence lines and bands are usually observed in compound semiconductors such as IIIb-Vb and IIb-Vf1b compounds.

(2). Localized type

Here, the luminescence excitation and emission process are confined in a localized luminescence centre. Various kinds of metallic impurities intentionally incorporated in ionic crystals and semiconductors often create efficient localized luminescence centres. Localized type centres are classified into allowed and forbidden transition type in terms of electric dipole transitions. The electric dipole transition can take place between energy levels only with different parities i.e. $\Delta l = \pm 1$, $l$ being the azimuthal quantum number. When atoms and ions are incorporated in crystals, the forbidden character of the dipole transition is altered by the perturbation of the crystal electric field, so that the forbidden transition becomes allowed to some degree.

1.2.11. Development of ZnS based nanophosphors

Huge amount of research is being expanded during the recent years in order develop nanophosphors that come under the category of doped
nanocrystals (DNC) [39]. To utilize the phenomena of quantum confinement further, device fabrication with nano dimensions is being done worldwide. The challenge is great but will be equally rewarding. Materials that convert absorbed energy to visible light without going to high temperatures i.e. incandescence are known as luminescent materials and also referred as phosphors. Such materials find applications in displays like television i.e. cathode ray tubes (CRT), plasma display panels (PDP), Electroluminescence (E.I.) based displays and field emission displays; in light sources like fluorescent tubes, compact fluorescent lamps and cold cathode lamps; as detectors for X-rays, temperature and pressure sensors. Phosphors are generally in crystalline powder form with size ranging from 1-100 µm. Phosphors with one dimension <100 nm are called nanophosphors, possess strikingly different absorption and emission characteristics with improved efficiency and life times [40].

Out of the generally used luminescent nanophosphors, ZnS based phosphors are widely used as one of the best candidate. ZnS occurs in two common polytypes, zinc blende (also called sphalerite) and wurtzite. The two types have these features in common: Zinc blende/sphalerite is based on a fcc lattice of anions whereas wurtzite is derived from an hcp array of anions. In both structures, the cations occupy one of the two types of tetrahedral holes present. The mineral crystallizes in the cubic crystal system. In the crystal structure, zinc and sulfur atoms are tetrahedrally coordinated. The structure is closely related to the structure of diamond. The lattice constant for zinc sulfide in the zinc blende crystal structure is 0.596 nm,
The first report on doped nanocrystals (DNCs) that showed all features such as increased band gap, shift of excitation and emission spectra of nanosized semiconductor was by Bhargava \textit{et al} \cite{41} in 1994. They synthesised manganese doped nanocrystals of zinc sulfide. Following the encouraging results of Bhargava \textit{et al} on Mn doped ZnS nanoporphor, Khosravi \textit{et al} \cite{42} reported synthesis of manganese doped ZnS nanoparticles by aqueous method and synthesis of copper doped zinc sulphide quantum particles \cite{43}. Method used by Weller \textit{et al} \cite{44} for the synthesis of CdS was employed for the purpose. Yu \textit{et al} \cite{45} prepared zinc sulfide nanoparticles with homogeneous Mn distribution and studied optical properties along with other characteristics. Stanic \textit{et al} \cite{46} reported in 1997 the sol–gel synthesis of nanosized ZnS, a key material to a large number of phosphors.

Yang \textit{et al} \cite{47} in 2001 synthesised ZnS nanocrystals co-activated with Cu and rare-earth metals like Ce, Y, Nd, Er and Tb. Doped zinc sulfide nanoparticles were made by precipitation from homogeneous solution. Ebenstein \textit{et al} \cite{48} in 2002 reported fluorescence quantum yield of CdSe/ZnS core/shell nanophosphors synthesised by them. Nandakumar \textit{et al} \cite{49} in 2002 synthesised CdS quantum dots in polymer matrix Nafion following ion exchange reaction. Synthesis and photoluminescent properties ZnS nanocrystals doped with Cu and halogen was reported by Manzoor \textit{et al} \cite{50} in 2003. For undoped ZnS, emission is reported to be peaked at 434 nm with a shoulder at 464 nm on excitation with 319 nm. The emission called self-activated emission and is attributed to sulfur vacancies contrary to Zn
vacancy related activated luminescence in bulk ZnS. The authors have studied undoped ZnS and some other ZnS:Cu,F samples with variation in stoichiometry. Lee et al [51] studied in 2004, the effect of synthesis temperature on particle size/shape of ZnS:Cu nanocrystals. The band diagram for copper doped ZnS nanophosphors is shown in figure 1.3. The additional sets of energy levels created due to the presence of defects are displayed clearly in the diagram.

