1. Introduction

Abstract

A preface to nanoscience and nanotechnology provides the theoretical background of nanomaterials, their nomenclature and classification. Here we elucidate some of the relevant charismatic properties of these low dimensional structures. Nanomaterials are employed for diverse potent applications by exploiting their novel characteristics and therefore, nanotechnology is often referred as the 'technology of tomorrow'. The work presented in this thesis mainly deals with the synthesis and characterization of semiconductor nanomaterials in general and ZnS & CdS nanoparticles in particular. A brief account of the few popular procedures to fabricate these nanomaterials along with their fundamental properties is provided. The motivation behind our work is driven by the blooming interest in the investigation of the exciting and unforeseen properties of ZnS & CdS nanoparticles, which make them smart materials for a wide range of applications.
1.1 Preface to Nanoscience and Nanotechnology

1.1.1 Historical Review and Basic Definitions

Nanoscience is the study of the properties of materials (living or non-living) and their manipulation at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale. Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale. Nanotechnology is based on the smallest unit of matter to engineering new materials and devices atom by atom, aiming at achieving superior properties and performance through atomic-scale architecture [1].

The prefix ‘nano’ is derived from the Greek word for ‘dwarf’. One nanometer (nm) is equal to one-billionth of a meter, $10^{-9}$ m. A human hair is approximately 80,000nm wide, and a red blood cell approximately 7000nm wide. Although a broad definition, International Union of Pure and Applied Chemists (IUPAC) categorizes nanomaterials as those which have structured components with at least one dimension less than 100nm.

The conceptual underpinnings of nanotechnologies were first laid out in 1959 by the physicist Richard Feynman, in his foresightful lecture ‘There’s plenty of room at the bottom’ at the winter meeting of the American Physical Society at Caltech [2]. Feynman explored the possibility of manipulating material at the scale of individual atoms and molecules, imagining the whole of the Encyclopaedia Britannica written on the head of a pin and foreseeing the increasing ability to examine and control matter at the nanoscale. The term ‘nanotechnology’ was not used until 1974, when Norio Taniguchi, a researcher at the University of Tokyo, Japan used it to refer to the ability to engineer materials precisely at the nanometer level [3].

The size range that holds so much interest is typically from 100nm down to the atomic level (approximately 0.2 nm), because it is in this range (particularly at the lower end) that materials can have different or enhanced properties compared to the same materials at a larger size. The two main reasons for this change in behaviour are an increased relative surface area, and the dominance of quantum effects. An increase in surface area (per unit mass) will result in a corresponding increase in chemical reactivity,
making some nanomaterials useful as catalysts to improve the efficiency of fuel cells and batteries. As the size of matter is reduced to tens of nanometers or less, quantum effects can begin to play a role, and these can significantly change a material's optical, magnetic or electrical properties. In some cases, size-dependent properties have been exploited for centuries. For example, gold and silver nanoparticles (particles of diameter less than 100 nm) have been used as coloured pigments in stained glass and ceramics since the 10th century AD [4]. Depending on their size, gold particles can appear red, blue or gold in colour. The challenge for the ancient (al)chemists was to make all nanoparticles the same size (and hence the same colour), and the production of single-size nanoparticles is still a challenge today.

Nanoscience is concerned with understanding these effects and their influence on the properties of a material. Nanotechnologies aim to exploit these effects to create structures, devices and systems with novel properties and functions due to their size. The changes in the physicochemical properties of these 'Tailor-made' materials can be tuned by controlling their sizes and as a result nanomaterials can be exploited for numerous vital applications.

Nanotechnologies can be regarded as genuinely interdisciplinary, and have prompted the collaboration between researchers in previously disparate areas to share knowledge, tools and techniques. An understanding of the physics and chemistry of matter and processes at the nanoscale is relevant to all scientific disciplines, from chemistry and physics to biology, engineering and medicine. Indeed, it could be argued that evolutionary developments in each of these fields towards investigating matter at increasingly small size scales has now come to be known as 'nanotechnology'.

