CHAPTER I

INTRODUCTION

NANOSCIENCE AND BRIEF REVIEW OF LITERATURE

1 NANOSCIENCE AND NANOTECHNOLOGY

1.1 INTRODUCTION

Nanotechnology is the technology which uses phenomena and structures that can only occur at the nanometer scale, which is the scale of single atom and small molecules. Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometer, where unique phenomena enable novel applications. Nanotechnology is sometimes called as molecular manufacturing and it is the branch of engineering that deals with design and manufacturing of extremely small electronic circuits, mechanical devices built at the molecular level of matter. Nanotechnology is the design, characterization, production and application of structures and devices at the nanoscale.

The related term nanoscience is used to describe the interdisciplinary fields of science devoted to the study of nanoscale phenomena employed in nanotechnology. It is the world of atoms, molecules, macromolecules, quantum dots, and macromolecular assemblies, and is dominated by surface effects such as Van der Waals force of attraction, hydrogen bonding, electronic charge, ionic bonding, covalent bonding, hydrophobicity, hydrophilicity, and quantum
mechanical tunneling, to the virtual exclusion of macro-scale effects such as turbulence and inertia. For example, the vastly increased ratio of surface area to volume opens new possibilities in surface-based science, such as catalysis [http://www.nanotechnology.com/docs/wtd0_15798.pdf](http://www.nanotechnology.com/docs/wtd0_15798.pdf); Nanotechnology Basics, 2008; [http://www.nanoscience.com/education/overview.html](http://www.nanoscience.com/education/overview.html); Small Wonders, 2002; [Nanoscience and Nanotechnologies, 2004](http://www.nanoscience.com/education/overview.html).

1.2 NANOMATERIALS

There are two definitions. The first - and broadest - definition states that nanomaterials are materials where the sizes of the individual building blocks are less than 100nm, at least in one dimension. This definition is well suited for many research proposals, where nanomaterials have a higher priority. The second definition is much more restrictive, and states that nanomaterials have properties which depend inherently on the small grain size and, as nanomaterials are usually quite expensive, such a restrictive definition makes more sense.

Nanostructures can be characterized on the basis of the number of dimensions in the nanoscale (1-100nm) (Autumn et al., 2000) as follows:

0-D nanostructures are confined in all three spatial directions e.g., nanoparticles, quantum dots etc.

1-D nanostructures are confined in two spatial directions e.g., nanowires, nanotubes, etc.
2-D nanostructures are confined in one direction e.g., interfaces, membranes, thin films, Multi-layers etc.

1.3 SEMICONDUCTOR NANOPARTICLES

Almost all materials system including metals, insulators and semiconductors show size dependent electronic or optical properties in the quantum size regime. Among these, the modification in the energy band gap of semiconductors is the most attractive one because of the fundamental as well as technological importance (Rossetti et al., 1984). Semiconductors with widely tunable energy band gap are considered to be the materials for next generation flat panel displays, photovoltaic, optoelectronic devices, laser, sensors, photonic band gap devices, etc. When dimension of a material is continuously reduced from macroscopic size to nanometers, the physical and chemical properties drastically change.

Semiconductors derive their great importance from the fact that their electrical conductivity can be greatly altered via an external stimulus (voltage, photon flux, etc), making semiconductors critical parts of many different kinds of electrical circuits and optical applications (Sang et al., 2002). Optical properties of the quantum dots can be easily tuned with the particle size (Alivisatos, 1996a). The band gap can be controlled with the change in size of the nanomaterial, so that the different colored emission can be observed from the same material. These quantum dots of same material can be used for fabrication of LEDs having emission over the whole visible spectrum.
1.4 PROPERTIES OF NANOMATERIALS

In nanoparticles, the properties (physical, chemical, biological etc.) can be selectively controlled by engineering the size, morphology, and composition of the particles. Nanomaterials are known to exhibit markedly different properties compared to micron sized ones. These new substances will have enhanced or entirely different properties from their bulk counterparts (Cao, 2004).

Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. These factors can change or enhance the properties such as reactivity, strength and electrical characteristics. As growth and catalytic chemical reactions occur at surfaces, a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles (Ogawa et al., 1982).

It has been shown that the various material properties such as electrical, mechanical, optical, magnetic etc are highly influenced by the fine-grained structure and there is generally improvement in the concerned properties. Using a variety of synthesis methods, it is possible to produce nanostructured materials in the various forms like: thin films, powder, quantum wires, quantum wells, quantum dots, etc.

Nanocrystalline systems have attracted much interest for their novel optical properties, which differ remarkably from bulk crystals. Nanocrystalline materials are exceptionally strong, hard, and, ductile at high temperature, wear-resistance and chemically very active.
Nanocrystalline materials are also much more formable than their conventional, commercially available micron counterparts (Knauth and Schoonman, 2002).

1.5 UNIQUE PROPERTIES AT NANOSCALE

Four important ways in which nanoscale materials may differ from macroscale materials are as follows:

✓ Gravitational forces become negligible and electromagnetic forces dominate.

✓ Quantum mechanical model is used to describe motion and energy instead of the classical mechanical model.

✓ Greater surface area to volume ratio.

✓ Random molecular motion.

These can affect the optical, electrical and magnetic behavior of materials, particularly as the structure or particle size approaches the smaller end of the nanoscale. Materials that exploit these effects include quantum dots, and quantum well lasers for optoelectronics.

1.5.1 Quantum Confinement

Nanotechnology has yielded a number of unique structures that are not found anywhere in nature. The idea behind confinement is all about keeping electrons trapped in a small area. The sizes for confinement have to be less than 30nm for effective confinement. Quantum confinement comes in several flavors. 2-D confinement is only restricted in one dimension, and the result is a quantum well (or
plane). 1-D confinement occurs in nanowires. 0-D confinement is found only in the quantum dot.

Confinement is important as it leads to new electronic properties that are not present in bulk semiconductor devices. The typical quantum dot is anywhere between 3-60 nm in diameter. That is still 30 to 600 times the size of a typical atom. Quantum dots are large enough to be manipulated by magnetic fields and can even be moved around with an STM or AFM. Many important atomistic characteristics can be deduced from a quantum dot that would otherwise be impossible to research in an atom.

Quantum confinement is responsible for the increase of energy difference between energy states and band gap (Fig. 1.1) which is a phenomenon tightly related with the optical and electronic properties of the materials. The quantum confinement effect can be observed once the diameter of the particle is of the magnitude as the wavelength of electron wave function (Cahay et al., 2001). When the materials are so small, their electronic and optical properties deviate substantially from those of bulk materials (Haug and Koch, 1990).

A particle behaves as if it is free when the confining dimension is large compared to the wavelength of the particle. During this state, bandgap remains at its original energy due to continuous energy state. However, as the confining dimension decreases and reaches a certain limit, typically in nanoscale, the energy spectrum turns to discrete. As a result, bandgap becomes size dependent. This
ultimately produces a blue shift in optical illumination as the size of the particles decreases.

Specifically, the effect describes the phenomenon resulting from electrons and electron holes being squeezed into a dimension that approaches a critical quantum measurement, called the exciton Bohr radius. Nanocrystals lie in-between the atomic and the molecular limit of discrete density of electronic states (Fig. 1.2) and the extended crystalline limit of continuous band (Alivisatos, 1996b).
Fig 1.2 Evolution of the density of the states as the dimensionality of the structure is reduced from the 3D (bulk) to 0D (quantum dot).

1.5.1.1 Exciton

An exciton is a bound state of an electron and an imaginary particle called an electron hole in an insulator (or semiconductor), or in other words, a Coulomb correlated electron-hole pair. It is an elementary excitation, or a quasiparticle of a solid.

A vivid picture of exciton formation is as follows: a photon enters a semiconductor, exciting an electron from the valence band into the conduction band. The missing electron in the valence band leaves a hole behind, of opposite electric charge, to which it is attracted by the Coulomb’s force. Exciton results from the binding of the electron with its hole; as a result, the exciton has slightly less energy than the unbound electron and hole. The wavefunction of the bound state is hydrogenic i.e., an "exotic atom" state akin to that of a hydrogen atom (Liang, 1970).
1.5.2 Surface to Volume Ratio

As surface area to volume ratio increases, a greater amount of a substance comes in contact with surrounding material as shown in figure 1.3. This results in better catalysts, since a greater proportion of the material is exposed for potential reaction.

Fig 1.3 Surface to volume ratio increases at small scale

1.5.3 Optical properties

The optical properties of a material result from the interaction of light with the composition and atomic structure of the material. Colour, luster, and fluorescence are examples of well-known optical properties. At the nanoscale, some interesting optical properties emerge. Gold nanoparticles and zinc oxide are interesting examples. These substances exhibit different properties as bulk samples compared to nanosized samples. Bulk gold is yellow in colour while nanosized
sample is red in colour. Bulk Zinc oxide (ZnO) is white in colour while nanosized particle of ZnO is transparent. The underlying principle governing the colour changes between a bulk sample and a nano can be explained as follows: When light is shone on a piece of metal, the photons strike the electrons in the metal. In bulk metal, electrons are free to move more or less randomly throughout the crystal structure of the metal. However, in a very thin film of metal lying upon an insulator (such as glass), the electrons are confined to a thin region. When the light strikes on these electrons the electrons will move in a coherent wave, rather than being free to move randomly. These coherent waves of electrons are called surface plasmons. The size of these waves of electrons depends upon the thickness of the film. If an incoming photon has just the right wavelength, its energy will be completely absorbed by the metal, and turned into a surface plasmon. This is called surface plasmon resonance, i.e. the incoming photon resonates with the kind of electron waves produced in the film. Photons that do not resonate with the metal film will be reflected back. Consequently when white light strikes upon such a metal film, the film selectively absorbs photons at a certain small range of wavelengths.