**Figure 1.3.** The energy band diagram of Cu doped ZnS ($V_{Zn}$ is the zinc vacancy, $Cu_{Zn}$ is the interstitial zinc and $V_{S}$ is the sulphur vacancy).

Luminescence properties are characterised by studying excitation and emission spectra.
Chapter 1

1.3. Metal nanoparticles

In recent years, researchers in the field of nanotechnology found that metal nanoparticles have all kinds of unexpected benefits in both the conventional and medical technology. Metal nanoparticles have served a variety of functions over time; gold and silver nanoparticles occupy the most popular position among the conventionally used metal nanoparticles in science and technology. They are non-toxic and appear to have endless medical applications; it has also been found that ingesting liquid gold nanoparticles has extremely beneficial effects on human health. Nanotechnology is fairly new to our civilization, but it turns out that colloidal gold has been in existence since ancient times and it was originally used to stain glass. It was rediscovered by Michael Faraday in the 1850s and almost immediately became one of science's favorite substances.

1.3.1. Surface plasmon resonance

Nanoparticle metal colloidal solutions of the noble metals of copper, silver and gold exhibit very intense colour which is absent in the bulk materials as well as for the individual atoms. This colouration is due to the collective oscillation of the free conduction electrons in metal nanoparticles induced by the interacting electromagnetic fields [52-55]. These resonances are called surface plasmon resonances (SPR). SPR originates from the field of plasmonics which constitutes the larger portion of nanophotonics. Nanophotonics is quite simply the study of the optical behaviour of nanometer scale objects [56].
Plasmonics is concerned with conduction electrons at metal surfaces and their interaction with electromagnetic radiation [57]. The quantization of the collective oscillations of electrons in the conduction band of a metal produces the plasmon. There are three types of plasmons: volume plasmons, surface plasmon polaritons and localized surface plasmons. Surface plasmons (SPs) are basically the quanta of plasma oscillations at a metal surface. When a surface plasmon couples with a photon, a quasiparticle called the surface plasmon polariton (SPP) is formed. Volume plasmons are the excitation of the conduction electron sea that occurs in bulk metals and localized surface plasmons are the excitations (non-propagating) of conduction electrons in metallic nanostructures coupled to the electromagnetic field.

Classical mechanics [58] and the Drude model can be used to describe plasmons and predict their behaviour [59, 60]. Surface plasmons (SPs) are coherent electron oscillations that exist at the interface between any two materials where the real part of the dielectric function changes sign across the interface (e.g. a metal-dielectric interface such as a metal sheet in air). The surface plasmon polariton (SPP) can propagate along the surface of a metal until energy is lost either via absorption in the metal or radiation into free-space. The existence of SPs was first predicted in 1957 by Ritchie et al [61]. Although a mathematical prediction of SPR was developed in the late 1890's, the SPR phenomenon was first physically witnessed in the early 20th century by Wood et al at Johns Hopkins University [62].
is the elementary charge, \( m \) is the mass of an electron, and \( \varepsilon_0 \) is the permittivity of free space) which brought together the Drude model and the Fermi-Dirac statistics from quantum mechanics.

\[
E_p = \hbar \sqrt{\frac{n e^2}{m \varepsilon_0}}
\]  

(1.20)

