CHAPTER I

INTRODUCTION TO

NANOSCIENCE AND BRIEF REVIEW OF LITERATURE

ABSTRACT

A brief introduction of nanoscience and nanotechnology, nanoparticles, quantum confinement effect, various properties, techniques for synthesis of nanoparticles, core-shell nanocomposites, importance of core-shell nanocomposites, applications for core-shell nanocomposites and selected material for this work ZnO, ZnS, CdS and available methods of synthesis are explained in detailed manner. The study and characterization of core-shell nanocomposites using various techniques by different workers with the help of available/accessible literature are presented. The objective of the present study is outlined.
CHAPTER I

INTRODUCTION

1.1 NANOSCIENCE AND NANOTECHNOLOGY

1.1.1 Introduction

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale. Thus, it is the science and technology of small things, in particular things that are less than 100nm in size and are termed as nanomaterials.

Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale (Shah and Tokeer Ahmad, 2010). In recent years nanotechnology has become one of the most important and exiting forefront fields in physics, chemistry, biology and engineering and technology The importance was emerged from Richard Feynman’s famous talk “There is plenty of room at the bottom” in 1959 at the annual meeting of the American Physical Society, where he addressed about manipulating things on a small scale (Feynman, 1960). His envision led to the development of nanotechnology.

The term nanotechnology was coined by Professor Taniguchi, Tokyo Science University in 1974 and was popularized in mid 80’s by Dr. K. Eric Drexler, through his books Engines of Creation: The Coming Era of Nanotechnology and Nanosystems: Molecular Machinery, Manufacturing, and Computation (Eric, 1986).

Term ‘Nano’ can be traced to a Greek root which means dwarf. On the length scale, nano is one billionth of a meter. The use of nanomaterials is documented from the times of Romans. Some of the examples that show use of nanoparticles are the Lycurgus Cup, which consists of gold and silver alloy nanoparticles (Freestone, 2007) and the ‘Damascus Sword’ containing the nanoscale carbon particles (Verhoeven et al., 1998) etc (Figure 1.1) Michael Faraday had demonstrated the synthesis of gold nanoparticles in 1857 in his paper titled ‘Experimental relations of gold (and other metals) to light’ published in Philosophical Transactions
(Thompson, 2007). But in last few decades this field has scaled new heights for many reasons including invention of revolutionary imaging methods and techniques that made the characterization of the materials at nanoscale very easy.

**Figure. 1.1 Examples of use of nanomaterials in ancient times.**

(A) The Lycurgus Cup, (B) The Damascus Sword and (C) The gold colloids prepared by Michael Faraday

(The pictures are taken from ref 3, 4 and 5)

One of the basic results of the materials science is the insight that most properties of solids depend on the microstructure. A reduction in the spatial dimension, or confinement of particles or quasi-particles in a particular crystallographic direction within a structure generally leads to changes in physical properties of the system in that direction. Hence the another classification of nanostructured materials and systems essentially depends on the number of dimensions which lie within the nanometer range. It is represented in figure 1.2; (a) 3D-systems confined in three dimensions, e.g. structures typically composed of consolidated equiaxed crystallites; (b) 2D-systems confined in two dimensions, e.g. filamentary structures where the length is substantially greater than the cross-sectional dimensions; (c) 1D-systems confined in one dimension, e.g. layered or laminate structures; (d) 0D-zero-dimensional structures, e.g. nano-pores and nano-particles.

The most well-known example of the correlation between the atomic structure and the properties of a bulk material is probably the spectacular variation in the hardness of carbon when it transforms from diamond to graphite. Comparable variations have been noted if the atomic structure
Figure 1.2 Schematic classification of nano – materials
(a) three – dimensional, (b) two – dimensional,
(c) one – dimensional and (d) zero – dimensional structures.

of a solid deviates far from equilibrium or if its size is reduced to a few interatomic spacing. An example of the latter case is the change in color of CdS crystals if their size is reduced to a few nano-meters. Figure 1.3 gives a partial list of zero-dimensional nanostructures with their typical ranges of dimensions (Microscopy and Histology Catalogue, 1993 and Itoh, 2003). One nanometer is approximately the length equivalent to 10 hydrogen or 5 silicon atoms aligned in a line. Small features permit more functionality in a given space, but nanotechnology is not only a simple continuation of miniaturization from micron meter scale to nanometer scale.

Figure 1.3 Examples of zero-dimensional nanostructures or nanomaterials with their typical ranges of dimension
Materials in the micrometer scale mostly exhibit physical properties the same as that of bulk form; however, materials in the nanometer scale may exhibit physical properties distinctively different from that of bulk. Materials in this size range exhibit some remarkable specific properties; a transition from atoms or molecules to bulk form takes place in this size range. For example, crystals in the nanometer scale have a low melting point (the difference can be as large as 1000°C) and reduced lattice constants, since the number of surface atoms or ions becomes a significant fraction of the total number of atoms or ions and the surface energy plays a significant role in the thermal stability.

Crystal structures stable at elevated temperatures are stable at much lower temperatures in nanometer sizes, so ferroelectrics and ferromagnetics may lose their ferroelectricity and ferromagnetism when the materials are shrunk to the nanometer scale. Bulk semiconductors become insulators when the characteristic dimension is sufficiently small (in a couple of nanometers). Although bulk gold does not exhibit catalytic properties, Au nanocrystal demonstrates to be an excellent low temperature catalyst. In general, nanotechnology can be understood as a technology of design, fabrication and applications of nanostructures and nanomaterials. In the United States, nanotechnology has been defined as being “concerned with materials and systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size” (http://www.nano.gov, 2000).

In order to explore novel physical properties and phenomena and realize potential applications of nanostructures and nanomaterials, the ability to fabricate and process nanomaterials and nanostructures is the first cornerstone in nanotechnology. Nanostructured materials are those with at least one dimension falling in nanometer scale, and include nanoparticles (including quantum dots, when exhibiting quantum effects), nanorods and nanowires, thin films, and bulk materials made of nanoscale building blocks or consisting of nanoscale structures.
1.1.2 Technology

Many technologies have been explored to fabricate nanostructures and nanomaterials. These technical approaches can be group different fabrication and processing techniques such as top-down and bottom-up approaches, spontaneous and forced processes.

1.1.2.1 Top down approaches

In top-down method the large scale object or patterns are gradually reduces its dimensions. This can be accomplished by a technique called lithography. In which a bulk material is selectively degraded to produce smaller, often patterned, features. For example, in the case of microlithography, light is shone through a mask to selectively etch either a positive or a negative pattern into a surface, yielding the desired microscopic topography. Size reductions to nanolithography are driven in large part by the computer industry, responding to the demand for smaller resistors and stronger computing power. To reach feature sizes <100 nm, researchers rely on shorter wavelengths of light, or even e-beam lithographic techniques. Top down processing can also be generated through selective chemical etching, although this relies much more on the initial properties of the bulk material. This approach is shown in figure 1.4.

1.1.2.2 Bottom up approaches

In bottom up methods, the atoms and molecules are assembled into the smallest nanostructures (dimensions of typically 2 to 10 nm) by carefully controlled chemical reactions, which make this technique cheaper as compared to the lithographical methods (Figure 1.4). Self-assembly of atoms and molecules into nanostructures can be classified as a bottom up method. In nature, self assembly is often used to make complex structures. At present, the mastery of self-assembly is limited to relatively simple systems. To achieve complex systems hierarchical self assembly can assist, where the products of one self-assembly step is a base for the next one. The formation of self-assembled mono layers (SAMs), that are produced when a substance spontaneously forms a molecular monolayer on a surface, could be successfully combined with
standard lithographical methods to achieve large-scale and better controlled structures. In one type of bottom up synthesis, individual molecules are triggered to self-assemble into larger objects with nanoscale dimension.

The formation of micelles from individual charged lipids is a classic example of this method. In such systems, aggregate shape and size are pre-programmed through the specific features of the component molecules, often through the inclusion of selectively compatible and incompatible components. When we deliberately create molecules with such opposing segments (e.g. hydrophilic and hydrophobic; rigid and flexible; directional hydrogen-bonding or π–π stacking; etc.), multiple molecules are forced to reduce their entropic/enthalpy balance through aggregation.

![Figure.1.4 Schematic of top-down and bottom-up fabrication process, showing removal and addition of material to reach final structure](image)

Substantial advances have been made in this field of “supramolecular self-assembly” over the past 30 years, and researchers have a continual eye on advances in understanding nature’s own methods for assembling proteins, nucleic acids, and other biomolecules. Bottom up methods are also used, for instance, for the fabrication of carbon nanotubes (CNT) and nanoparticles.
1.2 NANOMATERIALS

Nanomaterials or nanophase materials are the materials which are made of grains that are about 100 nm in diameter and contain less than few ten thousands of atoms. Nanocrystals are crystalline clusters of a few hundred to a few thousand atoms with sizes of a few nanometres, although more complex than individual atoms. Their properties are different from bulk crystals. Due to their small size, much of their chemical and physical properties are dominated by their surfaces and not by their bulk volume (Alivisatos, 1997). Nanocrystals can be synthesized from metallic materials such as gold (Brust et al., 1995 and Brown et al., 1999), silver (Quaroni et al., 1999 and Rivas et al., 2001) or cobalt (Ershov, et al., 2000 and Puntes et al., 2001), from semiconductor materials such as cadmium sulphide (Murray et al., 1993 and Merkoçi et al., 2006), cadmium selenide (Steigerwald et al., 1990 and Colvin et al., 1990), cadmium telluride (Eychnmüller et al., 2000 and Talapin et al., 2001), gallium arsenide (Olshavsky et al., 1990) or indium phosphide (Guzelian et al., 1996 and Micic et al., 1997), and from insulators such as iron oxide (Rockenberger et al., 1999 and Santra et al., 2001) or titanium oxide (Trentler et al., 1999).

Three properties are important for the quality of colloidal nanocrystals. Firstly, nanocrystals obviously should be crystalline and thus preferentially consist of only one domain. Secondly, their size distribution should be as narrow as possible and the third part, there should be a unique, uniform shape to nanocrystals in a particular sample. Colloidal nanocrystals are dispersed in a solvent and should be stabilized in a way that prevents agglomeration. Besides spherical nanocrystals, more complex geometries such as rods (Peng et al., 2000 and Jana et al., 2001), prisms (Jin et al., 2001) and tetra pods (Manna et al., 2000) can be synthesized in a controlled way.

1.3 PROPERTIES OF NANOMATERIALS

Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most micro structured materials have similar properties to the corresponding bulk materials, the properties of
materials with nanometer dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials. Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable to length, the entire material will be affected by the surface properties of nanomaterials. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum effects. The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic and optical properties of the materials. For example, lasers and light emitting diodes (LED) from both of the quantum dots and quantum wires are very promising in the future optoelectronics. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are also an important factor in determination of the properties of the nanomaterials.

Nanosturctures and Nanomaterials favours of a self purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, the mechanical properties of nanomaterials will be better than the bulk materials. The superior mechanical properties of carbon nanotubes are well known. Due to their nanometer size, nanomaterials are already known to have many novel properties. Many novel applications of the nanomaterials rose from these novel properties have also been proposed.
1.3.1 Surface to Volume Ratio

Figure 1.5 shows nanomaterials have an increased surface to volume ratio compared to bulk materials. This means that for a given total volume, the external surface is greater if it is made of an ensemble of nanomaterial sub-units rather than of bulk. The increased surface to volume of nanomaterials impacts the material physical properties such as its melting and boiling points, as well as its chemical reactivity. Reactions that occur at material surface are particularly affected such as catalysis reactions, detection reactions and reactions that require the adsorption of certain species at the material surface to initiate.

Figure 1.5 Schematic drawing showing how surface to volume increases when moving from bulk material to nano-sized particle

1.3.2 Quantum Confinement Effect

According to band theory, the solid atoms have energy bands and isolated atoms possess discrete energy levels. Nano materials are the intermediate state to solids and atoms. When the material size is reduced to nanoscale, the energy levels of electrons change. This effect is called quantum confinement effect. This affects the optical, electrical and magnetic properties of nanomaterials. An example of quantum effect in nanosized particle is colour. The gold in a ring is notably yellow, but if gold is shrunk to a nanoparticle (10 nm to 100 nm in size) it becomes red. Moreover, nanoparticles emit a specific colour depending on their nanometer size. Nanocrystals of materials with larger band gaps produce green or blue emission while low band gap materials emit red colour.
1.3.3 Exciton

The concept of excitons was first proposed by Yakov Frenkel in 1931 (Frenkel, 1931), when he described the excitation of atoms in a lattice of insulators. He proposed that this excited state would be able to travel in a particle-like fashion through the lattice without the net transfer of charge. An exciton can form when a photon is absorbed by a semiconductor. This excites an electron from the valence band into the conduction band. In turn, this leaves behind a positively-charged electron hole (an abstraction for the location from which an electron was moved). The electron in the conduction band is then attracted to this localized hole by the Coulomb force. This attraction provides a stabilizing energy balance. Consequently, the exciton has slightly less energy than the unbound electron and hole. The wave function of the bound state is said to be hydrogenic, an exotic atom state akin to that of a hydrogen atom. However, the binding energy is much smaller and the particle's size much larger than a hydrogen atom. This is because of both the screening of the Coulomb force by other electrons in the semiconductor (i.e., its dielectric constant), and the small effective masses of the excited electron and hole.