Another factor is larger surface area/volume ratio. Since the nanoparticles have dominating surface, the Surface Plasmon Resonance (SPR) effect takes place (Jönsson and Malmqvist, 1992).
1.5.4 Electron Conduction Properties

Nanoparticles exhibit properties intermediate of isolated atom and bulk material. This is also true for the electron conduction properties. The electron conduction of nanoparticles of metals is altered due to the reduced density of states in the valence and conduction bands for these systems. The continuous density of state for the bulk state of metal is modified to the formation of discrete energy levels. The separation between these levels can be comparable or larger than thermal energy \( k_B T \) as the particle size is reduced; \( k_B \) being the Boltzmann constant and \( T \) the temperature in Kelvin. This separation can be measured in terms of average spacing between the successive quantum levels, known as the Kubo gap, and given by

\[
\delta = \frac{4 E_F}{3n} \quad \text{-------------------------- (1)}
\]

where \( E_F \) is the Fermi level energy and \( n \) is the number of valence electrons in the cluster (Kubo, 1962).

Due to the presence of discrete levels of energy, the electron conduction is not continuous in the case of metal nanoparticles. In fact, nanoparticles exhibit discrete charging events (Green, 2002). These systems exhibit a transition from metal-like properties to molecule-like charging (Ringel et al., 2002 and Liu et al., 2004). These ligand capped nanoparticles also exhibit very small capacitances in attofarad range due to the presence of low dielectric surrounding medium (Verheijen et al., 2006 and Chiang et al., 2001). During electron conduction, the electrons have to overcome the cluster
charging energy \( (E_c) \) before it can tunnel through the cluster. This occurs only at fixed bias voltage, and thus results in incremental increase in the current at potentials where the electron addition to the system is energetically favorable. This results in the current-voltage (I-V) graph exhibiting equally spaced steps. This is commonly known as the “Coulomb staircase” phenomenon (Ostermann et al., 2006). It occurs whenever the charging energy \( (E_c) \) is greater than the thermal energy \( (k_B T) \), i.e.

\[
E_c = \frac{e^2}{2C} > k_B T
\]  

where \( e \) is the electronic charge and \( C \) is the Capacitance of the system.

The constant spacing between the staircase steps \( (\Delta V) \) is given by equation

\[
\Delta V = \frac{e}{C_{du}}
\]

The capacitance associated with the cluster \( (C_{Clu}) \) is determined by the I-V curves as seen in cyclic voltammetry or the Differential Pulse Voltammetry (Lee et al., 2004).

1.5.5 Superparamagnetism in magnetic nanoparticles

Magnetic nanoparticles like different oxides of iron as well as nanoparticles of nickel and manganese have also been successfully synthesized in size-controlled manner. They have important implications in the information storage magnetic materials and as phase contrast reagents for Magnetic Resonance Imaging (MRI).
They have already proved to be much better than the currently utilized phase contrast reagents like complexed gadolinium salts. Due to quantum effects, they also exhibit superparamagnetism. It implies that their magnetic susceptibility is intermediate between a paramagnetic material and a ferromagnetic material. For iron oxides, this happens only below an average size of 25 nm.

1.5.6 Chemical reactivity

Just as changes in the optical and electronic properties of nanoscale materials are anticipated based on quantum confinement effects, changes in chemical reactivity of nanoscale materials have also been anticipated. As chemical reactions are governed by electrons, relative electron affinities or ionization potentials, and electron orbital densities, a natural coupling exists between chemical reactivity and the electronic character of the reactants and any reaction catalysts. In transition metal atom clusters, ionization potential increases as the cluster size drops below the bulk limit. The increase in ionization potential does not, however, always vary monotonically with cluster size. Nanoparticles can also be arranged into layers on surfaces, providing a large surface area and hence enhanced activity, relevant to a range of potential applications such as catalysts (Elschenbroich, 2008).

1.5.7 Mechanical strength

For materials such as crystalline solids, as the size of their structural components decreases, interface area becomes greater;
which can greatly affect both mechanical and electrical properties. For example, most metals are made up of small crystalline grains; the boundaries between the grain slow down or arrest the propagation of defects when the material is stressed, thus giving strength. If these grains can be made very small, or even nanoscale in size, the interface area within the material greatly increases, which enhances its strength. For example, nanocrystalline nickel is as strong as hardened steel (Timoshenko and Young, 1968).

1.5.8 Melting point

Melting Point is the temperature at which the atoms, ions, or molecules in a substance have enough energy to overcome the intermolecular forces that hold them in a fixed position in a solid. At nanoscale, surface atoms require less energy to move because they are in contact with fewer atoms of the substance as shown in figure 1.4.

![Surface atoms at nanoscale](image)

**Fig 1.4** Surface atoms at nanoscale

1.6 TECHNIQUES FOR SYNTHESIS OF NANOPARTICLES

Nanomaterials are not simply another step in the miniaturization of materials. They often require very different production approaches. There are several processes to create nanomaterials. Two main
approaches are used in nanotechnology. In the "top-down" approach, nano-objects are constructed from larger entities without atomic-level control. In the "bottom-up" approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition.

The top-down approach (Fig. 1.5) often uses the traditional workshop or micro fabrication methods where externally-controlled tools are used to cut, mill and shape materials into the desired shape and order. Micro patterning techniques, such as photolithography and inkjet printing belong to this category.

The biggest problem with top-down approach is the imperfection of the surface structure. The conventional top-down techniques such as lithography can cause significant crystallographic damage to the processed patterns, and additional defects may be introduced even during the etching steps (Das et al., 2000). For example, nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on the surface. Such imperfections would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials, since the surface over volume ratio in nanostructures and nanomaterials is very large. The

![Image of bulk and fine particles](image-url)
surface imperfection would result in a reduced conductivity due to inelastic surface scattering, which in turn would lead to the generation of excessive heat and thus impose extra challenges to device design and fabrication. Techniques for inorganic materials such as lithography and milling fit this description. Production processes by using top-down approach are:

- High energy milling
- Chemical mechanical milling
- Vapour phase condensation
- Electro-explosion
- Laser ablation
- Sputtering

Bottom-up approach (Fig. 1.6) uses the chemical properties of single molecules to cause single-molecule components to (a) self-organize or self-assemble into some useful conformation, or (b) rely on positional assembly. These approaches utilize the concepts of molecular self-assembly and/or molecular recognition. Such bottom-up approaches should be able to produce devices in parallel and much cheaper than top-down methods, but could potentially be overwhelmed as the size and complexity of the desired assembly increases.

Fig 1.6 Bottom-up approach
Bottom-up approach refers to the build-up of a material from bottom: atom-by-atom, molecule by-molecule, or cluster-by-cluster. In crystal growth, growth species, such as atoms, ions and molecules, after impinging onto the growth surface, assemble into crystal structure one after another. For most materials, there is no difference in physical properties of materials regardless of the synthesis routes, provided that chemical composition, crystallinity, and microstructure of the material are identical (Vieu et al., 2000). Of course, different synthesis and processing approaches often result in appreciable differences in chemical composition, crystallinity, and microstructure of the material due to kinetic reasons. Consequently, the material exhibits different physical properties. Although the bottom-up approach is not new, it plays an important role in the fabrication and processing of nanostructures and nanomaterials. When structures fall into a nanometer scale, there is little choice for top-down approach. Production processes by using bottom-up approach are:

- Crystallisation
- Sol-gel
- Chemical vapour deposition
- Solvothermal/Hydrothermal
- Micelle and micro emulsion synthesis
- Spray pyrolysis
- Template Synthesis: Electrochemical and Electroless
Bottom-up approach also promises a better chance to obtain nanostructures with less defects, more homogeneous chemical composition, and better short and long range ordering. This is because the bottom-up approach is driven mainly by reduction of Gibbs free energy, so that nanostructures and nanomaterials thus produced are in a state closer to a thermodynamic equilibrium state. On the contrary, top-down approach most likely introduces internal stress, in addition to surface defects and contaminations.

1.7 STABILIZATION OF MATERIALS IN NANOMETER SIZE

The extremely small size of nanomaterials implies that their surface area-to-volume ratio is very high. This means that a very large fraction of atoms in them are on the surface where their valency is unfulfilled. This gives the nanoparticles very high surface energy, and hence extreme thermodynamic instability. The matter in nanometer regime has inherent tendency to form bigger aggregates. Material needs to be stabilized \textit{kinetically} in their nano regime. Figure 1.7 shows Steric and electrostatic stabilization of nanoparticles (Teranishi and Miyake, 1998).