The excitation of SPs by light is denoted as an SPR for planar surfaces or a localized surface plasmon resonance (LSPR) for nanometer-sized metallic structures. For nanoparticles, localized surface plasmon oscillations can give rise to the intense colours of suspensions or sols containing the nanoparticles. Nanoparticles or nanowires of noble metals exhibit strong absorption bands in the ultraviolet-visible light regime that are not present in the bulk metal. This extraordinary absorption increase has been exploited to increase light absorption in photovoltaic cells by depositing metal nanoparticles on the cell surface [63]. The energy (colour) of this absorption differs when the light is polarized along or perpendicular to the nanowire [64]. Shifts in this resonance due to changes in the local index of refraction upon adsorption to the nanoparticles can also be used to detect biopolymers such as DNA or proteins. This phenomenon is the basis of many standard tools for measuring adsorption of material onto planar metal (typically gold and silver) surfaces or onto the surface of metal nanoparticles. It is behind many colour based biosensor applications and different lab-on-a-chip sensors.

SPR relies on the ability of a "source" to excite the SPs that reside in the conduction band of a noble-type metal thin film. Standard excitation
sources are electromagnetic radiation and electron beams. If a light source is used, it must be p-polarized (parallel to the plane of incidence). Wood's early work demonstrated that using s-polarized light would not produce the same excitation (in electronic surface plasmons) outcome as p-polarized light [61]. Common light sources can be in the far-infrared (10-1000 µm), mid-infrared (2.5-10 µm), near-infrared (750 nm-2.5 µm), or visible light ranges (400-700 nm). Lasers that operate at the desired wavelength are often used since they are monochromatic and coherent. The major class of metal nanoparticles discussed in the present thesis are gold and silver nanoparticles.

1.3.2. Gold nanoparticles

Gold is a chemical element with the symbol Au (Latin: *aurum*, "shining dawn") and an atomic number of 79. The atomic mass of the gold atom is 196.967amu and the atomic radius is 0.1442nm. The arrangement of outer electrons around the gold nucleus is related to gold's characteristic yellow colour. The colour of a metal is based on transitions of electrons between energy bands. The conditions for the intense absorption of light at the wavelengths necessary to produce the typical gold colour are fulfilled by a transition from the d band to unoccupied positions in the conduction band. The crystal structure for metallic gold is face centred cubic (fcc) with lattice parameter a=0.40788nm (see figure 1.5). This crystal structure contributes to gold's very high ductility since fcc lattices are particularly suitable for allowing the movement of dislocations in the lattice. Such dislocation movement is essential for achieving high ductility.
use as a dental alloy), and as a result there are a number of direct
applications of gold as a medical material.

Gold also possesses a high degree of resistance to bacterial
colonisation and because of this; it is the material of choice for implants that
are at risk of infection, such as the inner ear. It is important to draw a
distinction between the properties of gold in the bulk form and those
properties it exhibits when present in the form of nanoparticles. The unique
properties of gold at the nanoscale lead to its use in a growing number of
applications including colloids for optical limiting applications, biomedical
applications and as catalysts in chemical processing and pollution control.

Colloidal gold, also known as "nanogold", is a suspension (or
colloid) of sub-micrometer sized particles of gold in a fluid (usually water).
The liquid is usually of either an intense red color (for particles less than
100 nm), or a dirty yellowish color (for larger particles). Properties and
applications of colloidal gold nanoparticles depend upon shape. For
example, gold nanorods have both transverse and longitudinal absorption
peak and anisotropy of the shape affects their self-assembly [65]. The colour
of the colloidal gold solution changes with the increase in the size of the
nanoparticles dispersed in the media. The figure 1.6 shows how the colour
of the colloidal gold nanoparticles solution shifts form wine red to blue
color as the particle size is gradually increasing.
The fundamental mechanisms of optical limiting, their applications and their theoretical background are detailed well in chapter 3.