1.3.4 Quantum Dots

Colloidal semiconductor nanocrystals, which are also called quantum dots (QDs), consist of 1-10 nm diameter semiconductor nanoparticles that have organic ligands bound to their surface. Quantum dots are popular alternatives to organic dyes as fluorescent labels for biological imaging and sensing due to their small size, tuneable emission and photostability. Figure 1.6 shows an energy level diagram of bulk semiconductor, quantum dot and molecule. The luminescent properties of quantum dots arise from exciton decay (recombination of electron hole pairs) which can proceed through a radiative or nonradiative pathway. The radiative pathway involves electrons relaxing from the conduction band to the valence band by emitting photons with wavelengths corresponding to the semiconductor's band gap.
Nonradiative recombination can occur through energy release via phonon emission or auger recombination. In this size regime, quantum confinement effects lead to a size dependent increasing bandgap with observable, quantized energy levels (Reiss et al., 2009). The quantized energy levels observed in quantum dots lead to electronic structures that are intermediate between single molecules which have a single HOMO-LUMO gap and bulk semiconductors which have continuous energy levels within bands (Murphy et al., 2002).

1.3.5 Optical properties

One of the most fascinating and useful aspects of nanomaterials is their optical properties. The significant reduction in the size of materials affects the optical properties. The change in optical properties is caused by two factors, the quantum confinement of electrons within nanoparticles and the plasma resonance. Surface Plasmons (SP) are the origin of the color of nanomaterials. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photoelectrochemistry and biomedicine. The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including
doping and interaction with the surrounding environment or other nanostructures. Likewise, shape can have dramatic influence on optical properties of metal nanostructures.

1.3.6 Electrical Properties

Nanomaterials can hold considerably more energy than conventional because of their large grain boundary (surface) area. They are materials in which an optical absorption band can be introduced, or an existing band can be altered by the passage of current through these materials. Nanocrystalline materials are good candidates for separator plates in batteries because they can hold considerably more energy than conventional ones. Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydrides are envisioned to require far less frequent recharging and to last much longer. As the size is reduced from the bulk, the electronic bands in metals become narrower and the delocalized electronic states are transformed to more localized molecular bonds. At the nanoscale, electrical properties are not necessarily the same as they are on the macroscale. Materials that are conductors on the macroscale may lose their conductivity at the nanoscale and vice versa. For instance, when an insulator becomes thin enough, it can be rendered conductive through a process called quantum tunnelling, a non-classical effect that is only observed at the nanoscale or smaller scale.

1.3.7 Mechanical Properties

Due to the nanometer size, many of the mechanical properties of the nanomaterials are modified to be different from the bulk materials including the hardness, elastic modulus, fracture toughness, scratch resistance and fatigue strength etc. An enhancement of mechanical properties of nanomaterials can result due to these modifications, which are generally resulting from structural perfection of the materials (Cao, 2004 and Herring and Galt, 1952). The small size either renders them free of internal structural imperfections such as dislocations, micro twins, and impurity precipitates or the few defects or impurities present cannot multiply sufficiently to cause mechanical failure. The imperfections within the nano dimension are highly energetic and will migrate to the surface to relax themselves under annealing, purifying the material and leaving.
perfect material structures inside the nanomaterials. Moreover, the external surfaces of nanomaterials also have less or free of defects compared to bulk materials, serving to enhance the mechanical properties of nanomaterials.

The enhanced mechanical properties of the nanomaterials could have many potential applications both in nano scale such as mechanical nano resonators, mass sensors, microscope probe tips and nano tweezers for nano scale object manipulation, and in macro scale applications structural reinforcement of polymer materials, light weight high strength materials, flexible conductive coatings, wear resistance coatings, tougher and harder cutting tools etc. Among many of the novel mechanical properties of nanomaterials, high hardness has been discovered from many nanomaterials system.

1.4 STABILIZATION OF NANOPARTICLES

Stability is one important factor that determines the application potential of the nanoparticles. Stability of nanoparticles especially as dispersion can be achieved by two methods.

a) Electrostatic repulsion.

b) Steric repulsion (using ligand/surfactants).

1.4.1 Electrostatic interaction

In metals, especially noble metals, stabilization of nanoparticles can occur through two modes: electrostatic repulsion and steric repulsion. In the first scenario, subsequent to their reductive preparation, the particles are surrounded by an electric double layer arising due to adsorption of reactant ions on the surface of nanoparticles. This results in two forces acting on nanoparticles, 1) Van der Waals force of attraction between metal cores and, 2) electrostatic force of repulsion (potential energy) due to charged ions on the surface. Stability of nanoparticles is dependent on the combination of these two forces. Figure 1.7 shows graph of potential energy versus distance from the surface of spherical particle. At a distance far from the surface, both Van der Waals attraction potential and
electrostatic repulsion potential is zero. Near the surface, a minimum is observed in potential energy due to Van der Waals attraction.

![Scheme illustration of stabilization of nanoparticles via electrostatic interaction](image)

**Figure 1.7  Scheme illustration of stabilization of nanoparticles via electrostatic interaction**

At a distance not very far away from the surface where electric repulsion dominates the Van der Waal’s attraction potential and the combination of these two opposing forces leads to a maximum in the energy curve. This maximum is known as repulsive barrier. If the barrier is greater than certain value, two particles cannot overcome the barrier and thus agglomeration is prevented (Cao, 2004 and Bonnemann et al., 2001). Electrostatic stabilization is kinetic stabilization process and it is useful only in the case of dilute solutions. Addition of electrolytes screens the double layer charge leading to aggregation. As can be noticed, such stabilization occurring due to electronic repulsion is highly dependent on several factors and the ideal condition for most stable dispersion can be achieved in a very narrow window.

### 1.4.2 Stabilization of nanoparticles using ligands/surfactants

Figure 1.8 indicates steric stabilization of metal nanoparticles. Steric stabilization of nanoparticles can be achieved by co-ordination of organic molecules on the surface of nanoparticles, which act as capping ligands. In this way nanoparticle cores are separated from each other and agglomeration is prevented. In case of metal nanoparticles system, ligands
that are commonly used as stabilizing agent include thiols, amines, silane, phosphines, carboxylic acid (especially for transition metals) etc.

**Figure 1.8 Steric Stabilization of metal nanoparticles**

**1.5 CORE-SHELL SEMICONDUCTING NANOCRYSTALS**

Core-shell semiconducting nanocrystals (CSSNCs) are a class of materials which have properties intermediate between those of small, individual molecules and those of bulk, crystalline semiconductors. They are unique because of their easily modular properties, which are a result of their size. These nanocrystals are composed of a quantum dot core and a shell of a distinct semiconducting material. It is shows in figure 1.9.

**Figure 1.9 Schematic diagram of Core-Shell system**
The core and the shell are typically composed of type II–VI, IV–VI, and III–V semiconductors, with configurations such as CdS/ZnS, CdSe/ZnS, CdSe/CdS, and InAs/CdSe (typical notation is: core/shell) (Loukanov et al., 2004).

1.6 IMPORTANCE OF CORE/SHELL NANOPARTICLES

Core/shell nanoparticles are gradually attracting more and more attention, since these nanoparticles have emerged at the frontier between materials chemistry and many other fields, such as electronics, biomedical, pharmaceutical, optics, and catalysis. Core/shell nanoparticles are highly functional materials with modified properties. Sometimes properties arising from either core or shell materials can be quite different. The properties can be modified by changing either the constituting materials or the core to shell ratio. Because of the shell material coating, the properties of the core particle such as reactivity decrease or thermal stability can be modified, so that the overall particle stability and dispersibility of the core particle increases. Ultimately, particles show distinctive properties of the different materials employed together. This is especially true of the inherent ability to manipulate the surface functions to meet the diverse application requirements (Daniel et al., 2004 and Caruso, 2001). Core/shell nanoparticles are also used to enhance the adsorption capacity for environmental remediation applications. An example is the Fe$_2$O$_3$ coating on MgO and CaO nanoparticles, which can enhance the adsorption capability of toxic materials, such as SO$_2$ and H$_2$S, from the environment compared with that of pure MgO and CaO (Carnes et al., 2002 and Decker et al., 1996).

1.7 APPLICATIONS

One of the most important properties of core-shell semiconducting nanocrystals (CSSNCs) is that their cores, which are quantum dots, fluoresce, which is important in their biomedical and optical applications. The shells are highly modular, and thus the bulk properties, such as solubility and activity of the CSSNCs can be changed.
1.7.1 Optical Applications

The size, shape, and composition of the core-shell structure are related to the band gap, which in turn is related to its optical properties. Thus, by modulating the size, shape, and material of the core, the optics can be tuned and optimized for use in optical devices and applications such as LEDs, detectors, lasers, phosphors, and photovoltaic’s.

1.7.2 LEDs

An advantage of CSSNC LEDs over organic LEDs is that CSSNC LEDs have narrower emissions, as narrow as 32 nm, than organic LEDs, which range from 50-100 nm (Coe et al., 2002). Specifically, the core-shell motif is desirable for use in LEDs because of their electroluminescence and photoluminescence quantum efficiencies and their ability to be processed into devices easily.

Current aims for LED displays include developing materials with wavelength emissions of 610–620 nm for red displays, 525–530 nm for green displays, and 460–470 nm for blue displays. This is because these wavelengths maximize the perceived power and they lie outside of the National Television System Committee standard colour triangle. CSSNCs have been synthesized that meet these wavelength emissions: (CdSe) ZnS for red emission, (CdS)ZnS for blue emission, and (Cd\textsubscript{x}Zn\textsubscript{1-x}Se)Cd\textsubscript{y}Zn\textsubscript{1-y}S for the green emission (Steckel et al., 2006). Using CdSe core and ZnS or CdS/ZnS shells, the maximum luminance values of red, orange, yellow, and green LEDs were improved to 9,064, 3,200, 4,470 and 3,700 cd m\textsuperscript{-2}, respectively; electroluminescent efficiency (1.1–2.8 cd A\textsuperscript{-2}), and turn-on voltages (3–4 V) were also increased (Sun et al., 2007).

1.7.3 Lasers

In CSSNCs with only one exciton, absorption and stimulated emission occur equally. In CSSNCs with more than one exciton, non-radiative Auger recombination occurs, which decays optical gain, an important quality in lasers. However, type II CSSNCs, CdS/ZnSe, were used in optical amplification from stimulated emission of single-exciton states, eliminating Auger recombination. This has the advantage that lasing threshold could be lowered under continuous wave excitation, enhancing the potential of CSSNCs as optical gain media. Type II CSSNCs
separate the electrons and holes of the exciton pair, which leads to a strong electric field and thus, reducing absorption losses (Klimov et al., 2007).

1.7.4 Phosphors

By combining the modularity of CSSNCs and stability of organic polymer, a broad range of colours of phosphors were developed. CdSe core/ZnS shell are used to generate bluish green to red colours, and (CdS)/ZnS quantum dots are used to generate violet to blue colours. By mixing the appropriate amounts of the different sizes of CSSNCs, the entire visible range with narrow emission profiles and high photoluminescence quantum yields can be achieved (Lee et al., 2000).

1.8 ELECTRONIC APPLICATIONS

Core/shell nanoparticles with either core or shell made of a semiconductor or a metal are equally important in the electronics field. Polymeric materials are easy to process, but these materials have low dielectric constant. On the other hand, ceramic materials have high dielectric constants but are more difficult to process. Interestingly, a combination of these two materials in the form of core/shell with ceramic core and a thin polymer shell increases the dielectric constant compared with the pure polymer. At the same time, it renders them more easily processable. Because of their high capacitance, these materials are used in electronics (Maliakal et al., 2005 and White et al., 2008). Silica shells are used to modulate the position and intensity of the colloidal metal surface Plasmon adsorption band (Ung et al., 1998).

1.9 CATALYTIC APPLICATIONS

Nanosized metal oxides (MgO, CaO) have destructive adsorption capacity of halogenated hydrocarbons and organo-phosphorous compounds but a coating of a transition metal oxide [Fe$_2$O$_3$, V$_2$O$_5$] (Schneider, 2001) onto the original metal oxide increases the destructive adsorption capacity several fold. Similarly, the catalytic conversion of CO to CO$_2$ by Fe$_2$O$_3$-coated Au nanoparticles supported on SiO$_2$ was studied by Yin et al (Yin et al., 2011). Their results showed that the conversion
efficiency is more than that for Au alone supported on SiO$_2$. They also found that the efficiency increases with preheating of the catalyst but that excess heating can decrease the efficiency mainly because of the increase in percentage of Au metal and crystalline nature of the Fe$_2$O$_3$.

Carbon-coated Fe$_3$O$_4$ is used for the solid phase extraction of polycyclic aromatic hydrocarbons from environmental water samples. The main application of the carbon coating on the metal or metal oxide nanoparticles is to increase the core particle stability with a subsequent increase in catalytic properties, biocompatibility, and no toxicity (Yu et al., 2010, Wang et al., 2010 and Galakhov et al., 2010).

1.10 BIOMEDICAL APPLICATIONS

1.10.1 Controlled Drug Delivery and Specific Targeting

Core/shell nanoparticles have many potential and exciting applications in the biomedical field. Although more than a decade some applications have already been developed there are major applications still at the innovation stage. In the biomedical field, core/shell nanoparticles are mainly used for controlled drug delivery, bio imaging, cell labelling, as biosensors and in tissue engineering applications etc. Recently, the performance of drug delivery systems has improved enormously because of the development of controlled release of drugs over the more traditional uncontrolled release. Advances in this area have become easier and more precise because of nanotechnology developments. Simultaneously, very specific drug delivery is now possible to a particular location inside the body or to an organ in what is called “targeted delivery”. There are two approaches used for drug controlled delivery purposes, (i) active and (ii) passive targeting. Active targeting is a more specific targeting with customized ligands attached to the drug-encapsulating nanoparticles, which can be selectively adsorbed by the target cell receptors. For example, folic acid or methotrexate are selectively used for cancer cell therapies because cancer cells have folate receptors (De et al., 2008, Landmark et al., 2008) that are over expressed on the cell surface. However, in the case of passive targeting, the encapsulated drugs target the body with appropriate surface modification so that they selectively
accumulate with the targeted cells due to physicochemical or pharmacological factors (Vasir et al., 2005 and Torchilin, 2010).