![Stabilization of nanoparticles](image)

Steric stabilization (Mostly in non-polar solvents)  
Electrostatic stabilization (Mostly in polar solvents)

Fig 1.7 Stabilization of nanoparticles
1.7.1 Electrostatic stabilization

Nanomaterials routinely carry excess charge on their surface. This can be due to the presence of ions of particular type (cations or anions) adsorbed on the nanoparticles surface. The counter ions are present in the vicinity of the nanoparticle surface too. Thus, each particle carries an electrical double-layer around it. For example, in citrate stabilization of nanoparticles, the citrate ions are adsorbed on the metal nanoparticle surface while the Na\(^+\) ions are present in the vicinity. The capping of nanoparticle surface with citrate ions give the gold nanoparticles a net negative charge, with the cations present as a second layer. This electric double layer on each particle repulses other particles and stabilizes the nanoparticle. This electrostatic stabilization, however, is very susceptible to the presence of salts in the medium. The ions released upon dissociation of salts screen the charges on the nanoparticle surface and decrease the energy-barrier for nanoparticle coalescence. The charge on the ions also plays an important role in this process. Greater the charge on the electrolyte, more efficient it is towards inducing nanoparticle aggregation. Indeed, preparation of nanoparticles by citrate method requires following strict condition of cleanliness and use of de-ionized water.
1.7.2 Steric Stabilization

The other method of nanoparticle stabilization is the *steric stabilization*. If the growing particle is capped with a bulky ligand, the particle growth is arrested due to steric constraints. The use of thiols or polymers to stabilize metals in colloidal state is a good example of steric stabilization. The affinity of the ligand towards the nanoparticle surface decides the average particle size.

The two methods of stabilizing nanoparticles are shown schematically in figure 1.8. An interesting aspect of nanomaterial synthesis was the preparation of highly monodisperse spherical nanoparticles by heating a polydisperse sample. This proceeds via the ‘Ostwald ripening’ concept of colloids, wherein bigger particles are formed at the expense of smaller ones. The greater thermodynamic instability of smaller particles coaxes these particles to coalesce together and form bigger particles (Stoeva et al., 2002 and Prasad et al., 2003). This method of preparation of monodisperse sample holds good promise for industrial preparations where large amounts of nanoparticles need to be prepared.

Recently, methods have been developed to cap the surfaces of the nanoparticles with organic or inorganic groups, so that the nanoparticles are stable against agglomeration. Suitable surfactants not only prevent agglomeration but also improve some optical properties of the nanoparticles. Some particular passivators have been used, such as polyethylene glycol (PEG) and pyrocatechol violet (PV)
(Konishi et al., 2001), acrylic acid (AA) (Bol and Meijerink, 2001a), methacrylic acid (MA) (Bhargava and Gallagher, 1994), polyvinyl alcohol (PVA) (Khosravi et al., 1995), mercaptoethanol (Yu et al., 1996), sodium hexametaphosphate (SHMP) (Ghosh et al., 2006) and polyvinyl pyrrolidone (PVP) (Rittner and Abraham, 1998). These are added during the chemical synthesis for capping the surface of the particles. Understanding the effect of capping on nanoparticles is one of the most important topics now-a-days.

The influence of surface passivation on luminescence quantum efficiency of ZnS:Cu$^{2+}$ nanoparticles has been discussed by Bol and Meijerink (2001b). The fundamental question that we are attempting to address in this thesis is how capping causes any noticeable improvement in luminescence quantum efficiency of nanoparticles. Keeping the above point in view, we studied optical properties of the ZnS:Cu$^{2+}$ nanoparticles using the following three surfactants.
(i) Trioctylphosphine oxide
(ii) Sodium hexametaphosphate
(iii) Cetyl trimethylammonium bromide

In this thesis we concentrate mainly on the steric stabilization to stabilize the nanoparticles.

1.8 TYPES OF LIGHT EMISSION

Light is a form of energy. There are two common ways for creating light which are, incandescence and luminescence.

1.8.1 Incandescence

Incandescence is light coming from heat energy. Something will begin to glow when heated to a high enough energy. When metal heated in a flame or an electric stove heater begins to glow “red hot”, that is incandescence. When the tungsten filament of an ordinary incandescence light bulb is heated still hotter, it glows brightly “white hot” by the same means. The sun and stars glow by incandescence (http://www.uvminerals.org/luminesce.htm). The different types of incandescence are shown in Figure 1.9.
1.8.2 Luminescence

Luminescence is the so called “cold light”, light coming from other sources of energy, which can take place at normal and lower temperatures. In luminescence, some energy source kicks an electron of an atom out of its ground or lowest energy state into an excited or higher energy state. The electron then gives back the energy in the form of light when falling back to its ground state. There are several varieties of luminescence, each named according to what the source of energy is, or what the trigger for the luminescence is (http://www.uvminerals.org/luminese.htm). The luminescence process is classified into:

- Phosphorescence,
- Electroluminescence,
- Bioluminescence,
- Chemiluminescence and
- Thermoluminescence.
1.8.3 Physical processes taking place during luminescence

Luminescence is defined as the phenomenon in which the electronic state of a substance is excited by some kind of external energy and the excitation energy is given off in the form of light. The word light not only includes electromagnetic waves in the visible region of 400 to 700 nm, but also those in the neighbouring region on both ends, i.e. the near ultra-violet and the near infrared regions (Figure 1.10) (Shionoya and Yen, 1999). Luminescence is divided into fluorescence and phosphorescence according to the duration time of the after-glow.

Fig 1.10 The spectrum of visible light

1.8.3.1 Fluorescence

When a molecule absorbs UV radiation it gets excited from a vibrational level in the electronic ground state to one of the many vibrational levels in the electronic excited state. This excited state is usually the first excited singlet state (Figure 1.11). Once a molecule arrives at the lowest vibrational level of an excited singlet state, it can do a number of things, one of which is to return to the ground state by photon emission. This process is called fluorescence. The lifetime of an excited singlet state is approximately $10^{-9}$ to $10^{-7}$ seconds and therefore the decay time of fluorescence is of the same order of magnitude,
1.8.3.2 Phosphorescence

Phosphorescence results when a molecule gets excited to the triplet state (Figure 1.11). It loses energy by emission of a photon. A radiative transition between the lowest triplet state and the ground state takes place and this type of emission is called phosphorescence. As phosphorescence originates from the lowest triplet state, it will have a decay time approximately equal to the lifetime of the triplet state. This lifetime is approximately $10^{-4}$ to 10 seconds. Phosphorescence is therefore often characterized by an after glow that is not observed for fluorescence.
1.8.4 Radiationless transitions

A molecule can also undergo some radiationless transitions. These processes are called the radiationless transfer of energy. These processes are explained in Figure 1.12. There are three processes that can occur, namely vibrational relaxation, intersystem crossing and internal conversion. When a molecule returns to the electronic ground state non-radiatively, the excess energy is converted to vibrational energy (internal conversion) and the molecule is placed in an extremely high vibrational level of the electronic ground state.

Fig 1.12 Possible physical processes following the absorption of a photon by a molecule

The excess vibrational energy is lost by collision with other molecules (vibrational relaxation). The spin of an excited electron can be reversed and this leaves the molecule in an excited triplet state. This is then called intersystem crossing. The triplet state is in a lower electronic energy than that of the excited singlet state. The probability that this will
happen is increased if the vibrational levels of these two states overlap (Oxtoby, 1981).

1.8.5 Types of phosphors

Phosphors are classified according to the transitions that take place when it is irradiated with either photons or electrons. One group includes phosphors where the transition occurs in the band gap and the other group includes phosphors where transitions are localized in luminescent centres such as rare-earth elements. These are referred to as band gap and intra-atomic transitions respectively (http://en.wikipedia.org/wiki/Phosphorescence).

1.8.5.1 Band gap transition phosphors

A typical semiconductor consists of a valence band and a conduction band. The energy gap between the bands is referred to as the band gap (Figure 1.13). The lower energy state or valence band is occupied by electrons originating from bound electrons of atoms. The higher energy bands or conduction bands are not occupied by electrons. The reason why these unoccupied states are called conduction bands is due to the fact that an electron in this band is almost freely mobile if it is excited from the valence band by some method: for example, by absorption of light quanta. In contrast, electrons in the valence band cannot be mobile because only two electrons (spin up and spin down) can occupy an electronic state. Electrons in the valence band must have empty states in order to move freely when an electric field is applied. After an electron is
excited to the conduction band, a hole that remains in the valence band behaves as if it was a mobile particle with a positive charge (Shionoya and Yen, 1999).

Excitation occurs due to energy transfer from the incident, high energy, particles to the electrons in the valence band. If the transferred energy is high enough the electrons get excited to the higher energy levels or conduction band. Free electrons and free holes are now generated in the conduction and valence bands respectively. If the crystal is perfect, i.e. free from lattice defects and impurities, the free electrons and holes can recombine directly and emit photons ((a) in Figure 1.14). The energy of these photons is equal to the band gap of the semiconductor. Localized energy levels or impurity levels are created in a crystal by the presence of activator impurities, incidental impurities and lattice defects. This provides effective recombination paths for the free electrons and holes as represented by (b), (c) and (d).
in Figure 1.14. (b) is the transition between a free electron in the conduction band and a hole trapped by an acceptor level. (c) represents a transition between an electron in a deep donor level and a free hole in the valence band and (d) represent a transition between a donor and acceptor level. A number of luminescent processes in the ZnS:Ag,Cl (blue) ZnS:Cu,Al,Au (green) and ZnS:Mn (orange) phosphors occur according to (d) (http://en.wikipedia.org/wiki/Phosphorescence).