1.1.2 Classification of Nanomaterials

There are several types of nanomaterials, which are either naturally occurring or can be artificially synthesized. Some of the most popular nanomaterials are nanoparticles, nanocrystals, nanowires, nanotubes, nanorods, nanobelts, nanowhiskers, nanodisks, nanocages, fullerene, buckyballs. When these nanomaterials achieve the size range of quantum mechanically confined systems, they are respectively called as quantum dots (QD), quantum crystals (QC), quantum wires, quantum wells and so on.
Materials that have one dimension in the nanoscale (and are extended in the other two dimensions) are layers, such as a thin films or surface coatings. Materials that are nanoscale in two dimensions (and extended in one dimension) include nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles, for example precipitates, colloids and quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials, made up of nanometer-sized grains, also fall into this category. Nanoparticles are often defined as particles of less than 100nm in diameter. In line with our definition of nanoscience and nanotechnologies, we classify nanoparticles to be particles less than 100nm in diameter that exhibit new or enhanced size-dependent properties compared with larger particles of the same material.

1.1.3 Synthesis of Nanomaterials

In some sense, nanoscience and nanotechnologies are not new. Many chemicals and chemical processes have nanoscale features — for example, chemists have been making polymers, large molecules made up of tiny nanoscaler subunits, for many decades. Nanotechnologies have been used to create the tiny features on computer chips for the past 20 years. The natural world also contains many examples of nanoscale structures, from milk (a nanoscale colloid) to sophisticated nanosized and nanostructured proteins that control a range of biological activities, such as flexing muscles, releasing energy and repairing cells. Nanoparticles occur naturally, and have been created for thousands of years as the products of combustion and cooking (food).

However, it is only in recent years that sophisticated tools have been developed to investigate and manipulate matter at the nanoscale, which have greatly affected our understanding of the nanoscale world. A major step in this direction was the invention of the scanning tunnelling microscope (STM) in 1982 [5, 6], and the atomic force microscope (AFM) in 1986 [7]. These tools use nanoscale probes to image a surface with atomic resolution, and are also capable of picking up, sliding or dragging atoms or molecules around on surfaces to build rudimentary nanostructures.

In a now famous experiment in 1990, D. Eigler and E. Schweizer at IBM moved xenon atoms around on a nickel surface to write the company logo, a laborious process which took a whole day under well-controlled conditions [8]. The use of these tools is not
restricted to engineering, but has been adopted across a range of disciplines. AFM, for example, is routinely used to study biological molecules such as proteins.

The technique used by Eigler and Schweizer is only one in the range of ways used to manipulate and produce nanomaterials, commonly categorized as either 'top-down' or 'bottom-up'. 'Top-down' techniques involve starting with a block of material, and etching or milling it down to the desired shape, whereas 'bottom-up' involves the assembly of smaller sub-units (atoms or molecules) to make a larger structure. The main challenge for top-down manufacture is the creation of increasingly small structures with sufficient accuracy, whereas for bottom-up manufacture, it is to make structures large enough, and of sufficient quality, to be of use as materials. These two methods have evolved separately and have now reached the point where the best achievable feature size for each technique is approximately the same, leading to novel hybrid ways of manufacture.

Some of the most popular methods, derived from the biological, chemical and physical sciences, to synthesize the nanomaterials are mentioned in the following sections.

1.1.3.1 Biological methods:
The atom-by-atom engineering approach starts from the most fundamental units of matters for constructing devices. The approach may not meet the needs of large-scale fabrication due to limited productivity. Hence one must on self assembly processes, such as in biology, to achieve atomic scale engineering at unmatched speed and precision.

Small living microbes in nature belong to the nanoscale. The diameter of a DNA molecule is less than 3nm, and the diameter of a protein molecule is about a few nanometers. Therefore, nanobiology and nanomedicine have many virgin fields that remain to be explored. As observed by a researcher: “When some matter can be designed and manufactured in biomolecular scales, the prospects will be wonderful. This is the excitement of nanoscience and nanotechnology” [1].

Self-assembly is the way that nature creates plants and animals – it is the self-organization, self-replica and self-repair process. Scientists have been learning of using self-assembly to create materials that can have some unique properties.
Of late researchers have demonstrated ordering of QDs using genetically engineered viruses. They could take advantage of these vital strong points by harnessing billions of phages to build various useful materials molecule-by-molecule [9, 10].