Among the commercially used optical limiting materials gold nanoparticles occupy a superior position. At the surface plasmon resonance (SPR) position the electric field inside the metal nanoparticle is much larger than the applied electric field. The ratio of the electric field inside the particle to the applied field is called the local field factor, $f(\omega)$. For a spherical particle with a radius that is very small compared to the wavelength of light, the local field factor is given by eqn.(1.21) [68, 69],

$$E_i = \frac{3\varepsilon_h}{\varepsilon_m + 2\varepsilon_h} E_0 = fE_0$$  \hspace{1cm} (1.21)

where $\varepsilon_h$ is the dielectric constant of the host medium and $\varepsilon_m$ is the complex dielectric constant of the metal. The local field factor becomes large when the real part of the denominator $(\varepsilon_m + 2\varepsilon_h)$ goes to zero.

Even when the inherent third order susceptibility $\chi_m^{(3)}$ of the metal inside the particle is very low, because of the local field enhancement the $\chi_m^{(3)}$ value could be very large. The third order optical nonlinearities of the materials are generally determined by the single beam method called Z-scan technique [70], the theory and experimental of the Z-scan setup are described in detail in chapter 3.

In addition to the nonlinear optical applications, colloidal gold has been successfully used as a therapeutic agent for rheumatoid arthritis in rats [71]. In a related study, [72] the implantation of gold beads near arthritic hip joints in dogs has been found to relieve pain. In cancer research, colloidal
gold can be used to target tumours and provide detection using SERS (surface enhanced Raman spectroscopy) in-vivo. Gold nanorods are being investigated as photo thermal agents for in-vivo applications. Gold nanorods are rod shaped gold nanoparticles whose aspect ratios tune the surface plasmon resonance (SPR) band from the visible to near infrared wavelength. Gold nanoparticles are promising probes for biomedical applications because they can be easily prepared and unlike other fluorescent probes such as quantum dots or organic dyes, they do not burn out after long exposure to light [73]. Gold nanoparticles are highly useful for a wide range of processes including general nanotechnology, electronics manufacturing and the synthesis of rare materials.

1.3.3. Silver nanoparticles

Silver is a metallic chemical element with the chemical symbol Ag (Latin: argentum, from the Indo-European root arg- for "white" or "shining") and atomic number 47. A soft, white, lustrous transition metal, it has the highest electrical conductivity than any element and the highest thermal conductivity than any metal. Metallic silver has an fcc lattice (shown in figure 1.7) with lattice parameter \( a = 0.408626 \text{nm} \). Its electronic configuration is [Kr] \( 4d^{10} 5s^1 \).
In addition to the nonlinear optical applications, silver nanoparticles are the best biomedical agents for antimicrobial activities. Impregnating materials with silver nanoparticles has been found to be a practical way to exploit the germ fighting properties of silver. The nano silver when in contact with bacteria and fungus will adversely affect cellular metabolism and inhibit cell growth. The nanosilver suppresses respiration, basal metabolism of electron transfer system, and transport of substrate in the microbial cell membrane. The nano silver inhibits multiplication and growth of those bacteria and fungi which cause infection, odour, itchiness and sores. Their very small size results in particles having a large surface area relative to their volume. In the case of silver nanoparticles, this allows them to easily interact with other particles and thus increases their antibacterial efficiency. Nano silver can be applied to a range of other healthcare products such as dressings for burns, scald, skin donor and recipient sites; plasters for surgical and trauma wounds and aqueous gel for spots.

1.4. Conclusions

A brief introduction to the principles, theoretical background and applications of semiconductor and metal nanoparticles is given. Such nanotechnologically enhanced materials will enable a weight reduction accompanied by an increase in stability and improved functionality of optical, luminescent and biological devices. Among the various types of nanostructured materials presented, a special attention is given to ZnO and ZnS (among the semiconductor based nanomaterials) and gold and silver
Chapter 1

(among the metal based structures) nanoparticles. Nanotechnology is essentially the increasing ability to manipulate (with precision) matter on previously impossible scales, presenting possibilities which many could never have imagined. Today's nanotechnology harnesses current progress in chemistry, physics, materials science and biotechnology to create novel materials that have unique properties.

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