1.10.2 Bio imaging

Different types of molecular imaging techniques, such as optical imaging (OI), magnetic resonance imaging (MRI), ultrasound imaging, positron emission tomography and others are used for the imaging of both in vivo and in vitro biological specimens. However, optical and magnetic resonance imaging techniques are the most acceptable because they utilize the inherent luminescent and magnetic properties of the nanoparticles. The two principal types of nanoparticles that have been used for imaging in vivo systems are luminescent nanoprobes for optical imaging and magnetic nanoparticles for magnetic resonance imaging. Normally, quantum dots (QDs) and dye-doped QDs are used for optical imaging purposes. Kircher et al., 2003 reported an MRI study for brain tumour cells of rats using Cy5.5 CLIO, which contains Fe nanoparticles. Au/Ag core/shell nanocomposite particles are used for sensing cancer and tumour cells in the body (Lee et al., 2008). Fe/Fe₂O₃ core/shell nanoparticles are selectively used for the detection of damaged DNA (Wang et al., 2009). Polymeric core/shell nanoparticles are commonly used as transplant materials. These can be either polymer/polymer or polymer/metallic material forming core/shell structures. They are used in dental braces and in joint replacements (Katti, 2004). Ultrahigh molecular weight polyethylene (UHMWPE)/silver, is one such material used in joint replacement (Morley et al., 2007).

Core/shell nanoparticles consisting of polymers, bio ceramics, and other inorganic materials appear to be better materials for joint replacement and bone regeneration because of superior mechanical properties, improved durability, and surface bioactivity compared with conventional polymers or composites.

Based on the various applications of core shell nanocomposites, the present study is aimed to improve the property of core shell nanocomposites by the way synthesizing the multi shell coated nanocomposites. For this, ZnO, ZnS and CdS were selected.
1.11 ZINC OXIDE (ZnO)

Zinc oxide (ZnO) is rapidly gaining credibility as a material with excellent possibilities. It is regarded as the key technological material, which exhibits semiconducting, piezoelectric and pyroelectric multiple properties. It is an inorganic compound with the formula ZnO. Zinc oxide crystallizes in two main forms, hexagonal wurtzite and cubic zincblende. The wurtzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. ZnO is a white powder that is insoluble in water. It is an n-type II-VI semiconductor with a direct wide-bandgap of about 3.37 eV at room temperature and a large exciton binding energy (60meV) (Norton et al., 2004).

ZnO displays multiple functions in electrical, piezoelectric and optical properties(Zhang et al., 2005). 1D ZnO with a large surface area and quantum confinement effect has stimulated much attention (Chen et al., 2009 and Zhang et al., 2009) owing to its potential applications in light emitting diodes (Sun et al., 2009), field effect transistors (Kim et al., 2006), solar cells (Zhang et al., 2009), chemical sensors (Ahn et al., 2009) and catalysts (Bae et al., 2009). Specifically, ZnO absorbs UV radiation due to transitions between conduction and valence bands (Subramanyam et al., 2000), it is expected as an excellent transparent conducting electrode in solar cells, flat panel displays, and as a window material in anti-reflection coatings and optical filters. ZnO nanostructures have also been used as a gas sensor (Gaskov et al., 2001 and Suchea et al., 2005) due to its conductivity changes upon exposure to gases such as H$_2$ and ozone with a relatively high sensitivity.

1.11.1 Properties of Zinc Oxide (ZnO)

Spherical shape of ZnO nanocrystals has a very large exciton binding energy (~ 60 meV), which results in more efficient excitonic emission at room temperature. Its elastic constants are smaller than those of relevant III-V semiconductors, such as GaN. The hollow sphere ZnO nanocrystals are a relatively soft material with approximate hardness of 4.5 on the Mohs scale. The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of ZnO are beneficial for
ceramics. Zinc Oxide exhibits semiconducting, piezoelectric and pyroelectric multiple properties.

1.12 ZINC SULFIDE (ZnS)

Zinc sulfide (ZnS) is one of the first semiconductors discovered and it has traditionally shown remarkable fundamental properties versatility and a promise for novel diverse applications. ZnS has two commonly available allotropes: one with a cubic zinc blende (ZB) structure and another one with a hexagonal wurtzite (WZ) structure. The cubic form is the stable low-temperature phase, while the latter is the high-temperature polymorph which forms at around 1296 K (Yeh et al., 1992). ZnS has a larger band gap of 3.72 eV and 3.77 eV (for cubic zinc blende (ZB) and hexagonal wurtzite (WZ) ZnS, respectively). Its atomic structure and chemical properties are comparable to more popular and widely known ZnO. ZnS is traditionally the most suitable candidate for electroluminescence devices. It is used as a key material for light-emitting diodes (LEDs), flat panel displays, infrared windows, sensors, lasers and bio devices. Zinc sulfide is also used as an infrared optical material, transmitting from visible wavelengths to just over 12 micrometers. It can be used planar as an optical window or shaped into a lens. ZnS is also an important phosphor host lattice material used in electroluminescent devices (ELD), because of the band gap large enough to emit visible light without absorption and the efficient transport of high energy electrons.

1.12.1 Properties of Zinc Sulfide (ZnS)

Zinc Sulfide is a direct-transition semiconductor with the widest energy band gap among the groups II-VI compound semiconductor materials, the most striking feature of ZnS nanocrystallites is that their chemical and physical properties differ dramatically from those of the bulk solids. As a nontoxic II-VI semiconductor material, ZnS spherical nanocrystals are chemically more stable and technologically better than other semiconductor materials such as ZnSe. It is considered to be a promising host material. The hollow ZnS spheres can be doped as either an n-type semiconductor or a p-type semiconductor.
1.13 CADMIUM SULPHIDE (CdS)

Cadmium sulphide (CdS) is a brilliant II–IV wide band semiconductor with direct band gap of 2.42 eV at room temperature with many outstanding physical and chemical properties, which has promising applications in multiple technical fields including photo-chemical catalysis, gas sensor, detectors for laser and infrared, nonlinear optical materials and various luminescence devices (El-bially et al., 2012, Dumbrava et al., 2010 and Rao et al., 2011).

In particular, CdS has been extensively studied because of its large value of band gap ($E_g$), which allows light emission between blue and red wavelengths. Due to the large band gap of CdS nanoparticles, it is used as window material in hetero junction solar cells (Romeo et al., 2004). In p–n junction solar cells CdS is used as n-type material along with p-type materials like gallium arsenide, indium phosphide and cadmium telluride (Nelson, 2003). CdS can be doped with B, Al, Ga and In to get n-type conductivity or with Cu, Ag and Au to obtain p-type conductivity.

CdS has three types of crystal structures namely hexagonal wurtzite, cubic zinc blend and high pressure rock-salt phase. Among these the hexagonal wurtzite has been intensively investigated because it is the most stable of the three phases and can be easily synthesized. Hexagonal phase has been observed in both the bulk and nanocrystalline CdS while cubic and rock-salt phases are observed only in nanocrystalline CdS (Banerjee et al., 2000).

1.13.1 Properties of Cadmium Sulphide (CdS)

Cadmium sulphide is a direct band gap semiconductor (2.42 eV). The conductivity of spherical CdS nanocrystals increases when irradiated with light. This property leads to use as photoresistor. When combined with a p-type semiconductor it forms the core component of a photovoltaic (solar) cell. It exhibit both piezoelectric and pyroelectric nature. It has a strong visible-light absorption and emission property. Hollow sphere CdS nanocrystals have lower crystallization temperature and shorter crystallization time.
1.14 MULTI SHELL NANOCOMPOSITES

Nanocomposites are advantageous because they can compensate for the disadvantages of the individual component, and induce a synergistic effect, such as an efficient charge separation and improvement of photostability.

The main advantages of multilayer semiconductor nanoparticles are higher quantum yield, higher photoluminescence efficiency, improved optical properties, increased half-life times of the semiconductor materials, easy detection of emission spectra because they are shifted toward higher wavelength in the visible range, photo-oxidation stability, improved appropriate electronic properties (band gap, band alignment), and finally better structural (lattice mismatch) properties than unlayered CS particles. The advantage of lattice mismatch between the core and shell material is that the shell can grow to a significant thickness without losing its luminescence properties. Over the past few years, researchers have concentrated mainly on this type of particle because of their exciting applications.

Rodríguez et al., (2005) showed that for multishell bimetallic nanoparticles, the final shape depends on the selection of the core metal. For Au Ag bimetallic multishell nanoparticles, the deposition of Ag on Au generates a pseudo spherical geometry. However, deposition of Au on Ag leads to the preferential formation of polygonal particles with sharp facet intersections.

The optical properties also change with the shell coating as shown in Figure 1.10. To begin, the gold colloid colour was deep red; upon deposition of a silver shell, it turned yellow, a second gold shell led to a blue hue. Finally, after deposition of the second silver shell, an orange colour was obtained.

Archana Maurya and Pratima Chauhan (2011) demonstrated the detailed study of the structural and optical properties of pure TiO$_2$ and that of CdS/TiO$_2$ composite nanoparticles.

CdS/TiO$_2$ nanocomposites were prepared by a simple Co-precipitation method. They reported that the composite sample is more conductive than TiO$_2$. Electrical and optical properties of CdS/TiO$_2$
nanocomposite reveals that sample could have its major application in white light nanodevices such as light emitting diodes (LEDs) and photocatalysis.

Meiying Ge et al., (2011) described the tunable CdS and ZnS shells by facile thermolysis of air-stable cadmium ethylxanthate \((\text{Cd(ex})_2\) and zinc ethylxanthate \((\text{Zn(ex})_2\) precursors for CdSe/CdS/ZnS core/shell nanocrystals (CCZ NCs). They reported the growth dynamical studies and the evolution details of red/blue-shift in the capping of CdS and ZnS layers on nanocrystals by the use of ethylxanthate precursors.

Figure 1.10 Colour changes in colloidal dispersion of Au/Ag nanoparticles with increasing number of layers

Geeta Rani and Sahare (2012) were successfully fabricated short length ZnO nanorods and ZnO@ZnS core–shell nanostructures by sulfidation of ZnO nanorods via a facile chemical synthesis. The study revealed that the products have two phases of ZnO and ZnS. The Nanorods share the characteristics of both ZnO and ZnS. They reported that the bare ZnO nanorods show no absorption in the visible region. A significant red shift in the absorption edge is observed in the UV-Vis spectra of the ZnO/ZnS core/shell nanorods because of deposition of the ZnS, and the photo absorption in the visible region at the range of 400–700 nm was obviously enhanced. The optical band gap was found to be increased with increasing sulfidation process. They also reported the following points.
The PL spectra of ZnO@ZnS core–shell nanostructure showed an enhanced broad blue emission and a disappeared orange emission, comparing to that of pure ZnO nanorods. The enhancement in blue emission could be explained as that ZnS nanoparticle has a higher band gap than ZnO and then it suppressed the tunnelling of the charge carriers from the cores to the ZnS nanoshell. As a result, more photo generated electrons and holes were confined inside the ZnO core, giving rise to a high quantum yield. The strongest blue emission of ZnO@ZnS core–shell in the range of 400–650 nm was supposed to origin from the synergic interactions of ZnO core and ZnS nanoshell. The broad blue emission and a passivated orange emission provides a good indication of tuning the visible emission of the core–shell nanostructures so, this is a promising material applied in the fabrication of nanoscale optical devices. The measurement of luminescence revealed that ZnO@ZnS core–shell structure integrated the luminescent effect of ZnO and ZnS.

Wang et al., (2009) prepared ZnO-ZnS-CdS heterostructures by a wet chemistry method. They reported the following points. The photo excited electrons in the ZnO-ZnS-CdS heterostructures have a much longer lifetime (>225 ns) than that of the sole ZnO, ZnS and CdS (<65 ns). The greatly prolonged lifetime of charge carriers in the hetrostructure is contributed to the improved photo catalytic H₂ evolution. It was found that ZnO-ZnS-CdS heterostructures are highly active photocatalysts for H₂ evolution under simulated solar light irradiation in an aqueous solution containing So₃²- and S²- ions as sacrificial reagents.

1.15 METHODS OF SYNTHESIS OF MULTI SHELL COATED NANOCOMPOSITES

Nowadays, the attention of many scientists is focused on the development of new methods for synthesis and stabilization of multi shell coated nanocomposites. Moreover, special attention is paid to monodispersed and stable particles formation. Nanocomposite materials formed by metallic or oxide particles dispersed in polymer, ceramic or vitreous matrices have important application in areas such as catalysis and electronics. Different metals, metal oxides, sulfides, polymers, core-
shell and composite nanoparticles can be prepared using a number of synthetic techniques, which are broadly classified into two categories, namely, physical methods and chemical methods.

**Physical Methods**
- a. Arc discharge method
- b. Laser ablation
- c. High-energy ball milling
- d. Sputtering
- e. Inert gas condensation

**Chemical Methods**
- a. Hydrothermal synthesis
- b. Sol-gel technique
- c. Sonochemical technique
- d. Micro emulsion technique
- e. Chemical precipitation

1.15.1 **Arc discharge Method**
A common technique for the production of single walled carbon nanotubes is the electric arc discharge method in which carbon is vaporized between two carbon electrodes. Nanoparticles of metal oxides, carbides and nitrides can also be prepared by carrying out the discharge in suitable gas medium or by loading the electrodes with suitable precursor.

1.15.2 **Laser ablation**
In laser ablation, higher power laser pulses are used to evaporate matter from target surface such that the stoichiometry of the material is preserved in the interaction. As a result, a supersonic jet of particles (plume) is ejected normal to the target surface. This method is applicable to high melting point elements and transition metals.

1.15.3 **High-energy ball milling**
The only top-down approach for nanoparticle synthesis has been used for the generation of magnetic, catalytic and structural nanoparticles. High-energy ball milling is an already established technology, however it has been considered dirty because of contamination
problem with iron. This method leads to fabricate alloys, which cannot be produce by conventional techniques.