1.1.3.2 Chemical methods:

Most popular procedures to prepare nanomaterials come under this category. Till date the largest number of chemical synthesis techniques have been proposed and many of them are widely practiced to fabricate nanostructured materials. Chemical precipitation method involves mixing of two or more chemical 'precursors', and/or a catalyst, to form a 'gel'. The gel is dried under pre-determined temperatures, and further reduced under H₂, to form nanopowders of various materials, e.g. SiC, BaTiO₃, and W-Cu, Mo-Cu etc.

Monodispersed metal and semiconductor nanoparticles are synthesized by employing the potential of reverse micellar method where an excellent control on the size of nanoparticles is achieved by the size of reverse micellar microreactor [11]. The major drawback of the chemical methods is their low yield of nanomaterials. For example, in the chemical precipitation technique the production rates are close to 10-50 g/day. Other major disadvantages are the agglomeration of powders and their oxidation due to use of liquid chemical precursors. Sol-gel technique in its present state encounters serious problems in providing a continuous size control and narrow size distribution [12].

1.1.3.3 Physical methods:
The synthesis of nanomaterials by physical methods can be broadly classified as originating from deposition, sputtering, plasma and growth techniques. A brief account of the most common practices to prepare these nanomaterials is presented here.

In the method of Ball milling/Mechanical Attrition metal or ceramic compounds (Fe, Co, Ni, NiAl, TiAl, and FeSn) are subjected to severe mechanical deformation with strain rates as high as 10⁷/sec to produce the powder of nanometer sized particles. Molecular beam epitaxy (MBE), Chemical vapour deposition (CVD) or Metallo-organic chemical vapour deposition (MOCVD) are few examples of epitaxial growth methods where a huge variety of thin (5-100Å) layers of different semiconductor heterostructures are fabricated on a substrate with interfaces of atomic precision [13]. InAs QDs are grown by MBE in a GaAs matrix. The dots are formed by an island growth process of
InAs onto GaAs due to large mismatch between the two lattices. The QDs usually have vertical alignment but lack lateral ordering, which is likely due to the strain effect from the bottom layer on the growth of the upper layer, while the simultaneous nucleation in the same layer leads to randomness in the dot size distribution [1].

Nanosized particles of Fe, MgO, Cu and TiO₂ etc. can be prepared by Vapour condensation techniques which are similar to physical vapour deposition; the only difference being the use of a liquid nitrogen column to let the vaporized materials condense.

In Laser ablation, a high energy focused laser beam, forms a plasma zone resulting in production of ultrafine particles of AlN, MnO₂, TiO₂, Ti etc.

Nanostructured materials of Al, Cu, Mn etc. can be produced by applying the DC /RF sputtering technique in which a DC/RF sputter source is used for vaporizing the material, instead of laser as in laser ablation.

Induction and microwave plasma techniques are adopted to prepare a wide variety of metal and compound nanoparticles. In the RF induction method, a RF generator, coupled to copper coils is used to ionize the plasma gas by achieving a temperature, as high as 1000°C or more. In this process, a material fed into the plasma zone, vaporizes and then re-condenses as nanoparticles on the chamber-walls. Nanopowders of Fe, AlN, Cu and other metallic borides, nitrides and carbides are synthesized employing this procedure.

In the Microwave plasma technique, at high plasma temperatures (1000°C or more) microwaves generate plasmas by the ionization of gases, which transfer the heat necessary for chemical reactions to occur. Nanoscale materials of Fe, Co, Mo, Ni, TiO₂, ZrO₂, and Al₂O₃ etc. are prepared by this method.

The fabrication and manipulation of low dimensional structures by assembling the atoms or molecules with atomic resolution can be precisely done with the help of a number of Lithographic techniques such as Photolithography, Nanolithography and Soft Lithography etc.

The rate of production of nanomaterials is very low in most of these (A, B and C) methods. For example, yield of nanomaterials is 6-8% for sputtering and 50% or less for plasma techniques. Although a fantastic control over the size of a nanostructure is
possible by lithographic techniques, the production rate is low. In the case of sputtering, a broad particle size distribution is obtained and only 6-8% of sputtered material is reported to be less than 100nm. A high-energy consumption is a prerequisite for laser ablation and plasma techniques. Broad size distribution, low production rate and above all the high consumption of energy make most of the physical methods highly expensive and therefore cannot be adopted for practical commercial applications.