![Diagram of band gap transitions in a phosphor](image)

**Fig 1.14 Model of band gap transitions in a phosphor**

**1.8.5.2 Intra-atomic transition phosphors**

Characteristic luminescence occurs by doping the host lattice with either transition (3d) or rare earth (4f) metal ions (impurities) that substitute the host lattice cations. When a moving particle (electron or photon) collides with an atom, an electron in the inner shell will be excited to a higher energy level. The electron relaxes to its original energy level and the extra energy is released in the form of a photon (Figure 1.15).
Rare-earth ions from Ce$^{3+}$ to Yb$^{3+}$ (atomic numbers 58 - 70) have partially filled 4f orbitals with energy levels characteristic to each ion and shows a variety of luminescent properties around the visible region. Many of these ions are used as luminescent ions in phosphors. The levels are not much affected by the environment, because 4f electrons are shielded from external electric fields by the outer 5s$^2$ and 5p$^6$ electrons. This is in strong contrast with the transition metal ions, whose 3d electrons, that is located in the outer shell, are heavily affected by the environment or crystal field (Shionoya and Yen, 1999). Figure 1.16 shows an energy level diagram of luminescent transitions within Eu$^{3+}$. The diagram shows that absorbed excitation (high energy electrons) induces transitions to higher $f$ levels where upon non-
radiative transitions to the $^5D_J$ ($J = 0, 1, 2, 3$) states occur. This is followed by radiative transitions to the ground state. Typical phosphors used in CRTs and FEDs consist of a host matrix doped with activators such as the rare-earths ($4f$) and transition metals ($3d$) (Srivastava and Ronda, 2003).

Fig. 1.16 Intra-atomic luminescent transitions in Eu$^{3+}$ ions

1.9 II-VI SEMICONDUCTORS

There are generally recognized eight II-VI semiconductor materials. They are ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe, and CdTe. Mercury, the other group IIIB metal, forms a liquid at standard temperature and pressure (STP) and therefore is not generally included in this list. Because of their uses in optoelectronics and
semiconducting applications, II-VI semiconductors have recently been the focus of intense research in nanomaterials. The II-VI semiconductors are typically wide band gap materials, serving as efficient light emitters. This makes them likely candidates to replace materials such as GaN in light emitting diodes (LED) (Gutowski et al., 2002). Each of the II-VI semiconductors demonstrates some unique properties, making them useful for unique applications. ZnS has a band gap of 3.54 eV for the zinc blende phase and 3.91 eV for the wurtzite phase (Ray, 1969). It displays a high refractive index of 2.2 and a high transmittance of light in the visible region of the spectrum (Jiang et al., 2001, Yamaga et al., 1988 and Elidrissi et al., 2001). These properties make ZnS a strong candidate for optoelectronic devices. Nanostructures of II-VI semiconductors have also been shown to have some unique properties. CdS nanowires have functioned as Fabry-Perot optical cavities and these nanowires have been used as electrically driven lasers (Duan et al., 2003). Also, CdSe nanorods can have up to 100% polarized luminescence and could be used as nano-emitters or high resolution detectors of polarized light (Hu et al., 2001).

This thesis will focus one particular non-oxide II-VI semiconductors, as they have offered the most potential for nanostructure applications. A brief portion of the thesis will first be given to ZnS nanostructures including a short consideration of the generalizability growth results of ZnS. Then, the bulk of the thesis will consist of a discussion of ZnS:Cu$^{2+}$ nanostructures, which have been
focused on due to the excellent optoelectronic and thermal properties of ZnS:Cu$^{2+}$ nanoparticles.

1.10 ZnS

ZnS type phosphors are presently very important as CRT phosphors. These phosphors have a long history, dating back about 130 years. At the International Conference on Luminescence held in 1966 in Budapest, presentation titled “The Century of the Discovery of Luminescent Zinc Sulfide” was given, in which the history of luminescent ZnS was discussed. In 1866, a young French chemist, Théodore Sidot, succeeded in growing tiny ZnS crystals by sublimation method. Although his original purpose was to study crystal growth, the crystals grown exhibited phosphorescence in the dark. The experiments were repeated, the observations confirmed and a note to the Academy of Science of Paris was presented. This note was published by Becquerel. These phosphorescent ZnS (zinc-blende) crystals were thereafter called Sidot’s blende. From present knowledge, one can conclude that Sidot’s blende contained a small quantity of copper as an impurity responsible for the phosphorescence (Shionoya and Yen, 1999). Zinc sulfide is a trimorphous mineral consisting of sphalerite, wurtzite and matraite.

1.10.1 Sphalerite
The mineral sphalerite is the chief ore of zinc. It consists largely of zinc sulphide in crystalline form, but almost always contains variable iron. When the iron content is sufficiently high it is an opaque black variety, marmatite. It is usually found in association with pyrite, galena and other sulphides along with dolomite, calcite and fluorite. The mineral will crystallize in the cubic crystal system. In the crystal structure, zinc and sulphur atoms are tetrahedrally coordinated. This structure is closely related to the structure of diamond (Figure 1.17). The hexagonal analogue is known as the wurtzite structure. The lattice constant for zinc sulfide in the zinc-blende crystal structure is 0.596 nm, calculated from geometry and ionic radii of 0.074 nm (zinc) and 0.184 nm (sulfide). It forms ABCABD layers. Its colour is usually yellow, brown or grey to grey-black, and it may be shiny or dull (Figure 1.18). Some of its characteristics are that it has a yellow to light brown streak, a hardness of 3.5 - 4 and a specific gravity of 3.9 - 4.1. The refractive index of sphalerite is 2.37. Some specimens of sphalerite are also fluorescent in ultraviolet light (http://en.wikipedia.org/wiki/Sphalerite).

1.10.2 Wurtzite

Wurtzite is a zinc sulfide mineral, a less frequently encountered mineral form of sphalerite. Its crystal structure is called the hexagonal wurtzite crystal structure, to which it lends its name (Figure 1.19). This structure is a member of the hexagonal crystal system and consists of
tetrahedrally coordinated zinc and sulphur atoms that are stacked in an ABABAB pattern. The unit cell parameters of wurtzite are $a = b = 3.81 \text{ Å}$ and $c = 6.23 \text{ Å}$. Its colour ranges from brownish black, orange brown, reddish brown to black (Figure 1.20). It can be characterized by a hardness of 3.5 – 4, a light brown streak and a specific gravity of 4.0 (http://webmineral.com/data/Wurtzite.shtml). It occurs in hydrothermal deposits associated with sphalerite, chalcopyrite, pyrite, barite and marcasite. It was first described for an occurrence in Pribram, Czech Republic in 1861 and named after the French chemist Charles-Adolphe Wurtz (http://en.wikipedia.org/wiki/Wurtzite).
Fig 1.18 Different types of sphalerite

Fig 1.19 The hexagonal wurtzite crystal structure
1.10.3 Matraite

Matraite is the rarest form of zinc sulfide. It has a hexagonal crystal structure, a hardness of 3.5 - 4, a yellow white streak and a brownish yellow colour (Figure 1.21). It was named after the Matra Mountains in Hungary (http://www.mineralatlas.com/mineral%20general%20descriptions/M/matraitepcd.htm)
1.11 ZINC SULFIDE DOPED WITH TRANSITION METALS

Since ZnS is a kind of wide band gap II–VI compound semiconductor materials with its band gap energy $E_g = 3.6$ eV, ZnS becomes good host material. It is commercially used as a phosphor and thin-film electroluminescence devices (Grlick and Gibson, 1949; McClean and Thomas, 1992; Yu and Senna, 1995 and Yu et al., 1995). Luminescence characteristic of impurity-activated ZnS nanocrystals differ markedly from those of the bulk ZnS. Yang et al., (2003) gave two reasons for this behaviour: First, ZnS nanocrystallites are the high disperse nanocrystalline system; second, the size-dependent properties of semiconductors ZnS nanoparticles are particularly interesting. It is well-known that the properties of pure ZnS nanoparticles are obviously different from the bulk materials, nanocrystals doped with optically active luminescence centers create new opportunities for luminescent study and application of nanosemiconductor materials (Bhargava et al., 1994 and Yi et al., 1993).

Doped ZnS nanocrystals have attracted more attention since 1994. Bhargava et al., reported for the first time that Cu$^{2+}$ doped ZnS nanosemiconductor could yield both high quantum luminescence efficiency and lifetime shortening at the same time. The results suggested that doped semiconductor nanocrystals form a new class of luminescent materials, which have a wide range of application in displays, lighting, sensors and lasers (Bhargava, 1996; Chen and Nie, 1998; Parsapour et al., 1996 and Waldrip et al., 2000). Many
literatures from different groups have reported the optical properties of various doped nanocrystals and the potential application of these luminescent materials. Today, various transition metal ions doped in nanocrystalline ZnS host, such as Cu$^{2+}$, Mn$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, single doped ZnS nanocrystallites. These semiconductors have been systematically studied, especially ZnS:Cu$^{2+}$ nanoparticles, and have achieved many successes.