1.15.4 Sputtering

Sputtering is a process whereby atoms are ejected from a solid target material due to bombardment of the target by energetic particles. It only happens when the kinetic energy of the incoming particles is much higher than conventional thermal energies. Sputtering is used extensively in the semiconductor industry to deposit thin films of various materials in integrated circuit processing.

1.15.5 Inert gas condensation

In this technique a metallic or inorganic material is vaporized using thermal evaporation sources such as a Joule heated refractory crucibles, electron beam evaporation devices, in an atmosphere of 1-50 m bar. Gas condensation allows producing nanoparticles with well controlled size distribution.

1.15.6 Hydrothermal Synthesis

Hydrothermal Synthesis can be defined as a method of synthesis of single crystal which depends on the solubility of minerals in hot water under high pressure. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called autoclave, in which a nutrient is supplied along with water. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value.

1.15.7 Sol-Gel Synthesis

Sol-gel method involves the formation of a concentrated suspension of a metallic oxide or hydroxide (sol), which is subsequently dehydrated by evaporation or solvent extraction, resulting in a semi-rigid mass (gel). A wide range of pure and mixed oxides can be produced on controlled heating of this gellated material. This process gives a good control over composition and particle size and a substantial reduction in the formation temperature.

1.15.8 Sonochemical process

In which molecules undergo a chemical reaction due to the application of powerful ultrasound radiation having frequency in the range
of 20 KHZ- 10 MHZ. This method extremely used in the synthesis of wide range of nanostructured inorganic materials for industrial applications.

1.15.9 Micro emulsion method

This method is exemplified by the synthesis of nanoparticles inside reverse micelles or in microemulsion. Synthesis of nanoparticles via microemulsion is a simple and powerful technique. It does not require expensive equipments. A wide ranging composition has been prepared as pure homogeneous phases.

1.15.10 Precipitation Method

Precipitation is the creation of a solid in a solution or inside another solid during a chemical reaction or by diffusion in a solid. When the reaction occurs in a liquid solution, the solid formed is called the precipitate. The chemical that causes the solid to form is called the precipitant. Without sufficient force of gravity (settling) to bring the solid particles together, the precipitate remains in suspension. Precipitation method is useful to form pure crystals

1.15.11 Co-precipitation Method

The co precipitation method is a useful method for the preparation of ceramic oxide powders. In the co precipitation method, the required amount of aqueous solution of desired metal ions were mixed together. The pH is adjusted somewhere in the region where the metal ions gets precipitated by adding aqueous solution of ammonia, ammonium hydroxide. The precipitate was washed with distilled water, dried and ground to obtain particles of size smaller than 5 um.

1.15.12 Thermal decomposition

Thermal decomposition is a reaction in which heat is used for breaking up a chemical substance in two or more substances. Because thermal decomposition is often endothermic it can be used to increase the heating value of a fuel. When metals are near the bottom of the reactivity series, their compounds generally decompose easily at high temperatures. This is because stronger bonds form between atoms towards the top of the reactivity series, and strong bonds break less easily.
1.15.13 Organometallic Synthesis

Compounds that contain a metal-carbon bond are known as organometallic compound. The high polarity of the metal-carbon bond is responsible for the high ionic nature of the organometallic compounds. The use of organometallic precursors allows the synthesis in mild conditions of metal nanoparticles displaying a controlled size, shape, structure and surface environment. Organometallic compounds are widely used in homogeneous catalysis.

1.15.14 Polyol Synthesis

Ethylene glycol has been widely used in the polyol process for the synthesis of metal (both pure and alloyed) nanoparticles due to its strong reducing power and relatively high boiling point. It has been widely used for the synthesis of nanocrystalline ceramic powders. Polyol Process is a low temperature process. It yields high pure organic free powders and ability to control the particle properties such as size, shape and uniformity, etc.

Among these methods, the chemical precipitation method is used in this 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.

Even though, numbers of techniques are available to characterise the nanocomposites, the following techniques were used in the present study for the characterization of nanocomposites.

1. X-Ray Diffraction
2. Scanning Electron Microscopy
3. Transmission Electron Microscopy
4. UV-Visible Spectroscopy
5. Photoluminescence Spectroscopy
1.16 BRIEF REVIEW OF LITERATURE

Zeng et al., (2003) successfully synthesized the Sb-doped ZnO nanoparticles in the atmosphere of a flowing mixed Ar + O$_2$ gas using Zn–Sb alloy with an atomic ratio of 6:1 as an vaporized material by the vapour condensation method. XRD pattern of the as-synthesized Sb-doped ZnO nanoparticles reveals a highly crystallized wurtzite structure and the average size of the nanoparticles were estimated as 52–60 nm. XPS analysis result clearly shows that the Sb element has doped into the ZnO crystal lattice and no metallic Zn as well as Sb exists in the Sb-doped ZnO nanoparticles. HRTEM image clearly indicates the two-dimensional lattice fringe of the wurtzite structure without any small area of zinc blende in this particle. The hexagonal nanoparticle is a perfect single crystal without any defects such as the dislocations and twins. The crystal growth of the ZnO nanoparticles could be controlled by the Sb doped element. The doped Sb$^{5+}$ ions lead to a considerable increase of the optical reflectivity and electrical resistivity in comparison with the undoped ZnO nanoparticles.

Yang Yang et al., (2004) prepared ZnO nanoparticles by thermal decomposition method. In this study, different organic additives such as β-cyclodextrin (β-CD), amylase, and polyethylene oxide polymer (PEO) were used to coat zinc acetate in order to investigate their roles on the thermal decomposition process of the precursor. XRD analyses and TEM observations showed that the morphology, dimension, and size distribution of the product ZnO are strongly affected with the presence of β-CD compared to the system of pure zinc acetate and amylase or PEO coated one. It is suggested that though the ultrafine carbon black from the decomposition of the organic compound might play an important role, the inclusion effect of β-CD should be the primary factor responsible for the formation of ZnO nanoparticles with regular shape and controllable dimension. When zinc acetate is coated on β-CD, the TGA plot shows the greatest weight loss in the range 300–500°C. The UV-Visible absorption curve gave a value at 385 nm (3.21 eV), which is near the band gap of ZnO 1S–1S electron transition (3.37 eV). A strong UV emission at 396 nm and a weak green emission at around 530 nm could be observed in PL spectra.
This method could also be used to prepare other nano scaled metal oxide from thermal decomposition process.

Takayuki Hirai and Yoko Asada (2005) prepared ZnO nanoparticles by NP-5/cyclohexane reverse micellar system and the photoluminescence properties for the resulting nanoparticles were investigated. The nanoparticles of nearly spherical morphology and narrow size distribution were obtained via the recovery of the \( \text{Zn(OH)}_2 \) precursor nanoparticles from the reverse micellar solution by in situ formation of polyurea (PUA) followed by calcination. XRD patterns of ZnO nanoparticles showed wurtzite-structure. The crystallite size of nanoparticles increased with increase in calcination time. The SEM images for the resulting ZnO nanoparticles showed spherical morphology and narrow size distribution. The as obtained ZnO nanoparticles demonstrated a near-UV emission and a green emission, and the photoluminescence properties depend on calcination conditions. They pointed out the most important factor which affects the photoluminescence properties of the ZnO nanoparticles was found to be the difference in the number of oxygen vacancies caused by the difference of the calcination condition, rather than the size, morphology, and crystallinity of the resulting nanoparticles.

Santi Maensiri et al., (2006) synthesised nanocrystalline ZnO powders by a simple method using zinc acetate dehydrate and polyvinyl pyrrolidone (PVP) as a chelating agent. The synthesized powders were characterized by TG-DTA, XRD, FT-IR, UV-VIS, PL, SEM and TEM. The TG curve shows a major weight loss in the range 400\(^\circ\)C - 550\(^\circ\)C. The weight loss is related to the combustion of organic matrix. On the DTA curve, a main exothermic effect was observed at 550\(^\circ\)C, indicating that the thermal events can be associated with the burnout of organic species involved in the precursor powders. XRD pattern of the calcined ZnO powders show typical wurtzite structure. The crystalline sizes of the powders were estimated as 51±21 nm. The FTIR spectra show main absorption bands at 3400, 2900, 1380 and 1600 cm\(^{-1}\). The synthesised powders exhibited the UV absorption below 2.99 eV. The powders also exhibited room temperature PL, having a strong UV emission band at 2.98 eV, a weak blue band at 2.82 eV, a weak blue-green band at 2.56 eV and a weak
green band at 2.34 eV. The strong UV emission with weak green emission intensity should be attributed to the high purity with perfect crystallinity of the synthesised ZnO powders.

**Guang Zhou and Jiancheng Deng (2007)** successfully synthesized Ag/ZnO nano-composites via the coordination homogeneous co-precipitation method. Thermo gravimetry-differential thermal analysis (TG-DTA), Fourier transform infrared (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM) and ultraviolet-visible (UV-Vis) were used to characterize the microstructure and morphology of the precursor and the products obtained at various temperatures. The particle size (20 to 50 nm) of the product increased with increasing calcining temperature. TEM micrographs of samples show well-distributed spherical particle with a size about 20 nm. The average particle size increased with increasing calcining temperature, suggesting a gradual growth of the nano particles during the heating process. The method is new, facile, and as it does not require unnecessary expensive raw materials or equipment, it is also easy for scale production, and can be extended to synthesize other nano-composites.

**Changchun Chen et al., (2008)** synthesised nano sized ZnO powders by direct precipitation method. ZnO powders were characterized by XRD, Brunauer-Emmet-Teller analysis (BET), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and TG-DTA. The XRD results showed that the synthesised ZnO powders had a pure wurtzite structure and the average nano particle sizes were about 35.2 nm. According to SEM photograph, the morphology of the nano sized ZnO particles takes on pseudo-spherical shape. TEM indicates that the ZnO particles are approximately spherical and the average diameter of the particles was 32 nm. The TGA curve shows a major weight loss in the range 50-220°C with no further weight loss observed at a temperature up to 700°C. The weight loss was related to the decomposition of the precursors of ZnO. On the DTA curve a main exothermic effect was observed between 200 and 250°C with a maximum at about 220°C, indicating that thermal events could be associated with the decomposition of the precursors of ZnO.
Jinghai Yang et al., (2009) have successfully prepared ZnO nanoparticles by chemical precipitation method at a low temperature of 200°C. X-Ray Diffraction (XRD), Transmission Electron Microscope (TEM), Photoluminescence (PL) and Raman were used to investigate the effect of annealing temperature on the structure and optical properties of nanoparticles. The XRD analyses revealed that the average size of the as-prepared samples was about 8 nm under 200°C, which had a good agreement with TEM images. All the diffraction peaks could be well indexed as hexagonal phase of ZnO. No excess peaks were detected, which indicated that crystalline ZnO had formed under 200°C and there were no impurities in the samples. The size of ZnO nanoparticles increased with increasing annealing temperature. In Raman spectra, a sharp strong peak is observed at 438 cm⁻¹, which is the characteristic scattering peak of the Raman-active dominant E₂ (high) mode of wurtzite hexagonal ZnO. Raman-scattering spectra confirmed that the as-grown products were wurtzite hexagonal phase and possessed good crystal quality with very few defects at the annealing temperature of 500°C. Room temperature PL spectra showed a sharp and strong peak in the UV region and a suppressed weak peak in the visible region. The position of Ultraviolet (UV) emission peak in PL spectra revealed a red-shift when the annealing temperature was increased. In addition, after annealing under 500°C the intensity of the UV peak became strongest and the intensity of the green emission almost disappeared, which indicated that ZnO nanoparticles have much better crystallization after annealing.

Navendu Goswami and Dhirendra Kumar Sharma (2010) reported the structural, electronic and optical properties of ZnO nanoparticles. The prepared ZnO nanoparticles were investigated employing X-Ray Diffraction (XRD), Transmission Electron Microscope (TEM) Atomic Force Microscope (AFM), Fourier Transform Infrared (FTIR), UV-Visible and Fluorescence Spectroscopy. In order to study the effect of annealing on ZnO nanoparticles, they have analysed pre and post-annealed nanoparticles. It was observed that annealing treatment removes the impurities and consequently enhances the purity of ZnO nanoparticles without influencing their wurtzite phase. The formation of nanocrystalline ZnO is
reflected through the broadening of the XRD characteristic lines for ZnO. The average size of the nanocrystallites was determined using Debye-Scherrer equation and estimated size of ZnO nanoparticles are 20.5 nm. The lattice plane (200), which was not distinctly observed for unannealed ZnO, is prominently distinguished for annealed ZnO. The TEM images of the pre- and post-annealed ZnO nanoparticles show spherical shape. The smallest size of the ZnO nanoparticles is about 18 nm whereas the average size of nanoparticles is around 24 nm. There is no difference in the AFM images for pre- and post-annealed ZnO nanoparticles. The particle size, shape and distribution were also examined by the surface topographic data with atomic resolution. It is inferred that the particle sizes are in the range of 20-40 nm. FTIR spectroscopy concomitant with the XRD results, confirms the formation of pure ZnO particles. The blue shift observed in the UV-Visible spectrum is the typical signature of size confinement in ZnO nanocrystals. The fluorescence study leads to an interesting conclusion that although crystal phase and other structural parameters of ZnO nanoparticles, as investigated through XRD, AFM, TEM and FTIR techniques, are not influenced by annealing process, fluorescence emissions are affected. This finding paves the way to the process of altering visible luminescence in ZnO nanoparticles without varying their size or shape.

**Nirmala and Anukaliani (2011)** prepared antibacterial activity of transition metals (Mn, Co) doped ZnO nanopowders by a DC thermal plasma method against Escherichia coli and Staphylococcus aureus were investigated. The phase and morphology studies have been carried out by X-ray diffraction, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) respectively. They concluded that TM (Co, Mn) doped ZnO nanoparticles prepared by dc thermal plasma method may be used as promising materials for biomedical applications and reducing the environmental toxicity.