1.2 Properties of Nanomaterials

In a bulk material, the intrinsic electronic properties originate from the bulk band structure whereas in the case of nanomaterials a number of electronic properties such as density of states (DOS), ionization potential and electron affinity etc. are directly governed by the crystallite size and shape [14].

There is no clear cut size-related definition of nanomaterials, but a common understanding is that nanomaterials must exhibit some unique size-dependent properties that are minimal or vanish for large bulk crystals. Nanomaterials are attractive because of their unique and superior electrical, magnetic, mechanical and other physicochemical properties, where the size of the grains approaches a few hundreds of nanometers. Many of the outstanding properties are strongly enhanced when the size of the object is smaller than the electron mean free path length. This is commonly known as the size-confinement or quantum confinement effect of nanomaterials.

1.2.1 Quantum Confinement and Density of States of Low Dimensional Structures

In semiconductors, the de Broglie wavelength of an electron and a hole, $\lambda_e$, $\lambda_h$, and the Bohr radius of an exciton, $a_B$, may be considerably larger than the lattice constant, $a_L$. Therefore, it is possible to create a mesoscopic structure, which is in one, two, or three dimension comparable to or even less than $\lambda_e$, $\lambda_h$ and $a_B$ but still larger than $a_L$. In these structures, elementary excitations will experience quantum confinement resulting in finite motion along the confinement axis and infinite motion in other directions.

In the case of the size restriction in one dimension, we get a two-dimensional structure, the so-called quantum well. In the case of the two-dimensional confinement the relevant one-dimensional structure is referred to as a quantum wire. Finally, if the motion
of electrons, holes and excitons is restricted in all three directions, we come to a quasi-zero-dimensional system, the so-called quantum dot [12].

In the two- and one-dimensional confined structures, quasiparticles at low concentration can be considered as an ideal gas similar to the picture in a three-dimensional crystal. The density of electrons and holes can be expressed in the general form

\[ \rho(E) \propto E^{(d/2)-1} \quad d = 1, 2, 3 \]

where \( d \) is the dimensionality, and the energy is measured from the bottom of conduction band (also known as lowest unoccupied molecular orbital or LUMO) for electrons and top of the valence band (also known as highest occupied molecular orbital or HOMO) for holes. In the three-dimensional system, \( \rho(E) \) is a smooth square-root function of energy. In the case of \( d=2 \) and \( d=1 \), a number of discrete subbands appear due to the quantum confinement effect, and the density of states obeys eqn. (1.1) within every subband (Fig. 1.1).

![Figure 1.1: Density of electron states for various dimensionalities. For \( d=1, 2, 3 \), the density of states can be expressed by the formula \( \rho(E) \propto E^{(d/2)-1} \). For a quasi-zero-dimensional system the density of states is described by a set of \( \delta \)-functions.](image-url)
1.2.2 Size-dependent Oscillator Strength

Nanometer-sized semiconductor particles have attracted much attention because of their novel electronic and optical properties originating from quantum confinement. Optical spectra, in principle, contain a wealth of detailed information about the actual structure of small semiconductor particles. The crystallites are too small to exhibit bulk band gaps in their optical spectra. In the band gap region, the small crystallites show a higher energy absorption threshold with a resolved spectral feature (quantum size exciton peak), not present in the spectra of larger crystals [15]. For nanocrystals the electrons and holes necessarily acquire quantum energies of spatial localization, thus shifting their energy higher than the bulk band gap.

Localization effects and energies of binding to attractive potentials become stronger as the dimensionality decreases. Similarly, the excitonic effects lead to a strong enhancement of the oscillator strength near absorption edge as the dimensionality decreases [13]. The smaller the crystal, the greater is the oscillator strength of this quantum size exciton state relative to the remaining higher energy ‘continuous’ absorption. This occurs physically because the oscillator-strength is a measure of the spatial overlap of the electron & hole. The overlap increases as the two carriers are progressively confined in smaller crystallites. The net result is the appearance of an exciton peak in small crystallites [16]. Therefore, enhancement of oscillator strength and of excitonic effects in low-dimensional systems makes excitonic effects easier to observe at room temperature even in materials like ZnS and CdS, where they can be seen well only at low temperatures in the bulk [13].