The impurity-activated ZnS host nano semiconductor luminescence materials have been studied for two decades. Many efforts have been made in experiment and theory. Among the printed reviews about nanometer semiconductor materials, all of them only reviewed the single semiconductor nanoparticles or nanocrystalline. For example, “Experiment and theory of electronic wave function in semiconductor clusters” reviewed by Brus (Brus, 1984), “Physicochemical properties of extremely small colloid metal and semiconductor particles” studied by Henglein (Henglein, 1989), “The material synthesis, quantum size effects and photophysical properties of nanometer-sized semiconductor or clusters” studied by Wang and Herron (Wang and Herron, 1991) and recently, “The synthesis, properties and perspectives of nanocrystalline semiconductor” reviewed by Trindade (Trindade et al., 2001). However, nobody focuses on the doped nanocrystalline semiconductor. The present work is focused on the wonderful characters of the doped nanomaterial, especially ZnS:Cu$^{2+}$ nanocrystals, such as the shift and broadening of spectrum, the high
luminescent quantum efficiency, the shortening of emission lifetime and up conversion emission.

1.12 COPPER DOPED WITH ZNS NANOPARTICLES

In order to understand the physical and chemical properties of Cu\(^{2+}\) doped ZnS nanoparticles, some experimental work has been performed in the past years. However many things are unclear. For example the effect of quantum confinement on the luminescence efficiency is a point of debate. Nevertheless, strong photoluminescence is observed from ZnS:Cu nanoparticles due to the Cu\(^{2+}\) in the ZnS host. Cu substitute for Zn as Cu\(^{2+}\) (3d\(^9\)) and produce a deep acceptor level in bulk ZnS. In cubic ZnS, the tetrahedral crystal field of the S\(^{2-}\) ligands splits the Cu 3d\(^9\) ground state into higher lying t\(_2\) states and lower e levels (Karar et al., 2004).

In ZnS:Mn nanoparticles, an orange luminescence has been well documented, which is attributed to the \(^{4}T_1\rightarrow^{6}A_1\) transition of Mn\(^{2+}\) ions excited via energy transfer from the host ZnS (Bhargava et al., 1994). Similar interatomic emission from the characteristic 4f\(^7\)–4f\(^6\) 5d\(^1\) transition of Eu\(^{2+}\) was also observed in ZnS:Eu nanoparticles (Chen et al., 2000). However, in the case of nanosized ZnS:Cu, the luminescence properties are of still controversial. Two emission bands (blue and green) were often observed together in the same sample, such as 420 and 520 nm by Lee et al., (2004) and 460 nm and 507 nm by Xu et al., (1998). On the other hand, a single emission peak was also observed at 480 nm (Khosravi et al., 1995) or at 415 nm (Huang et al., 1997).
Recently Bol et al., (2002) reported a red emission around 60 nm in ZnS:Cu nanoparticles and assigned it to be the recombination between a deeply trapped electron and Cu$^{2+}$ (Bol et al., 2002). The optical properties of these nanocrystals exhibit efficiency luminescence even at room temperature. This can be used as new functional materials for future optoelectronic devices (Shimet et al., 2001;). Thus the study of optical properties of ZnS:Cu nanoparticles is important for the development of nanocrystals phosphors with efficient luminescence efficiency and the understanding of the impurity related optical transition in semiconductor nanocrystals. Compared with the traditional technology of ZnS:Cu LED, it was much earlier to fabricate a single larger LED using ZnS:Cu nanocrystals/ polymer composite due to its good film process ability.

1.13 METHODS OF SYNTHESIS OF ZnS:Cu$^{2+}$ NANOPARTICLE

Different methods are available to synthesis of ZnS:Cu$^{2+}$ nanoparticle. All particle synthesis techniques fall into one of the three categories:

1. Solid-state synthesis of nanoparticles
2. Vapour-phase synthesis of nanoparticles
3. Soft chemical method

In this thesis, we focus the soft chemical method to synthesize ZnS:Cu$^{2+}$ nanoparticles. The reason for adopting this soft chemical method ascribed that the impurity more easily substitutes the host metal ions position in the lattice of nanocrystals in solution.
The soft chemical method is further classified as follows:

(i) Chemical precipitation method
(ii) Micro emulsion technique
(iii) Colloidal chemical method
(iv) Chemical synthesis method
(v) Organic method
(vi) Sol-gel method and
(vii) Ions implantation method

Among these methods the chemical precipitation is used in this thesis work. This method is the most popular technique that is used in industrial applications because of its cheap raw materials, easy handling and large-scale production.

1.14 BRIEF REVIEW OF LITERATURE

Brus (1984) implied a model, in an elementary way, the excited electronic states of semiconductor crystallites are sufficiently small (~50 Å D). The electronic properties differ from those of bulk materials. The diffraction of bonding electrons by the periodic lattice potential remains of paramount importance in the crystallite electronic structure was observed. He solved the Schrodinger’s equation at the same level of approximation, as used in the analysis of bulk crystalline electron-hole states (Wannier excitons).

Khosravi et al (1995) synthesized free-standing powder of zinc sulphide quantum particles using a chemical route. They studied X-ray diffraction analysis which showed that the diameter of the particles is
~21±2 Å. It is smaller than the Bohr exciton diameter for zinc sulphide. The UV absorption shows an excitonic peak centered at ~300 nm corresponding to an energy gap of 4.1±0.1 eV. These particles show a luminescence band at ~424 nm. The quantum particles could be doped with copper during synthesis without altering the UV absorption or X-ray diffraction pattern. Moreover, doping of Cu shifted the luminescence to 480 nm, green wavelength in the visible region.

Sooklal et al (1996) have found that the location of Mn$^{2+}$ in 50 Å ZnS nanoclusters profoundly affects the photophysics of the entire particle. Mn$^{2+}$ substituted for Zn$^{2+}$ in the ZnS lattice leads to the well-known Mn$^{2+}$ ($^4T_1$-$^6A_1$)-based emission in the orange, with emission lifetimes that are best fit by a biexponential decay and are intermediate between those found for big (micron) nanoclusters and smaller nanoclusters. They examined addition of Mn$^{2+}$ to the outside of preformed ZnS nanoclusters apparently stabilize near-band-gap emission in the ultraviolet with even shorter lifetimes. Further studies are underway to examine the effect of Mn$^{2+}$ location on the electroluminescent properties of thin films of these nanocrystals.

Huang et al (1997) synthesized ZnS:Cu nanocrystals in polymeric networks. X-ray photoemission spectroscopy and atomic absorption data show that the Zn and Cu ion mass contents were about 8.2% and 0.12%, respectively. The particle size of ZnS:Cu nanocrystals was about 3.0 nm, measured by UV-vis spectrum. Due to the quantum size effects, the band gap energy of ZnS nanocrystals was about 4.2 eV. The photoluminescence of ZnS was observed at 390 nm and the
photoemission of ZnS:Cu/polymer thin films was observed at 415 nm. The ZnS:Cu/polymer was also used to fabricate light-emitting diode (LED), as the emitting layer of LED, the blue light of electroluminescence was observed at room temperature, and its turn-on voltage was less than 4 V.

Xu et al (1998) prepared ultrafine ZnS:Mn, ZnS:Cu, and ZnS:Eu nanoclusters using microemulsion with hydrothermal treatment. They observed PL experiments, which show strong visible light emission from these doped ZnS nanocrystals at room temperature. These preliminary results show that the micro-emulsion with hydrothermal treatment may be a good method to directly synthesize doped nanocrystalline phosphors with high luminescence efficiency.

Que et al (1998) prepared Cu-doped nanocrystals of ZnS in an inverse microemulsion by the hydrothermal technique. They reported, that it was much easier to fabricate the single layer structure EL device using the Cu-doped ZnS nanocrystals/ polymer composite due to its good film processability. The single layer EL device had about 5 V turn-on voltage and the green emission was observed at room temperature.

Wang et al (2000) synthesized ZnS:Cu nanoparticles by the coordination chemistry method with glycine as ligand. The size of the prepared nanoparticles decreased with increasing of Cu$^{2+}$ doping concentration inferred from the blue-shift of absorption spectra. From the relative luminescence intensity of vacancies and Cu$^{2+}$ centers, it is deduced that Cu$^{2+}$ ions substitute Zn$^{2+}$ ions in the lattice. There is no
obvious luminescence enhancement with increasing dopant for fresh samples because some of Cu\(^{2+}\) ions are used to form CuS, which can also act as nucleus. Successive crystallization and reorganization of the particles increased the luminescence intensity. They reported the function of the ligand and glycine which can provide the solubility levelling effect and a certain extent of surface-protecting effect.

Kumbhojkar et al (2000) carried out optical measurements on ZnS nanoclusters to investigate surface effects along with quantum size effects. They synthesized ZnS in the range of 1.5–2.5 nm, using different chemical methods as well as electronic passivating procedures. The size of nanoparticles has been estimated from empirical pseudopotential calculations. They obtained a significantly narrower size distribution of ZnS nanocrystals than reported in earlier published results. They observed band gap luminescence in mercaptoethanol capped ZnS nanocrystals. Effects of various defect levels on the luminescent behaviour of ZnS nanoparticles have been examined.

Mane & Lokhande (2000) have described the chemical bath deposition of metal chalcogenide thin films. They reported that the method is simple, inexpensive, convenient for large area deposition and capable of yielding good quality thin films. The presented data shows that the film formation could be carried out onto various substrates. They suggested that the physical and chemical properties of such semiconductors are comparable with the semiconductors prepared by other methods. The devices such as solar cells,
photoconductors, detectors, solar selective coatings etc. made from such films show the promise of the method in modern thin film technology.