**Chandrasekaran et al., (2012)** synthesised ZnO nanoparticles by sol–gel process using three different capping agents such as Ethylene diamine tetra acetic acid (EDTA), Triethanolamine (TEA) and Tetraethylammonium Bromide (TEABr). The size and morphological
changes of ZnO nanoparticles were investigated by using Transmission electron microscopy (TEM) and UV–Vis optical absorption spectroscopy. TEM images of the uncapped ZnO have no particular morphology and the particles were highly agglomerated. TEM and HRTEM images of EDTA, TEA capped ZnO particles shows that highly dispersed with hexagonal morphology. The sizes of the nanoparticles are in the range of 20 to 25 nm. From the TEM analysis, the morphologies of the ZnO nanoparticles are clearly changed with the capping agents. The XRD spectra of the synthesised samples confirmed that the synthesised products were wurtzite structure. The absorption curves for all the samples exhibits a strong absorption peak in the range of 365 to 370 nm. The uncapped and capped ZnO samples show excellent UV absorption and high transparency in the visible region. The presence of various capping agents in the synthesised ZnO nanoparticles were analysed through FTIR technique. Moreover, they concluded that the higher in the concentrations of the capping agents have no influence in the morphological changes.

Wageh et al., (2003) have succeeded in synthesizing ZnS quantum dots using mercaptoacetic acid as a stabilizer. The formation of samples occurs as a result of a thermodynamically controlled cluster growth. The effect of refluxing time on the preparation of these samples was measured using UV-Vis absorption and photoluminescence. The UV-Vis absorption and photoluminescence phenomena results showed that the band edge emission was improved by increasing the refluxing time. The luminescence spectra showed some new characteristics. The emission band observed at 463 nm appeared for samples attributed to dangling sulphur bonds at the interface of ZnS grains. The obtained quantum dots had a diameter of less than 4 nm and a band gap of about 4.2 eV, which is larger than the bulk ZnS (3.66 eV).

Yong Ding et al., (2004) have reported phase controlled synthesis of ZnS nanobelts: zinc blende vs wurtzite. Using VLS deposition process, by adjusting the synthesis conditions, they controlled the deposited ZnS nanostructures as zinc blend phase, wurtzite phase or a mixture. The formation of the nanosaw morphology was explained using a combination of vapour–liquid–solid (VLS) and the self-catalyzed growth process in two
steps. The SEM images showed the morphologies of the ZnS nanostructures with an average deposition thickness of 5 nm. The HRTEM images showed the main body of the nanosaw as wurtzite structure but the teeth are zinc blende structure. They pointed out that the transformation from wurtzite to zinc blend occurs at root of the saw teeth. The SAED pattern suggested that the zinc blend (as indicated by arrowheads) and wurtzite (rectangle marked diffraction spots) structures co-existence in the nanosaw. This study gave guidance for controlling the phase of the as-synthesized ZnS nanostructures.

Feng Wei et al., (2005) have presented a simple method for preparing the spindle-like ZnS nanostructures using a simple surfactant emulsion template by hydrothermal process. The morphologies of ZnS nanostructures were characterized by transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and field-emission scanning electron microscopy (FE-SEM). It was found that most of the products including twin ellipsoids with connected hollow cores are reminiscent of spindle-like structures. The lengths, widths and the thickness of the shell were in the range of 1-2 mm, 300-450 nm and 20-40 nm, respectively. Selected area electron diffraction (SAED) and X-ray powder diffraction (XRD) patterns show that the shell was composed of sphalerite ZnS polycrystals. The optical properties of spindle-like ZnS nanostructures have been studied by photoluminescence (PL) spectroscopy. A PL emission spectrum (λ_ex = 290 nm) recorded at room temperature showed two broad emissions, one around 360 nm and the other around 460 nm. They pointed out that this could be attributed to interstitial emission and trapped surface states emission, respectively. However, a weak peak near 400 nm could be attributed to sulfur vacancies emission.

Zhengshui Hu et al., (2006) synthesized mono-dispersed semiconductor ZnS hollow spheres with the diameter of 300-500 nm and the shell thickness of about 100-150 nm by solvothermal method. The synthesised particles were characterized by XRD, size distribution investment, UV-Vis, TEM, and SEM. TEM image of a single ZnS hollow sphere showed that the surface of the shell as coarse. The SEM image of
hollow ZnS spheres showed that the obtained products disperse homogeneously over a large area with the outer diameter of about 300-500 nm. The particle size of about 22.5 nm for the primary ZnS microcrystal can be calculated using XRD pattern. The UV-Vis measurement indicated that there was a broad absorption at 210-280 nm, which is likely to be caused by “hollow-effect”. A growth mechanism of ZnS hollow spheres has also been put forward and discussed.

**Lihong Dong et al., (2007)** fabricated uniform ZnS hollow nanospheres with different diameter and shell thickness controllably in a large scale by a one-pot, simple, economical method. Small and monodisperse ZnS hollow nanospheres with outer diameter ranging from 60 to 70 nm and wall thickness of 15-20 nm were fabricated in a large scale by a simple surfactant polyethylene glycol (PEG) assisted method. They pointed out that the diameter and the wall thickness of the hollow nanospheres could be controlled by manipulating the amount of PEG and the aging time, respectively. The product was characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), UV-Vis spectrum and fluorescence spectroscopy. The XRD pattern of the hollow nanospheres confirmed that the product was zinc blende structure. An average crystallite size of about 4 nm was estimated. UV-Vis spectrum revealed the quantum size effects of the hollow nanospheres. The fluorescence spectrum exhibits a strong and stable green emission centring at 521 nm, which may be caused by the presence of some self-activated luminescence centres, probably vacancy states or interstitial states related to the peculiar nanostructures. The photocatalytic investigation indicated that the prepared ZnS hollow nanospheres had good photocatalytic activity.

**Qi Xiao and Chong Xiao (2008)** synthesized water-soluble Mn$^{2+}$-doped ZnS quantum dots (Mn:ZnS d-dots) using thioglycolic acid (TGA) as stabilizer in aqueous solution in air. The sample was characterized by X-ray powder diffraction (XRD), UV-Vis absorption spectra and photoluminescence (PL) emission spectroscopy. The sizes of Mn:ZnS d-dots were determined to be about 2 nm using XRD measurements and the UV-Vis absorption spectra. The XRD patterns of Mn:ZnS d-dots were
shown cubic zinc blende structure. UV-Vis absorption spectra of Mn:ZnS d-dots with different Mn\(^{2+}\) concentration (0, 1.5 and 3\%) showed blue shift. The effects of Mn\(^{2+}\) concentration and TGA/(Zn + Mn) molar ratio on PL of Mn:ZnS d-dots have also been investigated. It was found that the Mn\(^{2+}\): \(^{4}\)T\(_{1}\) - \(^{6}\)A\(_{1}\) emission intensity of Mn:ZnS d-dots significantly increased with the increase of Mn\(^{2+}\) concentration, and showed a maximum when Mn\(^{2+}\) doping content was 1.5\%.

Baoyou 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. The oriented attachment mechanism was used to explain the epitaxial growth of nanorods. XRD patterns of the ZnS nanorods and ZnS:Cu nanorods reveals that the as-synthesized nanorods were hexagonal structure. TEM images of products showed rod-shaped with the diameter about 4 nm and length about 15 nm. The HRTEM images showed that the nanorods have a hexagonal wurtzite structure with high crystalline, which were consistent with the XRD results. The absorption spectra showed a minor red shift with increasing of Cu doping concentration. Photoluminescence showed red shift and the intensity of defect luminescence emission would be enhanced as the concentration of Cu ions (0.2-0.4\%) increased. They pointed out that the optical properties of the products could be controlled easily by changing Cu doping concentration. They suggested that this synthetic strategy might exploit a favourable route to synthesize metal-doped semiconductor nanostructures, which are potentially important for optoelectronic nanodevices.

Kuppayee et al., (2011) synthesized undoped and Cu\(^{2+}\) doped (0.2-0.8\%) ZnS nanoparticles through chemical precipitation method. Tri-n-octylphosphine oxide (TOPO) and sodium hexametaphosphate (SHMP) were used as capping agents. The synthesized nanoparticles were analyzed using X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier transform infrared spectrometer (FT-IR), UV-Vis spectrometer, Photoluminescence (PL) and Thermo gravimetric-Differential scanning calorimetry (TG-DTA) techniques. X-ray diffraction (XRD) patterns revealed that the particles exhibited cubic crystal structure. The estimated size of
the uncapped ZnS, ZnS:Cu and surfactants capped ZnS:Cu was found to be in the range of 6–3 nm. The TEM result revealed that the prepared particles were monodispersed by the addition of surfactants. The doping ions were identified by electron spin resonance (ESR) spectrometer. Photoluminescence spectra were recorded for ZnS: Cu$^{2+}$ under the excitation wavelength of 320 nm. The prepared Cu$^{2+}$-doped sample showed efficient PL emission in 470-525nm region. The capped ZnS:Cu emission intensity was enhanced than the uncapped particles. The shifting was observed by increasing the doping concentration. The absorption spectra of the all samples were highly blue shifted due to the quantum confinement effect. The addition of surfactants yielded enhanced emissions. In addition, the optimum levels of the capping agent were determined by increasing photoluminescence emission. The stability of the ZnS:Cu nanoparticles examined by TG-DTA analysis.

**Somayeh Nazerdeylami et al., (2011)** synthesised ZnS:Mn$^{2+}$ nanoparticles by chemical method using PVP (polyvinylpyrrolidone) as capping agent in aqueous solution. The structure and optical properties of the resultant product were characterized using UV-Vis optical spectroscopy, X-ray diffraction (XRD), Photoluminescence (PL) and Z-scan techniques. XRD pattern of Mn$^{2+}$ doped ZnS samples showed cubic zinc blende structure. The average crystalline sizes of ZnS: Mn$^{2+}$ with different Mn$^{2+}$ concentrations (1%, 5% and 10%) was estimated as 2.35, 2.24 and 2.30 nm respectively. 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. The band gap of nanoparticles was obtained as 4.25 eV. The room temperature photoluminescence (PL) spectrum of ZnS: Mn$^{2+}$ exhibited an orange-red emission at 594 nm. The PL intensity increased with increase of Mn$^{2+}$ ion concentration. A nonlinear absorption (NLA) was detected and was mainly associated with saturable absorption effect. They concluded that the increase in concentration of Mn$^{2+}$ ions in ZnS: Mn$^{2+}$ nanoparticles enhanced the non-linearity properties of these nanoparticles.

**Tiwari et al., (2012)** have prepared copper doped ZnS nanoparticles stabilized by sodium hexametaphosphate (SHMP) through
wet chemical method using thiourea and sodium sulphide as chalcogenide sources. The XRD pattern showed that ZnS nanoparticles had zinc blende structure. The crystallite size was obtained as 2.0 nm and 3.3 nm. Absorption measurements were done for three different dopant concentrations. An absorption edge around 310 nm was observed, which does not appreciably change with the variation of the dopant concentration. The PL emission spectra for SHMP capped and uncapped ZnS:Cu nanoparticles show the strong luminescence peak in the ultraviolet region. It seems that there is a complex interaction between capping agent and dopant ion with the host ZnS giving raise to different luminescence centres. The strong and narrow excitonic emission and very deep level emission suggested that the SHMP capped ZnS:Cu nanoparticles are of excellent optical quality.

Junjie Zhu et al., (2001) have prepared nanoparticles of CdS, ZnS by a very simple fast reaction between CdCl$_2$ or Zn(Ac)$_2$ and thioacetamide in aqueous solution using microwave irradiation. The nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), Reflectance and Photoluminescence spectra. XRD showed the particle size as 9 and 3 nm for CdS and ZnS, respectively. The TEM observations for the as-prepared ZnS and CdS nanoparticles show spherical shape. The optical refection edge of CdS and ZnS showed 460 and 300 nm, respectively. The absorption edges of both CdS and ZnS were blue-shifted from the absorption edge of bulk CdS and ZnS. The excitation wavelength was observed at 300 and 200 nm for CdS and ZnS, respectively. A broad emission peaks were observed at 505 and 460 nm for CdS and ZnS respectively. They pointed out that it is a simple and efficient method for producing nanoparticles.

Jun Zhang et al., (2002) synthesized uniform CdS nanoparticles from 4 to 8 nm via a quaternary reverse micelle method. The size of the nanoparticles can be controlled and modulated by adjusting the W (W = [H$_2$O]/[CTAB]) value. In order to eliminate the surface defects and improve the optical properties of CdS nanoparticles, the reflux treatment was employed. A typical TEM image show that most of CdS nanoparticles prepared at different W was spherical and uniform. Average size of the
nanoparticles (4, 6 to 8 nm) increased with increasing of W (5.01, 16.35 to 24.45) respectively. UV-Visible spectra noticed that the absorption onset is blue shift, which is the evidence of quantum confinement effect. The emission band at around 550 nm was observed. The possible mechanism of effective surface modification was discussed and the highest quantum yield of CdS nanoparticles at room temperature was estimated as 11%. Strong excitonic emission instead of traps was obtained and the luminescence efficiency was improved dramatically.

Wenzhong Wang et al., (2003) have reported a solid-state synthesis of CdS nanoparticles in the presence of a nonionic surfactant $C_{18}EO_{10}$ at ambient temperature. The structural nature and the chemical composition of CdS nanoparticles were analyzed by X-ray diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), UV-VIS optical absorption spectrum and X-ray photoelectron spectrum (XPS). XRD pattern of CdS show that the cubic phase. TEM images of CdS nanoparticles showed that spherical shape with an average diameter of ca 5 nm. HRTEM image of the sample revealed crystallinity of the nanoparticles. UV-VIS optical absorption spectrum of CdS nanoparticles showed blue shift. They suggested that this method may be extended to the synthesis of other materials of nanoparticles, such as semiconductors ZnS, CuS, NiS, FeS.