1.2.3 Surface States of Nanomaterials

Structural properties of any material are greatly influenced by its surface states. These states are created due to either surface atom reconstruction or dangling bonds. Real crystallites usually exhibit ionization and redox processes involving electrons of the surface states, in large crystals as well as in small ones [14]. Since the surface to volume ratio (i.e. aspect ratio) is enhanced in case of nanomaterials, the surface or interface energy dominates the total energy of the system and as a result most of the physical and chemical properties of the nanomaterials are driven by its surface structure.
In short, nanomaterials usually show unique properties through nanoscale size confinement, predominance of interfacial phenomena and quantum effects. Therefore, by reducing the dimension of a structure to nanosize, many inconceivable properties are expected to appear and may lead to different applications [17].

1.3 ZnS and CdS Nanoparticles

General information and facts about bulk ZnS and CdS along with their important properties from the application point of view are provided here. Nanomaterials of these semiconductors are of great importance as they exhibit improved optoelectronic and structural properties. A number of synthesis procedures are adopted to fabricate these technologically vital substances.

1.3.1 Bulk ZnS and CdS

Zinc sulphide (ZnS) and cadmium sulphide (CdS), are members of the II-VI chalcogenide family. Both are highly polar, direct and wide band gap semiconductors. Zinc sulphide is an off-white powder that occurs naturally as ‘blend’ and is prepared by precipitation of a zinc salt solution with ammonium sulphide. It is produced at a relatively low cost so many of its applications are as a substitution for other materials. ZnS is insoluble in water, but soluble in acid. ZnS may exist in both cubic zinc blende (sphalerite) and the hexagonal wurtzite structure, though the most stable bulk form of ZnS is cubic. Bulk ZnS transforms to wurtzite at 1020°C. Blende ((Zn, Fe)S) is the major ore of ZnS whereas wurtzite is the minor ore. Sphalerite (Zinc Blende) is one of the very few minerals those have a total of six directions of cleavage. In Greek, sphalerite means ‘treacherous rock’, while the meaning of Blende in German is ‘blind’ or ‘deceiving’. Sphalerite is a polymorph with two minerals, wurtzite & matraite.

A. Crystal structure of ZnS & CdS:

Zincblende, sometimes called sphalerite, consists of two interpenetrating face centered cubic (fcc) sublattices of Zn and S. One sublattice is displaced by 1/4 of a lattice parameter in each direction from the other sublattice, so that each site of one sublattice is tetrahedrally coordinated with sites from the other sublattice. Therefore, one atom is
situated on a fcc sublattice at the positions 0 0 0, ½ ½ 0, ½ 0 ½ and 0 ½ ½, and the other atom on a second fcc sublattice displaced from the first by the amount ½ ½ ½ along the body diagonal, as shown in the right to Fig. 1.2. That is, each atom of (say Zn) is at the center of a regular tetrahedron formed by four atoms of the opposite type (say S). A closely related structure is wurtzite also has tetrahedrally coordinated lattice sites. In zinc blende, the stacking of the ZnS dimers along the (111) direction is the repetition of ABC. While in the wurtzite which is the hexagonal analog of the zinc blende lattice, the stacking of the ZnS dimers is the repetition of AB. ZnS may take on either of these structures. The crystal structure for zinc blende and wurtzite are shown below in Fig. 1.2.

![Diagram of Crystal Structures](image)

**Fig. 1.2:** Cubic close packing ABC repeat in zinc blende (left) and hexagonal close packing AB repeat in wurtzite (right) crystal structures.

In nature CdS occurs in the form of ores like ‘Greenockite’ (hexagonal structure) and ‘Hawleyite’ (cubic structure). CdS appears as a yellow-to-orange coloured crystalline solid. The basic crystal structures of CdS are similar to as shown in Fig. 1.2 for ZnS.