Yang et al (2001) synthesized nanometer scale ZnS, ZnS:Cu, ZnS:Pb, and ZnS co-doped with Cu$^{2+}$ and Pb$^{2+}$ using a Chemical Precipitation method. Their X-ray Diffraction analysis shows that the diameter of the particles is 2–4 nm. The results of their PL experiments show strong visible-light emitting from these co-doped ZnS nanocrystals at room temperature. The emission band of ZnS nanoparticles is at 450 nm. They observed two emission bands for Cu$^{2+}$-doped ZnS nanocrystals. One is at 450 nm while the other is at 530 nm. The emission band of Pb$^{2+}$-doped ZnS nanocrystals is at 480–530 nm. But its fluorescence intensity is weaker than that of pure ZnS. The emission band of ZnS nanoparticles co-doped with Cu$^{2+}$ and Pb$^{2+}$ is at 500–550 nm and their fluorescence intensity is dramatically enhanced than that of ZnS nanocrystals.

Bol et al (2002) reported luminescence measurements on nanocrystalline ZnS:Cu$^{2+}$ particles as a function of particle size and temperature. The yielded results show that the green emission from these particles is due to recombination of a shallowly trapped electron and Cu$^{2+}$. They observed PL emission, shifted to slightly higher energies due to smaller size. They observed quenching temperature for the emission about 135 K. Temperature quenching is accompanied by a decrease in the emission lifetime from 20 ms at 4 K to 0.5 ms at 300 K.
In addition, a red emission band is observed which is assigned to recombination of a deeply trapped electron and Cu\(^{2+}\). The red emission is characterized by a longer lifetime (40 ms at 4 K) and a higher quenching temperature. They observed intensity of the red emission band is strongly dependent on the synthesis procedure.

**Yang et al** (2002) synthesized doped ZnS nanoparticles as free-standing powders using chemical precipitation method. They observed PL spectra of Cu\(^{2+}\) -and Cu\(^{+}\) -doped ZnS nanocrystals which consists of two emission peaks. One is at 450 nm and the other is at 530 nm. For Cu\(^{+}\) -and Cu\(^{2+}\) -doped ZnS nanocrystallites, Cu\(^{+}\) and Cu\(^{2+}\) are assumed to substitute for Zn\(^{2+}\) ions or to be interstitial ions. The luminescent centers of Cu\(^{+}\) and Cu\(^{2+}\) are formed in ZnS nanocrystallites. The relative fluorescence intensities decrease with increasing impurity mole ratios of Cu\(^{+}\) -and Cu\(^{2+}\). They obtained PL emission peaks which are shifted to longer wavelength and become broad. The emission spectra of Cu\(^{+}\)-doped samples are different from those of Cu\(^{2+}\)-doped samples because the luminescence mechanism of Cu\(^{+}\) and its synthesized process are different from those of Cu\(^{2+}\) luminescent centers.

**Zhu et al** (2003) synthesized ZnS nanobelts by heating ZnS powders in N\(_2\) atmosphere with a small amount of CO and H\(_2\). The as-prepared ZnS nanobelts have a hexagonal wurtzite structure and grow along the [001] direction. The formation of these nanobelts is a spontaneous growth process through the evaporation of a precursor followed by the nucleation and growth. They observed PL of the nanobelts which shows
a weak emission band at 450 nm and a strong emission band around 600 nm.

Lee et al (2004) synthesized ZnS:Cu nanocrystals by solution synthesis technique which has the cubic structure (β-ZnS). They examined by increasing the synthesis temperature. But the crystal structure was not changed. However, the grain size increased slightly with an increase of preparation temperature, as evidenced by the intensity increase of XRD peaks and the shift of absorption edge in optical transmittance spectrum. PL intensity is maximum for the sample prepared at 85 °C for the temperature range used in their study. The results obtained from XPS measurement show that, for lower synthesis temperature (< 85 °C), the binding energy is 932.2 eV (Cu2p3/2 of metallic Cu), and for higher synthesis temperature (>90 °C), the binding energy is 933.5 eV (Cu2p3/2 of CuO). From the observation, they reported that Cu is transformed into CuO when the sample is prepared at high temperature. The CuO plays an undesirable role on the substantial decrease of PL intensity.

Chang et al (2005) shifted the phosphors in CRTs which were coated with In$_2$O$_3$ conductive layer derived from the hydrolysis of Indium chloride. They found that brightness of the phosphors rises initially with an amount of InCl$_3$, reaches a maximum at 10 wt.% InCl$_3$ and then decreases when more InCl$_3$ was added. With 10 wt.% InCl$_3$ coating, the brightness of ZnS:Cu, Al phosphor increases by 24% at 800 V and 1 mA while very little changes were observed in the
luminescent emission peak and CIE color loci. The luminescence decay times increase with an increase of the conductive coating. However, they are shorter than 0.7 ms for samples with the amount of coating ranging from 0 to 20 wt.% InCl$_3$ and are suitable for display applications. Conductive coating affects the surface chemistry of the phosphor particles, enhances the zeta potential of ZnS:Cu, Al in IPA solution, and, consequently, increases the electrophoretic deposition rate of the phosphors onto substrate.

Warrad et al (2005) have successfully synthesized the quantum dots of manganese doped zinc sulfide by a simple precipitation reaction using aqueous route resulting in primary particle sizes of 60–80 nm. The nanoparticles were sterically stabilized using polyphosphates of sodium namely STTP and SHMP. The authors reported that SHMP was a superior capping agent than STTP. Moreover, they observed that the particle sizes are dependent on the amounts of stabilizing agents (SHMP) used during synthesis making it possible to alter the particle sizes by changing the concentrations of stabilizing agents used during synthesis.

Han et al (2005) synthesized Bigger-sized spherical particle of ZnS:Cu, Cl using a new eutectic mixture as flux. The best composition of the flux was the mixture of BaCl$_2$ 2H$_2$O, MgCl$_2$ 6H$_2$O and NaCl in the mole percentage ratio of 13.8:39.9:46.2. The total amount of the mixture was 6% of the total weight of ZnS prepared. The phosphor was synthesized by firing at higher temperatures in two steps. First step firing at 1150°C gave the hexagonal phase of the ZnS phosphor.
particles. Low intensity ball-milling of the phosphor pastes in solvents converted hexagonal phase partially to the cubic phase of the phosphor, which is an essential step. Mixing with copper sulfate or copper (I) halides and magnesium chloride and then firing (second step) at 750°C gave a phosphor with better luminescent characteristics and converted to almost 100% cubic phase. The particles were coated twice with the TiO₂ sol and finally calcined at 400°C in nitrogen atmosphere.

Ishizumi et al (2005) studied the optical properties of ZnS:Cu,Al nanocrystals fabricated by sequential implantation of Zn⁺,S⁺,Cu⁺, and Al⁺ ions into Al₂O₃ matrices. They reported that the ZnS:Cu, Al nanocrystals exist in Al₂O₃ matrices and exhibit the intense green luminescence related to the DA (Al–Cu) pair recombination. The spectroscopic studies show that sequential ion implantation is a useful method for synthesizing nanocrystals doped with luminescence centers.

Manzoor et al (2005) used a simple, surfactant-free, room-temperature self assembly method for the preparation of functionalized (doped) semiconducting nanorods. ZnS nanoparticles doped with Cu⁺–Al³⁺ pairs or Mn²⁺ prepared with excess S²⁻ (Sₙ²⁻) ions, aggregated in aqueous medium and grown into nearly mono-crystalline nanorods by Ostwald-ripening and oriented-attachment based coarsening mechanisms. They observed nanorod geometries which show conclusive evidences for the annihilation of larger concentration of surface dominated lattice-vacancies, increase in the doping concentration, modifications in the local environment around the
dopant ions, etc, which all leads to significant enhancement in the dopant-related photoluminescence of nanorods. This study demonstrated that the individual nanoparticles can be used as the fundamental building blocks for the creation of functionalized, ordered and extended nanosolids with enhanced luminescence properties for their applications in futuristic displays or lasers.

Kumar et al (2006) synthesized the nanoparticles of ZnS through a chemical route using TEA as the capping agent. The XRD pattern of the unimplanted samples showed cubic phase of ZnS and the grain size was estimated about 2.4 nm after correction due to lattice strain. Pellets of the nanostructured ZnS samples were implanted with Cu$^+$ ions at doses of $5 \times 10^{14}$, $1 \times 10^{15}$ and $5 \times 10^{15}$ ions/cm$^2$. Raman spectrum of unimplanted nanostructured ZnS show peaks at 258 and 344 cm$^{-1}$. The peak at 258 cm$^{-1}$ is attributed to the LOPC (L-) mode and the peak at 344 cm$^{-1}$ is attributed to the LO mode of ZnS. They reported the peak at 412 nm, which was attributed to transitions from sulfur vacancy states to the valence band and the peak at 518 nm was attributed to the transitions of electrons between sulfur and zinc vacancy states. Implantation with Cu$^+$ ion at a lower dose of $5 \times 10^{14}$ ions/cm$^2$ produced a photoluminescence peak around 490 nm which was attributed to the transition between the impurity levels formed by Cu$^+$ ion and the valence band.