Sivasubramanian et al., (2006) have investigated the structural phase transformation of as-prepared CdS nanoparticles upon annealing. With increase in particle size, the structure progressively changed from cubic to hexagonal. The CdS nanoparticles were investigated using X-ray diffraction (XRD), Raman, photoluminescence (PL) and infrared (IR) absorption spectroscopy. In the Raman spectra, the ratio of $I_{2LO}/I_{1LO}$ increases monotonically during the annealing process, indicating an enhancement of electron-phonon coupling with increasing particle size for both cubic and hexagonal phases (although with different enhancement factors). XRD pattern showed that the size of as-synthesized nanoparticles as 5 nm. With increase in annealing temperature, the size increased to 37 nm. Moreover, it shows that the cubic-CdS undergoes phase transition around 620 K. PL peak position showed a marginal decrease for annealing
up to 573 K. The changes in the optical properties are attributed to those arising from particle growth and structural transformation. A defect-induced mode at 195 cm\(^{-1}\), TO mode at 240 cm\(^{-1}\) and the Frohlich mode at 278 cm\(^{-1}\) were observed from IR absorption measurements.

Ronghui Xu et al., (2007) have reported a hydrothermal route to the production of high-quality CdS semiconductor nanocrystallites. The synthesis is based on the separation of the nucleation and growth stages by controlling some crucial factors such as temperature, pH and concentration of reactant mixture. These measures provide temporally discrete nucleation and permit controlled growth of quantities of nanocrystallites. CdS semiconductor nanocrystallites show sharp excitation features and strong “band-edge” emission which is maintained very strongly 10 months after precipitation. Transmission electron microscopy and X-ray powder diffraction indicate the presence of bulk structural properties in crystallites as small as 5 nm in diameter. The high-resolution TEM image confirmed that the nanoparticles were highly crystalline and a little aggregated on the carbon-coated copper grids. Ultrastability and super strong photoluminescence emission of as-prepared CdS semiconductor nanocrystallites indicate its potential practical value. They found that the semiconductor nanocrystals of CdS produced via hydrothermal method are of potentially practical value, because they are not only ultrastable but also highly luminescent.

Rodriguez et al., (2008) have synthesized CdS nanoparticles through chemical precipitation technique, using starch as capping material. The morphology and crystalline structure of such samples were measured by high-resolution transmission electron microscopy and X-ray diffraction, respectively. TEM images show uniform sphere-shaped nanoparticles, with particle size in the range of 5 nm. This value was consistent with the results obtained by XRD. The XRD pattern exhibits prominent broad peaks which confirm that CdS nanoparticles are cubic phase. The PL spectrum of CdS nanoparticles at T = 15 K shows broad peaks near 1.81 eV associated to electron–phonon interaction and the size distribution of the nanoparticles.
Kotkata et al., (2009) synthesised amorphous CdS nanoparticles capped with cetyltrimethyl ammonium bromide (CTAB) under various conditions using a co precipitation method. A blue shift in the band gap was observed in the UV-Visible absorption spectra indicating the formation of nanoparticles of an approximate size of 8nm. The recorded transmission electron micrographs confirmed this result. The blue shift reveals quantum size effect in the synthesised CdS amorphous sample. The phase-nature, phase transformation as well as the structure of the synthesised CdS nanoparticles has been extensively characterized using X-ray diffraction (XRD), Radial Distribution Function (RDF), Differential Scanning Calorimeter (DSC), Fourier Transform Infrared (FT-IR), Raman Scattering (RS) and/or Heat Stage X-ray diffraction (HSXRD). The TEM images clearly show that the nanoparticles of the samples are quantum dots with a good uniformity in size and shape. Also, the dots appeared quite spherical with no shape asymmetry. From DSC analysis three exothermic peaks were observed due to crystallization. Analysis revealed that the synthesised amorphous CdS nanoparticles could be transformed into CdS nanocrystals having a zinc blende or a wurtzite structure, relying on the applied heat treatment scheme. The rate of nano crystal growth depends on the aging period, prior filtering the reacted materials, and its relation to the quality of the capping process. They pointed out that five days aging period enhance the stability of the grown phase with a remarkable surface stability.

Vineet Sing et al., (2010) achieved tuning of size of thioglycerol capped cadmium sulphide nanoparticles by controlling the capping reagent concentration as well as annealing temperature through chemical precipitation method. The results arrived from UV-Vis absorption spectra, XRD, HRTEM and Raman spectra indicated that the particle get smaller sizes on increasing capping reagent concentration and becomes larger on increasing the annealing temperature due to agglomeration as well as thermal driven mass transfer phenomena. XRD, TEM and HRTEM pattern of CdS samples confirmed that the as grown samples have hexagonal phase. On increasing the capping reagent concentration the 1LO peak position in Raman spectra was shifted towards higher wave number as the
particle size gets smaller and peak gets progressively broader. From XRD pattern, increasing annealing temperature from 50°C to 200°C, there is no any effective change in XRD peak intensity while at 350°C and 500°C all the peaks of hexagonal phase were well resolved and their peak intensity also increases, indicating increasing crystallinity of the corresponding CdS products. Thermal annealing causes the growth in particle size which affects the UV-Vis, XRD, TEM, Raman and PL spectra. The High Resolution Transmission Electron Microscopy (HRTEM) images of sample shows clear lattice fringes with interlayer distances measured as 0.3375 nm and 0.361 nm respectively corresponding CdS. PL study attributes an enhancement of the peak intensity due to interstitial sulphur with increasing the capping reagent concentration while on post annealing of the sample peak intensity reduces, which can be further attributed due to detachment of capping molecules.

Priya et al., (2012) synthesised CdS nanocrystals by a simple and novel solvothermal method using a domestic microwave oven. They prepared in three molecular ratios. X ray diffraction measurements indicated that the crystallite size is controlled for all three samples less than 14 nm. UV visible absorption spectral measurements show an optical band gap within the range of 2.62-2.77 eV. Energy dispersive X-ray absorption spectral, DC and AC (with a fixed frequency of 1 kHz) electrical (at various temperatures ranging from 40-110°C) measurements were also carried out for all the samples. This indicated that the electronic contribution plays a dominant role in charge transport process and polarisability. A very significant change of conductivity (both AC and DC) takes place due to change in the sulphur content of CdS nanocrystals.

Saravanan et al., (2012) have synthesised cerium doped cadmium sulphide nanoparticles (Ce:CdS) by coprecipitation method with three different concentrations of cerium (1, 2 and 3 mol%). Powder X-ray diffraction pattern reveals the formation of cadmium sulfide nanoparticles with hexagonal (wurtzite) structure. It was also observed that the presence of ceria does not alter the structure of CdS. Average particle size was measured as ~3 nm. The presence of cerium was confirmed by EDX and ICP-OES analyses. EDAX spectrum shows the presence of major chemical
elements namely cadmium, sulfur and cerium. Using UV absorption edge values, the bandgap energy was estimated. Ce: CdS nanoparticles shows a blue shift in comparison with the bulk CdS, which may be ascribed to the quantum confinement effect. The samples show luminescence in the blue region, with an emission peak positioned around 350-450 nm. The peak position of NBE emission slightly shifted toward longer wavelength region with higher intensity, from 363 nm to 375 nm when the concentration of dopant increases to 3 mol%. They pointed out that luminescence property of CdS nanoparticles enhanced when Ce$^{3+}$ was introduced into the CdS. PL and XRD analyses demonstrated the Ce$^{3+}$ ions uniformly substituted Cd$^{2+}$ sites or interstitial sites in CdS lattice which influences the optical properties.

Elango et al., (2012) have successfully synthesized Manganese doped cadmium sulfide nanomaterials with different Mn concentrations using non-aqueous solution method. The materials were characterized by X-ray diffraction method (XRD), Electron Microscopic Method (HRTEM), UV-Visible absorption spectroscopy (UV-Vis), Fourier Transform Infrared spectroscopy (FT-IR) and Vibrating Sample Magnetometer (VSM) analysis. X-ray diffraction study revealed the cubic zinc blend structure of CdS:Mn as primary phase and cubic structured $\alpha$-MnS as secondary phase. The diameter of the crystallite size was found as 17 to 23 nm (under zero strain). The morphology of the particles was spherical in shape. The 5, 10 and 15 wt. % Mn doped CdS nanoparticles show mono dispersity with less agglomeration. The optical absorption spectra of the materials exhibited varying blue shifts in their characteristic $\lambda$ max region as a function of Mn in CdS host material. The presence of metal sulfur bonding and weak interaction between the anion ($S^{2-}$) and cations (Cd$^{2+}$ and Mn$^{2+}$) were confirmed by FT-IR spectroscopic data. An appreciable magnetic behaviour (super paramagnetic state) as the result of spin moment caused by Mn$^{2+}$ in the crystal structure of CdS:Mn was identified by VSM.

Cannas et al., (2003) synthesized ZnO-SiO$_2$ nanocomposites through impregnation of commercial mesoporous silica with zinc nitrate aqueous or ethanolic solutions. The samples treated at 700$^\circ$C exhibit the presence of nanocrystalline ZnO particles (zincite phase) dispersed onto
amorphous silica. XRD patterns of the samples show the series of peaks ascribed to the zincite phase. They are superimposed to that of silica matrix, with a sensible variation in intensity among the various preparations, which is consistent with the different ZnO concentration. The dark field observations show that these particles resulted to be aggregates of nanocrystals belonging to zincite phase, as confirmed by SAD pattern and in agreement with XRD patterns. A narrower and more homogeneous distribution of particles with mean sizes of about 7.5 nm are obtained using ethanolic instead of aqueous solutions. At higher temperatures the system evolves towards the formation of a zinc silicate phase. TEM bright field images of the samples treated at 700°C show the presence of some portions of still naked porous silica and other parts where the porous structure was partially covered by quite large particles.

Alexander et al., (2004) described photoluminescence, depending on the ZnS shell thickness of CdS/ZnS core-shell semiconductor nanoparticles. The synthesis was done by the microemulsion method in AOT surfactant reverse micelles containing water. The precursor amount was varied by two different ways one is increasing water content at a given precursor concentration or increasing the precursor concentration at given water content. It was found that the nanoparticle diameter and the shell thickness almost linearly increase when the water content trapped in the reverse micelles increases. Similarly, the diameter increases with the precursor concentration inside the micelles. The nanoparticle size also increases with the time of aging in an inert gas because of the increase of the ZnS shell thickness. The average nanoparticle diameter calculated from the absorption spectra as 3.2 nm for CdS and 2.36 nm for CdS/ZnS nanoparticles. The CdS/ZnS nanoparticle diameter linearly increases with the time due to the shell thickness increase. The CdS core also increase in size with time at a bigger growth rate than the shells.

Jianling Zhang et al., (2004) prepared well-dispersed ZnS/CdS composite nanoparticles by synthesizing the ZnS/CdS nanoparticles in AOT reverse micelles, and then the composites can be recovered by precipitation using compressed CO₂ as an antisolvent. The phase structures and morphologies of the obtained composites were
characterized by X-ray diffraction and transmission electronic micrographs. The results illustrate that the smaller molar ratio of water to surfactant of the reverse micelles and higher pressure of CO$_2$ are favourable for producing smaller particles. The absorbance of ZnS/CdS was centred at 367 nm, which is between that of pure CdS (392 nm) and that of pure ZnS nanoparticles (270 nm) in reverse micelles. The absorbance was decreased gradually with the increase in pressure and disappears as the pressure reaches a high enough value. This indicated that the CdS and ZnS nanoparticles in the reverse micelles can be co-precipitated completely by controlling the pressure. XRD results reveal that the product is a composite consisting of face centered cubic ZnS and CdS nanoparticles. The particle size and size distribution data were obtained by measuring the diameter of the particles in the TEM micrographs. The size and size distribution of the composites can be tuned by controlling the water in the reverse micelles and CO$_2$ pressure. They pointed out that this method has many potential advantages for the production of composite nanoparticles.

Lixin Cao et al., (2004) successfully prepared ZnS/CdS/ZnS quantum dot quantum well in AOT micelles and were characterized by absorption spectroscopy and fluorescence spectroscopy. The absorption spectrum has two large shoulders at 280 and 380 nm attributed to the electron transition of size-quantized ZnS and CdS nanoparticles, respectively. This is a characteristic of the superposition of the ZnS spectrum and the CdS spectrum. Luminescence in the region of 350-600 nm was observed. The luminescence from CdS was enhanced by the complete ZnS shell, which may be the result of the decrease in the defects on the surface of the CdS well, which were assumed to act as centers for radiationless recombination.

Dumitrache et al., (2005) have demonstrated the synthesis of iron core–oxide shell nanocomposite by a two-step method. In a first step, using a cross-flow configuration, the laser radiation heated a gas phase mixture containing iron pentacarbonyl (vapours) entrained by an ethylene flow. Secondly, a carefully controlled in situ passivation of the freshly formed pyrophoric iron nanoparticles created a protective iron oxide shell.
The produced nanoparticles with core–shell features were analyzed by TEM, XRD, SAED and Raman spectroscopy. They were produced iron particles with 14 nm in diameters and about 4 nm in oxide shell thickness. Raman spectroscopy was used to monitor the oxidation/passivation process. Much more XRD analysis clarified the SAED interpretation in the sense that in the region 0.21–0.20 nm α-Fe peak brings the most important contribution. The morphology of the nanocomposite particle was determined as being formed by α-Fe core surrounded by γ-Fe₂O₃/Fe₃O₄ shell.