Ehlert et al (2006) developed a new and facile synthetic method for the preparation of Cu and/or Pb (co-)doped ZnS nanocrystals without
injection of precursors. They prepared nanoparticles having the cubic structure and a particle size of about 5 nm with a narrow size distribution. The doping ions occupy regular lattice sites and were confirmed by photoluminescence spectroscopy. The prepared particles show blue (undoped ZnS), green (ZnS:Pb core, ZnS:Cu,Pb core, and ZnS:Cu, Pb/ZnS core/shell), or white (ZnS:Pb/ZnS core/shell) luminescence. Covering of the particles with a layer of undoped ZnS reduces the effect of surface defects and, related to them, the quenching of luminescence. In Pb-doped ZnS particles, the fraction of Pb$^{2+}$ on regular sites increases after the shelling procedure. They reported that the homogeneous synthetic route can be further exploited for the synthesis of other doped, sulfide based semiconductor materials.

Kim et al (2006) prepared ZnS:Cu nanocrystals by solution synthesis technique. The systematic investigation was carried out for the surface capping effect in which the particle size could be controlled and the particle agglomeration could be reduced. The optical characteristics such as photoluminescence (PL) intensity and emission wavelength were also observed. Sodium polyphosphate (SPP) was used as a surface capping agent, and the new results about the effects of SPP capping on structural and optical properties of ZnS:Cu nanocrystals were obtained. They observed, PL emission wavelength was blue-shifted, and it was decreased from 518 to 462 nm with the increase of SPP from 0.0 to 1.89 g.
Peng et al (2006) synthesized ZnS:Cu nanoparticles of about 3.5 nm by a simple wet chemical route. They observed a cubic zinc blende structure of ZnS for all the samples and no other crystalline phase was detected. Moreover, they observed a quantum confinement effect, for the small nanoparticles. The PL spectra of the doped samples are broad and asymmetric and can be deconvoluted into three Gaussian peaks. They observed a green luminescence peak related with copper impurities while two blue luminescence peaks can be attributed to native defects of ZnS. They also observed with an increasing of Cu$^{2+}$ concentrations, the green emission peak was systematically shifted to longer wavelength. Further, the overall PL intensity is decreased at the Cu$^{2+}$ concentration of 2%. They also reported, concentration quenching of the luminescence may be caused by the formation of CuS compound.

Wang et al (2006) have successfully prepared ZnS:Cu/PVA nanofibers with various concentrations of Cu doping by electrospinning method. The Cu-doped ZnS nanocrystals with diameter about 3 nm were well-dispersed in PVA nanofibers through the coordination between –OH and Zn$^{2+}$:Cu, which prevented the ZnS:Cu nanoparticles from aggregation in the nanofibers. Furthermore, they observed PL measurement and luminescence decay time measurement, demonstrated that the luminescence properties of Cu-doped samples were changed significantly compared with the undoped sample. This was caused by the influence of copper induced t$_2$ level. Therefore, they anticipated that this ZnS:Cu/PVA composite nanofibers with good
photo luminescence property can be exploited for fabrication of optoelectronic nanodevices.

Yazici et al (2007) presented experimental results about novel ZnS:Cu nanophosphors obtained by spray pyrolysis method. They observed good thermoluminescence properties and its TL intensity enhanced with decreasing particle size. Additionally, due to the high linear correlation between dose and TL response for beta-particle radiation, ZnS:Cu nanophosphors may be considered as a promising material to be used in thermoluminescence dosimetry for ionizing radiation and as well as non-ionizing (UV) radiation due to its low band gap.

Datta et al (2008) have prepared Cu-doped (0.1–15 mol%) ZnS nanorods (diameter 12–18, length 200–250 nm) by solvothermal process. Undoped and up to 1 mol% Cu-doped ZnS nanorods were found to crystallize in wurtzite structure with preferential growth along the [001] direction. They observed with an increasing of the dopant concentration, the wurtzite ZnS nanorods gradually phase transformed to cubic structure and the growth direction of the nanorods were changed along the (111) plane. Phase transformation was also found to induce noticeable defects in the ZnS lattices including twins and stacking faults.

Sambasivam et al (2008) reported that ligand thiophenol acts as a template in controlling growth of ZnS and ZnS:Cu$^{2+}$ nanoparticles. This study also demonstrated that the incorporation of Cu$^{2+}$ ions in lower
concentrations in ZnS lattice suppresses the growth of nanoparticles of different sizes and confines the particles size to a narrow range, without appreciable decrease in PL intensity. They observed TEM micrographs which indicated nearly narrow distribution of grain size. ESR spectrum reveals that the Cu$^{2+}$ ions enter into the Zn$^{2+}$ site in the lattice with distorted tetrahedral environment. This observation suggested that lower dopant concentration might be better in order to retain Cu$^{2+}$ states in the lattice host of ZnS with tetrahedral environment without marked drop in PL intensity. For the preparation of ZnS:Cu samples, thiophenol can also be used as ligand in place of amino acids to control the size in the nanorange.

Arai et al (2008) have prepared ZnS particles with unique morphology named as “ZnS-shell” using ZnO particle as precursor. ZnS-shell had hollow shell structure with the shell consisting of particles with a smaller lattice constant than ZnS. This particle showed higher activity than the ZnS prepared by co-precipitation method in photosplitting hydrogen sulfide. Furthermore, visible light response of ZnS-shell particle was realized by doping with Cu ions. The result of this study has demonstrated that the activity of a well-known material such as ZnS could be improved drastically by controlling the composition and morphology of the particle.

Song et al (2008) synthesized a monodispersed spherical ZnS particles as well as doping with Cu, Mn from metal–EDTA with TAA. They prepared nanoparticles tuned from 50nm to 1 mm by changing
the nucleation temperatures and molar ratio of reactant. They observed that the total emission intensity was increased continuously with increasing the grain size. For the ZnS microspheres annealed at 550–800°C, there are two emission sites when excited at 325 nm. One emission site of the blue band around 454 nm is associated with the trapped luminescence arising from the surface states; the other emission site of the green band around 510 nm may be related to the stoichiometric vacancies. The dominant emission site was red-shifted from 454 nm of pure ZnS to 508 nm of ZnS:Cu, and further also the fluorescence intensity was increased sharply when ZnS was doped with Cu$^{2+}$. The addition of Mn$^{2+}$ to the ZnS colloid did not have a significant effect on the emission site, but has effects on the emission intensity compared to the pure ZnS. The observed green fluorescence emission (510 nm) of the monodispersed ZnS microspheres could provide an interesting application in the development of novel luminescent devices.

Zheng et al (2008) produced a small, water-soluble, and stable colloidal Cu-doped ZnS quantum dots using a physical method: femtosecond laser ablation. They prepared five samples with different mean sizes by simply controlling the laser fluence. They prepared quantum dots which show narrow and symmetric Cu-related emission with a small luminescence decay time. The observed PL emission is ascribed to a transition between the conductor band of ZnS and the Cu impurity level. Moreover, they observed a quantum confinement effect. The characteristics of the as-prepared quantum dots make them very attractive for biomedical labels. Because of its intrinsic advantages
compared with other methods, laser-induced ablation of a doped solid target will be widely used to prepare various doped quantum dots.

Geng et al (2009) have successfully synthesized the rod-like ZnS:Cu$^{2+}$ nanocrystals by thermolyzing a mixture of Zn(Mer)$_2$ and Cu(Mer)$_2$ precursors which are easily controllable, safe and convenient. They used an oriented attachment mechanism to explain the epitaxial growth of nanorods. By selecting proper synthetic parameters, the adopted synthetic route was expected to the preparation of nanorods with tunable photoluminescence emission. The authors observed that this method may be employed to prepare other monodisperse transition-metal doped semiconductor nanostructures, which are potentially important for optoelectronic nanodevices.

Kao et al (2009) have synthesized ZnS:Cu, Al containing In$_2$O$_3$. The luminous performance of the phosphors using diode structure of FED is influenced by space distance and phosphor-layer thickness. In their case, samples prepared by performing once or twice the screen-printing process reveal better luminous performance. The spacer distance is also an important parameter of the luminous performance. When the spacer distance is reduced, the luminance increases; simultaneously, risk of phosphor damage is augmented. In their study, a spacer distance of 0.25mm is the most proper one to obtain intense emission and keep the anode plate undamaged. The luminance of the sample prepared by performing twice the screen-printing process is 6231cdm$^{-2}$ when a 6V$\mu$m$^{-1}$ electric field and a 0.25mm spacer are applied. The
intense green emission infers that the ZnS:Cu, Al phosphor is a very promising candidate for fabricating commercial FED.

Pouretedal et al (2009) synthesized nanoparticles of zinc sulfide. They also used manganese, nickel and copper as photocatalyst in the photodegradation of methylene blue and safranin as color pollutants. They examined the Photoreactivity of zinc sulfide with various dopants, mole fraction of dopant to zinc ion, pH of solution, dosage of photocatalyst and concentration of dye. The characterization of nanoparticles was studied using X-ray powder diffraction (XRD) patterns and UV–vis spectra. The maximum degradation efficiency was obtained in the presence of Zn$_{0.98}$Mn$_{0.02}$S, Zn$_{0.94}$Ni$_{0.06}$S and Zn$_{0.90}$Cu$_{0.10}$S as nanophotocatalyst. The effect of dosage of photocatalyst was studied in the range of 20–250 mg/L. It was seen that 150.0 mg/L of photocatalyst was an optimum value for the dosage. The most degradation efficiency was obtained in alkaline pH of 11.0 with study of photodegradation in pH amplitude of 2–12. The degradation efficiency was decreased in dye concentrations above of 5.0 mg/L for methylene blue and safranin dyes. In the best conditions, the degradation efficiency was obtained 87.3–95.6 and 85.4–93.2 for methylene blue and safranin, respectively.