Yu Xiaodan et al., (2006) prepared photoactive ZnS/TiO₂ nanocomposites via microemulsion-mediated solvothermal method. The structure, composition, physicochemical property, and morphology of the composites were characterized by powder X-ray diffraction (XRD), Raman scattering studies, UV diffuse reflectance spectroscopy (UV/DRS), photoluminescence (PL) spectroscopy, and transmission electron microscopy (TEM). XRD results show that the composites were cube-shaped with particle sizes of 10 to 15 nm, and the phase structure for ZnS and TiO₂ in the composites was cubic and anatase, respectively. Raman scattering studies indicate that there exists the chemical interaction between the cubic ZnS and the anatase TiO₂ in as-prepared composites. The high magnification TEM images show that the ZnS/TiO₂ composite particles were cube-shaped with an average size of 10 to 15 nm. The composites exhibit new UV absorption characteristics compared with the bulk TiO₂ or ZnS. The composites show efficient visible-light photocatalytic activity to degrade the aqueous parathion methyl, which was higher than that of a commercially available anatase TiO₂, pure anatase TiO₂, or cubic ZnS nanoparticles. This efficient photocatalytic activity was attributed to the formation of the pre associated complex between the ZnS/TiO₂ composite. They pointed out that the strong adsorption interaction between the parathionmethyl molecules and the ZnS/TiO₂ composites were responsible for this enhancement photocatalytic activity.

Meng et al., (2007) have studied Photoluminescence properties of single crystalline ZnO/CdS core/shell one-dimensional nanostructures. ZnO/CdS core/shell one-dimensional nanostructures were synthesized...
using ZnO nanorod arrays as templates, which were fabricated by a vapour transport process. CdS shells with various thicknesses were epitaxially grown on the ZnO nanorod arrays by metal organic chemical vapour deposition. The photoluminescence properties of the ZnO/CdS core/shell nanostructures were varied with different CdS shell thicknesses. PL measurements indicated that the emission of CdS was improved by ZnO nanorods in the core/shell structures of ZnO/CdS. A carrier transition process from ZnO to CdS was assumed to induce the enhancement of CdS photoluminescence. XRD pattern of core/shell nanostructure show both ZnO and CdS have wurtzite structures. Selected area electron diffraction measurement revealed that both ZnO cores and CdS shells were single crystalline growing along the c-axis. SAED pattern showed such structures are single crystal, which may be interesting for future device applications.

**Suraj Kumar Tripathy et al., (2007)** reported the synthesis of II-VI semiconductor (ZnO\textsubscript{rod}@SnO\textsubscript{2}) nanocomposite materials with core-shell morphology. ZnO nanorods were grown by hydrothermal technique using zinc acetate as the reactant. SnO\textsubscript{2} was coated on the nanorods by a simple technique of colloid chemistry. The formation of tin dioxide shell on the ZnO nanorods was confirmed by the TEM images of the resultant materials. The formation of the nanocomposite was also supported by XRD pattern. The approximate size of the SnO\textsubscript{2} nanoparticles is 10 nm and the thickness of the shell is about 50 nm. From XRD pattern showed that both the materials exist in perfect crystalline phases and retain their physical structure and hence confirmed to form a nanocomposite rather than alloy. The effect of tin dioxide shell on the optical properties of ZnO was investigated by photoluminescence spectroscopy and Raman spectroscopy. From the PL spectra, they concluded that the optical response of the ZnO remains mostly unaltered by the coating. The enhancement of the band edge luminescent peak may be due to passivation of the ZnO surface by the tin dioxide shell, which effectively eliminates the dangling bonds or the surface states that form traps for photo generated carriers. The Raman spectra reveal the presence of zinc oxide and tin dioxide. At the same time,
the shift of the main Raman band of tin dioxide indicates that the coating material has distorted crystallinity.

**Hui Zhang et al., (2007)** have investigated the cathodoluminescence (CL) properties including intensity and distribution of the band to band and defect emission of the flower-like ZnO, ZnO/ZnS core–shell and tube-like ZnS nanostructures. The flower-like ZnO nanostructures show the two broad CL emissions, i.e. UV emission at 380 nm due to band to band emission and yellow emission at 600 nm induced by interstitial oxygen. Moreover, the UV emission distribution of the flower-like ZnO nanostructures consisting of ZnO nanorods with hexagonal plane was not uniform due to the waveguide. Furthermore, the UV emission of ZnO has been greatly enhanced and the yellow emission has been inhibited by the formation of ZnO/ZnS core-shell nanostructures in the sulfuration process due to the elimination of interstitial oxygen. The SEM and CL mapping images of the tube-like ZnS nanostructures show the uniform and weak defect emission due to S vacancies.

**Litty Irimpan et al., (2008)** presented the nonlinear optical properties of ZnO-TiO$_2$-SiO$_2$ nanocomposites prepared by colloidal chemical synthesis. Nonlinear optical response of these samples was studied using nanosecond laser pulses at an off-resonance wavelength. The nonlinearity of the silica colloid is low and its nonlinear response can be improved by making composites with ZnO and TiO$_2$. These nanocomposites show self-defocusing nonlinearity and good nonlinear absorption behaviour. The room temperature absorption spectra of ZnO-TiO$_2$-SiO$_2$ nanocomposites show red shift and the exciton oscillator strength increases as a function of the ZnO content. The nonlinearity of the sample is caused by two photon absorption followed by weak free carrier absorption and nonlinear scattering. The significant optical nonlinearities of the pure semiconductor nano colloid at 523 nm were reported to have the nonlinear refractive index of the order of $10^{-16}$ to $10^{-20}$ m$^2$/W. The nonlinear refractive index and the nonlinear absorption increases with increasing ZnO volume fraction. The large enhancement of the third-order nonlinearity of the silica aerogel is due to the quantum confinement effect of bound electrons, which was induced by the
nanostructure nature of the sample. ZnO-TiO$_2$-SiO$_2$ is a potential nanocomposite material for the development of nonlinear optical devices with a relatively small limiting threshold.

**Saraswathi Amma et al., (2008)** reported the optical properties of manganese (Mn$^{2+}$) doped, polyvinyl pyrrolidone (PVP) capped cadmium sulphide (CdS) nanoparticles coated with zinc sulphide (ZnS). Colloidal solution of Mn$^{2+}$ doped CdS nanoparticles capped with PVP was synthesized using methanol as solvent. PVP was used to control the particle size and to prevent agglomeration. The absence of exciton peak or a second absorption edge in the UV region as well as the red shift in the absorption spectra with an increase in zinc sulphide content indicates the formation of (CdS-PVP) Mn/ZnS coreshell structure. Mn$^{2+}$ doping is expected to help in increasing the CdS band edge photoluminescence (PL) emission. Photoluminescence emission spectra recorded for (CdS–PVP) Mn nanoparticles showed two emission peaks, one at 416 nm and the other at 586 nm which was attributed to Mn$^{2+}$ emission. Intensity of Mn$^{2+}$ peak increased with increase of Mn$^{2+}$ content. Mn$^{2+}$ emission disappears when ZnS was coated over the CdS core, resulting in pure CdS band edge emission. The PL intensity of (CdS-PVP) Mn/ZnS was more than that of (CdS-PVP) Mn nanoparticles. X-ray diffractogram of (CdS-PVP)/Mn/ZnS coreshell particles show cubic structure and no separate peaks corresponding to Mn or ZnS. The presence of a small foreign inclusion or a shell layer over the core does not affect the XRD peaks of the core particles. TEM images show well defined and nearly monodispersed core shell nanoparticles. The particle size of ZnS coated sample was comparatively larger (5 nm) than the uncoated ones (4 nm).

**Fang Na GU et al., (2008)** have synthesized a new photoluminescent ZnS/ZnO/SBA-15 mesoporous materials. In which, ZnO nanoparticles that are modified with ZnS and confined in SBA-15, has been prepared through the controllable sulfuration at relatively low temperature (40$^\circ$C). The resulting samples are characterized by XRD, nitrogen adsorption-desorption and photoluminescence (PL) spectroscopy. It possesses relatively high surface area and thermal stability and exhibiting dramatically enhanced blue emission at the expense of the UV
emission. The XRD patterns of the samples at the low-angle region (2θ = 0.5–7°) display three reflection peaks of typical SBA-15, indicated the preservation of hexagonal ordered structure in the composite after the incorporation of ZnO and the formation of ZnS particles. These novel ZnS–ZnO composites were confined in mesoporous SBA-15. The PL intensity of ZnS/ZnO/SBA-15 samples was affected by the temperature and time of sulfuration. They pointed out that these materials have potential applications for advanced luminescence materials.

Prinsa Verma et al., (2009) synthesized ZnO nanocrystals by a simple co-precipitation method and Zinc Oxide-Sulphide (ZnO-ZnS) core-shell nanocomposites were successfully fabricated by sulfidation of ZnO nanocrystals via a facile chemical synthesis at room temperature. The as-obtained samples were characterized by X-ray diffraction and Transmission electron microscopy. The XRD peak positions of the ZnO/ZnS core-shell nanocomposites had two structures of ZnO and ZnS phases. The results showed that the pure ZnO nanocrystals were hexagonal wurtzite crystal structures and the ZnS nanoparticles were spherical structure. The average size of the ZnS nanoparticles was calculated about 10 nm according to the Scherrer formula. Similarly, the average size of bare ZnO nanoparticles was 25 nm. TEM images of ZnO/ZnS core-shell nanocomposites show that ZnS nanoparticles with the size of about 10 nm grow on the surface of the ZnO nanocrystals. The ZnO/ZnS core-shell nanocomposites exhibited a spherical shape with a mean diameter of 20 nm. The PL spectra of ZnO/ZnS core-shell nanocomposites showed an enhanced broad blue emission. This enhancement was due to higher band gap of ZnS than ZnO. It suppressed the tunnelling of the charge carriers from the core to the ZnS nanoshell. As a result, more photo generated electrons and holes were confined inside the ZnO core, giving rise to a high quantum yield. The optical study of ZnO-ZnS core-shell nanocomposites revealed that integrated photo luminescent effect of ZnO and ZnS.

Yinshu Wang et al., (2009) have synthesized ZnO/ZnS core shell nanostructures from ZnO nanorods by a chemical route. ZnO core is wurtzite structured single crystal and ZnS shell consists of nanoparticles
with Zinc-blend structure. The morphology of ZnO and ZnO/ZnS core shell nanostructures studied through Transmission Electron Microscopy. TEM images show no cavities in ZnO nanorods. The SAD pattern indicates that the particles have zinc-blend structure. The formation of zinc-blend structured ZnS is due to the low growth temperature. The PL spectra of ZnO nanorod and ZnO/ZnS nano core shell have strong emission around 400 nm. The calculated band gap of ZnO and ZnS are 3.3 eV, 3.7 eV respectively. The emission centred at 400 nm was due to ZnO band edge emission. They pointed out that the stronger emission of ZnO/ZnS nanostructures indicates the growth of ZnS on ZnO nanorods, which enhance the ZnO nanostructure band edge emission.

**Anil Kumar et al., (2009)** synthesised and demonstrated photophysics of colloidal ZnS/PbS/ZnS nanocomposites. The formation of monolayer of ZnS at the interface of ZnS/PbS precursor results in the formation of ZnS/PbS/ZnS nanoheterostructure containing PbS in the well with significantly improved fluorescence. The electronic properties of the nanocomposite have been examined as a function of thickness of ZnS shell and in the presence of excess [Zn$^{2+}$]. The addition of Zn$^{2+}$ further improves the charge separation in this system. The monolayer of ZnS shell enhances the oscillator strength of optical transition in the core–shell structure due to increase in quantum confinement of charge carriers and radiative recombination in shallow traps, whereas the formation of multilayer induced the radiative recombination involving mainly deeper traps. The addition of excess Zn$^{2+}$ to these particles enhances their photostability and improves the charge separation. As prepared ZnS/PbS/ZnS nanocomposite has different nanodomains in which electronic interactions and the charge dynamics could be manipulated by exciting the nanocomposite as a whole. Manipulation of electronic properties in these systems can be exploited for the fabrication of optoelectronic devices and designing of fluorescent sensors. Such a system might be encountered in galena-sphalerite mixed sulfide ore occurring in nature consisting of excess ZnS and little PbS.

**Soumitra Kar et al., (2009)** have synthesised S-doped ZnO nanonails and ZnS/ZnO core shell nanorods by a low temperature based
simple one step solvothermal approach using Zn foils as the precursor as well as the substrate. These S-doped ZnO nanostructures exhibited intense green emission property at room temperature. The PL spectra of the ZnO/ZnS nanorods showed three emission (UV [358 nm], Blue [411 nm] and Green [490 nm]) peaks. The sharp UV peak could be attributed to the band edge emission of ZnS. The XRD pattern of the sample synthesised with 0.1 g TU reveal that the formation of cubic ZnS as the predominant phase along with weak wurtzite ZnO. TEM image of the S-doped ZnO sample show nail like morphology with hexagonal cap followed by a relatively thin long needle shaped stem portion. The HRTEM image of the stem region of S-doped ZnO nail show hexagonal crystal structure of ZnO. Similarly the HRTEM image of ZnS/ZnO core shell nanorods shows the formation of small ZnO nanocrystal surrounding the ZnS nanorods surface. The morphological and compositional identities of the nanorods were determined by EDAX pattern. The TEM and EDAX studies indicated that use of Zn foil as the source is the key for the formation of ZnS/ZnO core shell nanorods by solvothermal technique.

Sonalika Vaidya et al., (2010) synthesized core shell nanocomposites of CdS@TiO$_2$ and ZnS@TiO$_2$ by the reverse micellar route. Titanium hydroxyacrylate has been used for the first time as the shell forming agent for the formation of TiO$_2$ shell over CdS and ZnS, which ensures the formation of shell over the core nanoparticles due to its slow rate of hydrolysis and thus forms core-shell nanocomposites. Pure CdS was found to crystallize in a cubic structure with a crystallite size of 3 nm. PXRD pattern of CdS@TiO$_2$ core-shell nanocomposite (molar ratio of Cd and Ti as 1:0.1) shows the formation of cubic CdS of size 3-5 nm. CdS particles with size 5-6 nm were obtained through HRTEM. The lattice planes correspond to (111) plane of cubic CdS. CdS@TiO$_2$ core-shell nanocomposites particles with size 3-5 nm were also observed in the HRTEM image. HRTEM studies of ZnS nanoparticles obtained by the reverse micellar route show particles with size of 3-4 nm. The lattice planes correspond to (111) planes of cubic ZnS indicate single crystalline nature. From UV studies band at around 466 nm was observed for pure CdS nanoparticles while absorption bands at 445 and 450 nm were
observed for CdS@TiO$_2$ nanocomposites with molar ratio of Cd and Ti as 1:0.1 and 1:0.05 respectively. UV-Vis studies were also carried out on nanocrystalline ZnS and ZnS@TiO$_2$ core-shell nanocomposites. Blue shift was observed for pure nanoparticles and core-shell nanocomposites of ZnS which suggest strong quantum confinement. No change in the particle size of nanoparticles and nanocomposites of ZnS. PL studies of CdS nanoparticles show a band at 478 nm which is red shift. This red shift of the emission band of CdS nanoparticles can be attributed to the stoke shift. The emission band is blue shifted for CdS@TiO$_2$ core-shell nanocomposites. This could be attributed to the smaller particle size of CdS in CdS@TiO$_2$ core-shell nanocomposites. PL studies on cubic ZnS and TiO$_2$ nanoparticles show a band at 385 nm which is attributed to shallow donor-acceptor transitions for ZnS and radiative annihilation of excitons for TiO$_2$ nanoparticles. PL studies on ZnS@TiO$_2$ core-shell nanocomposites also show a band at 385 nm which can be attributed to either of the above transitions for ZnS or TiO$_2$ or both.

**Narjes Ghows and Mohammad H. Entezari (2011)** have synthesised core-shell nanocrystal (CdS/TiO$_2$) at low temperature by micro-emulsion under ultrasound. The nanoparticles were characterized by X-ray diffraction (XRD), UV-visible spectroscopy, energy dispersed analysis of X-ray (EDAX), HRTEM and SEM. CdS nanoparticles were easily combined with TiO$_2$ through a reaction in micro-emulsion by means of ultrasonic irradiation. The formation of a uniform layer of TiO$_2$ on the CdS leads to an increase of the size of the nanoparticles. Ultrasonic irradiation could control the hydrolysis and condensation of TTIP and the formation of a gradient TiO$_2$ shell around the CdS core. The crystalline phases of TiO$_2$ and CdS in the resulting particles were anatase and hexagonal respectively. The optical investigation revealed a red-shift in the absorption by increasing the amount of TiO$_2$ in the nanocomposites. The result of EDAX measurement reveals that the core-shell nanocrystals have a high purity. HRTEM images show that TiO$_2$ was uniformly coated on the surface of CdS and lead to an enlargement of the nanoparticle size. The average size of the bare CdS nanoparticles was about 2-3 nm in diameter and in case of core-shell structure the size was found to be about 9 nm.
The SEM and TEM images indicate that TTIP hydrolysis in the presence of CdS nanoparticles lead to the formation of large irregular aggregates.

**Murugadoss and Ramasamy (2012)** have successfully synthesized ZnO, ZnS and ZnO/ZnS nanocomposites by chemical method in an air atmosphere. Water–ethanol matrix was used as solvent. The as-obtained samples were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), UV-Visible and Photoluminescence (PL) spectrophotometer. The XRD results showed that the ZnS nanoparticles were cubic in structure with the size of about 5 nm grown on the surface of the hexagonal ZnO nanocomposites. The FWHM of the mixed structures of ZnO/ZnS nanocomposites was significantly increased than the uncoated ZnO crystalline structure. It may be due to effect of the mixed solvent in size reduction. The TEM images show the spherical shape ZnO/ZnS core–shell nanoparticles. The corresponding selected area electron diffraction pattern confirmed the formation of mixed structures, which is in good agreement with the XRD results. The SEM images of uncoated ZnO and ZnS nanoparticles showed that the particles were highly aggregated due to the absence of capping agent. The average diameter of the ZnO/ZnS core-shell nanoparticles was about 10 nm. The results obtained from XRD, SEM and TEM studies confirmed the existence of the ZnO/ZnS nanocomposites. A strong absorption peak of the ZnO/ZnS core-shell nanoparticles was centred at 316 nm. The optical absorption spectroscopy shows strong blue shift absorption edge of the prepared samples with respect to that of bulk. The blue shift is a distinct signature of nanocomposites formation. The optical study of ZnO/ZnS nanocomposites showed an enhanced PL emission in visible region. The photoluminescence property of the ZnO/ZnS core/shell nanocomposites was varied with respect to the shell thicknesses. PL quenching was observed by increasing of shell thickness on ZnO. For the first time, they observed the PL quenching (in UV and blue emission) in ZnO/ZnS composites. It was found that the interaction between the ZnO and ZnS nanoparticle greatly influenced the optical and electrical properties of the obtained ZnO/ZnS composites.
Murugadoss (2012) successfully synthesized uncoated ZnO, CdS and ZnO/CdS core-shell nanocomposites by a chemical method in an atmosphere. The obtained samples were characterized by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), UV-Visible and Photoluminescence (PL) techniques. XRD pattern shows mixed structure of ZnO (hexagonal)/CdS (cubic) nanocomposites. When the CdS nanoparticles were coated on ZnO nanowires, the width of the ZnO/CdS nanocomposites increased from 8 nm to 16-20 nm. The SAED pattern of the ZnO/CdS nanocomposites shows the formation of mixed structure ZnO/CdS nanocomposites. The TEM images confirmed the formation of well crystalline hexagonal ZnO nanorods and cubic CdS nanoparticles with particle size 6 and 4 nm respectively. The optical absorption shows strong blue shifted absorption edge of the prepared samples with respect to that of the bulk. Based on the peak positions in the absorption spectra, the calculated sizes are 6.2 nm for ZnO and 4.3 nm for CdS nanoparticles. Study on the PL spectra of core-shell ZnO/CdS nanocomposites at room temperature revealed narrow and enhanced blue emission. This result provide good indication of tuning the visible emission of the ZnO nanostructures by the formation of ZnO/CdS core-shell nanocomposites, which promise applications in the fields of luminescence, solar cell devices, electronics and sensors.

Shuling Liu et al., (2013) have synthesized urchin like ZnS/CdS semiconductor composites by combining solvothermal route with homogeneous precipitation process. The as obtained samples were characterized by XRD, EDX, TEM, HR-TEM and FE-SEM. The results show that the composites were comprised of the hexagonal structure ZnS and CdS. The CdS nanoparticles were assembled on the surfaces of the thorns of urchin-like ZnS. In addition, the optical properties and photocatalytic activities of the as prepared ZnS/CdS composites toward some organic dyes were separately investigated. It was found that the ZnS/CdS composites exhibit excellent photocatalytic degradation activity for the organic dyes under UV irradiation, as compared to corresponding pure ZnS and commercial anatase TiO$_2$. This enhanced activity may be related to the modification of CdS nanoparticles on the surface of ZnS urchins.
Jiangang Jiang et al., (2013) synthesized the uniform ZnO/ZnS/CdS core-shell nanorod film electrodes by a two-step ion exchange method. The crystal structure, morphology, composition and optical property of as-prepared films were characterized by X-ray diffraction (XRD), Raman, Scanning electron microscope (SEM), Transmission electron microscope (TEM), Energy dispersive X-ray Detector (EDX) and UV-Vis techniques. The results showed that the ZnO nanorod arrays can be used as sacrificial templates to synthesize uniform ZnS layer and further transform into CdS by simple ion-exchange approach. The intimate contact between core and shell can be observed by high-resolution TEM image. The CdS content in the films can be adjusted easily by changing the reaction temperature. They pointed out that the ZnO/ZnS/CdS nanorod films can be used in the photoelectrochemical (PEC) hydrogen production.

Fei Li et., (2009) prepared ZnO/ZnS nanostructured materials by a simple chemical synthesis. X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) techniques are used to characterize the ZnO nanorods and the novel ZnO/ZnS nanocomposites. The results show that the ZnO nanorods are wurtzite crystal structure and the ZnS nanoparticles are sphalerite structure with the average size of about 10 nm grown on the surface of the ZnO nanorods. The measurements of the optical properties reveal that ZnO/ZnS nanocomposites have integrated the photoluminescent effect of ZnO and ZnS.

Daixun Jiang et al., (2009) have synthesised Core/Shell ZnS:Mn/ZnO nanoparticles by precipitation method. The influence of ZnO shell thickness on the luminescence properties of Mn-doped ZnS nanoparticles was studied. The formation of ZnO shells on the surface of ZnS:Mn nanoparticles was confirmed by X-ray diffraction (XRD) patterns, high-resolution TEM (HRTEM) images, and X-ray photoelectron spectroscopy (XPS) measurements. The photoluminescence excitation (PLE) spectra exhibited a blue shift in ZnO-coated ZnS:Mn nanoparticles compared with the uncoated ones.
Benxia Li and Yanfen Wang (2011) have fabricated ZnO/CdS flowerlike nano heterostructure by a facile two-step precipitation method for use in photocatalytic degradation of organic dyes. The as-prepared samples were characterized by X-ray diffraction, scanning electron microscopy, and UV–vis spectroscopy, demonstrating that the microstructure of the ZnO/CdS nano-heterostructure is composed of flower-like ZnO modified by CdS nanoparticles.

Anita Jain et al., (2012) have prepared zinc sulphide (ZnS:Mn)/zinc oxide (ZnO) core-shell nanostructures by a chemical precipitation method and observed the effect of ZnO concentration on the fluorescent nanoparticles. The morphological studies have been carried out using X-ray diffraction (XRD) and transmission electron microscopy. It was found that diameter of ZnS:Mn nanoparticles was around 4-7 nm, each containing primary crystallites of size 2.4 nm which was estimated from the XRD patterns. Band gap studies were performed by UV-visible spectroscopy and red shifts in absorption spectra have been observed.

Kanmani et al., (2012) were synthesized Core/shell structured ZnO nanorod/CdS nanoparticles by chemical co-precipitation method. The structural characterization by XRD confirms the formation of high crystalline wurtzite structured ZnO and mixed phase of CdS. SEM images of the ZnO/CdS composites reveal the formation of ZnO nanorods with typical diameters of about 0.1–0.2 µm and the coated ~4 nm sized CdS nanoparticles on ZnO nanorods. UV-Vis absorption spectra of CdS covered ZnO nanorods extend its absorption band up to 521.8 nm, favouring the effective photon capture in visible region.

Sarmila Dutta et al., (2012) have been fabricated ZnO/ZnS core-shell structure by simple chemical method. XRD and HRTEM data reveal the formation of good shell coating over the ZnO core. Photoluminescence spectra shows that emission intensity is at least four times higher when coated with ZnS compare to bare ZnO. Band gap is also calculated using UV-vis spectroscopy.

Manu Sharma and P. Jeevanandam (2012) have been synthesised Cadmium sulfide coated zinc oxide hierarchical nanocomposites at room temperature by a simple solution based method. The nanocomposites were
synthesised using different concentrations of thioacetamide, cadmium salts, and also by varying the reaction time. The optical properties were investigated by UV–visible diffuse reflectance and photoluminescence spectroscopy techniques.

Simmi Sharma and Santa Chawla (2013) were prepared ZnO/ZnS core shell nanoparticles by co-precipitation method at room temperature. Formation of epitaxial hexagonal ZnS over wurtzite ZnO core particles have been confirmed by x-ray diffraction and transmission electron microscopy studies. The core ZnO nanoparticles show prominent UV emission which enhances appreciably due to ZnS shell formation in ZnO/ZnS core/shell particles.

Habibi MH and Rahmati MH (2014) has been synthesized ZnO@CdS core-shell nano-structure by simple chemical precipitation method. The morphology and structure of the ZnO@CdS core-shell nano-structures have been confirmed by field-emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) measurements. The results showed that the ZnO@CdS core-shell nano-structure is mixed cubic and hexagonal structures. Optical study showed that band gaps of ZnO@CdS core-shell nanocomposites were red shifted by increasing the cadmium concentration.

1.17 OBJECTIVE OF THE WORK

The studies of semiconductor core shell nanoparticles have advanced at a rapid pace because of the fact that their optical properties can be systematically tuned by varying their sizes. Core shells are compounds with specific characteristics and varied uses. Their high fluorescence and narrow spectrum shape makes them an excellent tagging alternative to conventional fluorescent dyes. During the past three decades, extensive research has been performed on the properties and uses of core shell nanoparticles. Overcoating nanocrystallites with higher band gap inorganic materials have been shown to improve the photoluminescence quantum yields by passivating surface non radiative recombination sites.
In the present work, ZnO, ZnS and CdS were selected based on their properties and applications. Hence an attempt has been made to synthesize water soluble ZnO/CdS/ZnS and ZnS/ZnO/CdS core shell nanocomposites through simple chemical method.

**The following are objectives of the present work.**

- To synthesis pure ZnO, ZnS and CdS nanoparticles.
- To synthesis ZnO/CdS/ZnS and ZnS/ZnO/CdS multilayer core-shell nanocomposites by varying the shell thickness.
- To choose the best concentration of shell thickness.
- To characterize the structural, morphological and optical properties of pure ZnO, ZnS and CdS nanoparticles.
- To study the structural, morphological and optical properties of ZnO/CdS/ZnS and ZnS/ZnO/CdS multi layer core-shell nanocomposites.
- To characterize the thermal properties of ZnO/CdS/ZnS and ZnS/ZnO/CdS multilayer core-shell nanocomposites.

Optical properties of both uncoated and multilayer coated nanocomposites materials were studied using UV-Vis and photo luminescence spectroscopy. The TEM and SEM were used to obtain morphological information of nanocomposites. Crystalline phases of nanocomposites were identified using XRD technique. Finally, the thermal properties of nanocomposites were studied by TGA-DTA technique.
CHAPTER II

MATERIALS AND METHODS