Khare (2010) prepared nanocrystalline (Zn–Cd)S films with the effects of Cu doping on electro-optical properties by a simple, versatile and in expensive CBD technique. They observed various results which show strong dependence of EL and PL characteristics on Cu
concentration. The XRD studies show prominent lines of base materials whereas SEM studies present irregular distribution of circular grains. Further they reported that the SEM and XRD studies show particle size lie in nanometer range. The PL spectra were observed in the blue–green regions. The PL intensity was found to diminish above a particular concentration of dopant. The observed EL studies were lower threshold and higher brightness for smaller particles. The optical absorption spectra exhibit increase in band gap and its mechanism is based upon direct transition. Linear voltage–current characteristics indicate Ohmic nature and lower impedance for smaller particles.

Khare (2010) fabricated nanocrystalline (Zn–Cd)S films which were co-deposited on glass slide substrates by chemical bath deposition (CBD) technique at 70°C for 75 min. Electroluminescent (EL), photoluminescent (PL) and structural characteristics of these films doped with Cu have been investigated. Cu doping has significant effects on the growth, structural and optical properties of the deposited (Zn–Cd)S films. EL studies show the essentiality of copper for EL emission. The effect of Cu concentration is examined on XRD, SEM, UV–Vis spectroscopy, etc. The morphology of these films investigated with SEM and XRD was used to determine crystalline nature of the films. The optical absorption coefficient of the films has been found to increase with increase in Cu concentration. Voltage and frequency dependence shows the effectiveness of acceleration–collision mechanism. The trap-depth values are calculated from temperature dependence of EL brightness.
Kozak et al (2010) prepared ZnS nanoparticles and deposited on montmorillonite (MMT) in the presence of cetyl trimethyl ammonium (CTA). They reported the analysis of UV spectrometry and transmission electron microscopy (TEM) and proved the formation of nanoparticles with diameters ranging from 3 nm to 5 nm. Selected-area electron diffraction (SAED) patterns revealed the presence of romboedric ZnS. The band gap energy of nanosize ZnS was estimated at 3.89 ± 0.03 eV. Photoluminescence spectra exhibited a strong emission band between 300 nm and 600 nm which were explained by the vacant ZnS nanostructure.

Yuan et al (2010) have prepared, zinc sulfide (ZnS) nanoparticles on DNA network/mica and mica surface, respectively. This was carried out by first dropping a mixture of zinc acetate and DNA on a mica surface for the formation of the DNA networks or zinc acetate solution on a mica surface, and subsequently transferring the sample into a heated thiourea solution. The Zn$^{2+}$ adsorbed on DNA network/mica or mica surface would react with S$_2^-$ produced from thiourea and form ZnS nanoparticles on these surfaces. X-ray diffraction and atomic force microscopy (AFM) were used to characterize the ZnS nanoparticles in detail. Their AFM results showed that ZnS nanoparticles were distributed uniformly on the mica surface and deposited preferentially on DNA networks. They also found that the size and density of ZnS nanoparticles could effectively be controlled by adjusting reaction temperature and the concentration of Zn$^{2+}$ or DNA.
Klausch et al (2010) synthesized highly stable dispersions of hydrophilic ZnS:Cu nanocrystals using 3-mercaptopropionic acid. Through varying the reaction temperature and time, crystallinity and luminescence properties were studied. The particle size was determined by DLS, XRD, TEM and SAXS and is in a range of 3–10nm. Increasing dopant concentrations yield a red shift of the luminescence, allowing to adjust the emission color from blue to green was observed. It was also observed that the functionalization with octylamine transfers the particles into hydrophobic solvents and allows for the integration into polymers. Dispersion into laurylacrylate followed by in situ-polymerization leads to highly transparent and luminescent nanocomposites.

Kim et al (2010) Zn$_{1-x}$Cd$_x$S:Cu QDs ($x = 0$, 0.5, 1) with a diameter of 3.6 nm synthesized by a reverse micelle approach and their Cu-related emission properties with host composition were compared. First, ZnS:Cu QDs showed inefficient Cu-related green and orange emission bands. The low efficiency of Cu emission in ZnS QD host was postulated due to a large difference in solubility product constants between ZnS and CuS phase. The actual composition of Zn$_{0.5}$Cd$_{0.5}$S:Cu QDs was indirectly determined to be Zn$_{0.08}$Cd$_{0.92}$S:Cu, revealing that the actual composition of formed alloy QDs is far from the solution composition under the current synthetic conditions. Luminescent properties of CdS:Cu and Zn$_{0.5}$Cd$_{0.5}$S:Cu QDs were similar, showing a relatively bright red emission compared to ZnS:Cu QDs. A higher QY
was found from alloy QDs, indicating that a ZnCdS ternary QD would be a more advantageous host over a binary one.

Kumar et al (2011) reported the observation of copper impurity related peak at around 485 nm in the photoluminescence spectra of nano-particles of ZnS implanted with Cu$^+$ ions at the doses of $5 \times 10^{14}$, $1 \times 10^{15}$ and $5 \times 10^{14}$ ions/cm$^2$ and annealed at 200° and 300°C. The intensity of the Zn$^+$ vacancy peak observed in the PL spectra of the sample implanted at a higher dose of $5 \times 10^{15}$ ions/cm$^2$ decreased with annealing temperature, indicating impurity activation. Their results suggest that ion implantation is an efficient method to achieve controlled doping copper into ZnS nanoparticles.

Fang et al (2011) provided a comprehensive review on the synthesis of ZnS nanostructures, starting from 0D nanostructures (0D nanocrystals, 0D core/shell nanocrystals and 0D hollow nanocrystals), continuing with 1D nanostructures (nanowires, nanorods, nanotubes, nanobelts, nanoribbons, aligned nanowires and nanobelts, complicated nanostructures, longitudinal heterostructured nanostructures, coaxial (core/shell), heterostructured nanostructures and finishing with 2D nanostructures such as nanosheets. In addition, they also presented the novel properties and potential applications of these materials. Especially the luminescence properties (photoluminescence, cathodoluminescence, electro-luminescence, electrochemiluminescence, thermoluminescence, and luminescence mechanism), chemical and physical properties of the nanostructures
produced under different synthetic conditions and with diverse nanoscale morphologies were analysed.

Nazerdeylami et al (2011) synthesized ZnS:Mn$^{2+}$ nanoparticles by chemical method using PVP (polyvinylpyrrolidone) as a capping agent in aqueous solution. They reported structure and optical properties of the resultant product which were characterized using UV–vis optical spectroscopy, X-ray diffraction (XRD), photoluminescence (PL) and z-scan techniques. UV–vis spectra for all samples showed an excitonic peak at around 292 nm, indicated that concentration of Mn$^{2+}$ ions does not alter the band gap of nanoparticles. XRD patterns showed that the ZnS:Mn$^{2+}$ nanoparticles have zinc blende structure with the average crystalline sizes of about 2 nm.

Ehrlich et al (2011) reported the process of ZnS nanoparticles which includes two stages: rapid formation of a crystal “core”, covered by amorphous “shell”, with subsequent slow ripening of this shell. As follows from the ZnS particle size this shell may consist of several atomic layers of zinc and sulfur. The ripening process includes its crystallization with formation of the luminescent centers. Luminescence of ZnS nanoparticles was caused by zinc ions located on the surface. Zinc and sulfur vacancies ($V_{Zn}$ и $V_{S}$) or zinc and sulfur interstitial atoms were attributed to such type of defects.

Tiwari et al (2011) have reported the ML characteristic of the capped ZnS:Cu nanophosphors. It was found that γ-irradiation results in the increase of density of the filled electron traps. The nature and the density of these traps alter according to the kind of capping agent used.
and hence the ML intensity varies. They also observed the mechanism of ML which could be understood on the basis of piezo-electrically induced charge carrier detrapping model was reported. It seems that trapping and detrapping of charge carriers in materials can be studied using ML.

1.15 OBJECTIVE OF THE WORK

As seen in the introduction and literature review, ZnS:Cu\textsuperscript{2+} nanoparticles have attracted much attention in the past 15 years due to change in their optical properties in accordance with narrow and small size and its applications in electroluminescence devices, field emission display, biosensor in biological, laser etc. Because of these properties and applications, the present study is focused on the ZnS:Cu\textsuperscript{2+} nanoparticles.

The objective of the present research can be summarized as follows.

- To synthesize Cu\textsuperscript{2+} -doped ZnS nanoparticles in aqueous medium in an air atmosphere without using any complicate or high cost instrument.
- To select the optimum concentration of doping ion in ZnS i.e., Cu\textsuperscript{2+} ion.
- To reduce the particles size and increase the monodisperse using three different polymers.
- To characterize optical and thermal properties using different techniques.