In the two modifications of ZnS, the cubic zinc blende structure and the hexagonal wurtzite structure, the valence band maximum is split into three levels say A, B and C by crystal field and spin-orbit interaction. In hexagonal CdS the conduction band (minimum at Γ) originates from the Cd 5s states. The valence band (A, B, C maxima at Γ split by crystal field and spin-orbit interaction) results from the s-3p states [18]. A list of the values of various basic physical and chemical properties of ZnS and CdS is provided in the Appendix B.
B. Applications of ZnS & CdS:

ZnS and CdS are technologically vital materials due to their wide variety of applications. Both are used in infrared (IR) optics and as substrates. ZnS is used as evaporation sources and as a friction material to carry sulphur, which harden rotor surfaces and thereby reduces wear. CdS is used as polarizers, beam splitters and $\frac{1}{2}$ & $\frac{1}{4}$ waveplates. Other applications of ZnS are in printing inks, UV-hardness systems, powder coatings, adhesives, insulating & sealing compounds, thermoplastic pigmentation, thermosets; flame resistant plastics, glass-fiber reinforced plastics, pigment concentrates elastomers, flexible fibers, paper, mastics, lubricants, electroluminescent lamps, infrared windows & domes and optical elements.

A lot of resemblance in the physicochemical properties of ZnS and CdS results in similar applications of CdS. Synthetic Cd pigments based on CdS are valued for their good thermal stability in many polymers, for example in engineering plastics. Due to the useful optoelectronic properties, CdS is being used as photoresistors and many other photosensitive and photovoltaic devices [19].

1.3.2 ZnS and CdS Nanoparticles: Properties and Applications

A. Band structure and luminescence of ZnS and CdS nanoparticles:

In quantum physics, the electronic structure of a material is analyzed in terms of the density of electron states (DOS). Transport of the charge (electron or hole) in the periodic lattice potential produces the characteristic semiconductor band structure — a complex set of anisotropic relationships between energy and momentum [14]. In bulk crystals, each electron band consists of a continuum of electron states. However, the energy spacing of electron states increases with decreasing QD size, and therefore the energy spectrum of an electron band approaches a set of discrete lines in nanocrystals.

Nanoparticles of semiconductors (quantum dots) were theorized in the 1970s and initially created in the early 1980s. The first report correlating the semiconductor particle size with the optical properties was made in 1967 by Berry who studied both CdS and AgI particles [20]. If semiconductor particles are made small enough, quantum effects come into play, which limit the energies at which electrons and holes can exist in the
particles. Quantum confinement effects become pronounced in the region of strong confinement, where the size of the quantum dot is less than the exciton Bohr diameter of the semiconductor. This parameter has a value of 6 nm for CdS. The Bohr exciton diameter of ZnS is about 5 nm; consequently, ZnS nanoparticles exhibit strong quantum size effect in the nanometer regime. The blue shift of the threshold, relative to that of bulk-phase ZnS results from 'quantum-confinement' [21].

The fine tuning of the fluorescence emission within each colour is controlled by the size of QDs. The colour change of the fluorescence is governed by the 'electron in a potential box' effect. A simple potential box model explaining the shift of the luminescence wavelength is shown in the Fig. 1.3.

![Fig. 1.3: Luminescence in a bulk (left) and nanocrystalline (right) semiconductor.](image)

The quantization of electron states exists in the nanocrystals, where discrete energy levels are more distant than the band gap of the larger crystals [17]. QDs illuminated by UV light emit light at a wavelength that depends both on the material composition and the size of QDs. Large differences in the fluorescence wavelength result from different band gaps of the materials. Within each colour, the wavelength is defined by the different sizes of QDs [17]. It has been shown for many semiconductor QDs that a full spectrum of luminescence (see Fig. 1.4) can be achieved by engineering the size of QD.
Fig. 1.4: A family of QDs with varying sizes can be made to emit a full spectrum of colours when excited with a single excitation source.

The quantum efficiency of semiconductor nanocrystals enhances as compared to their bulk counterpart. Further it has been shown that doping improves the quantum efficiency of semiconductor NCs. Bhargava et al. reported that coated nanocrystals of Mn-doped ZnS with sizes varying from 3.5nm to 7.5nm could yield high luminescent efficiency of 18% [22].

B. Surface properties of ZnS and CdS nanoparticles:

The surface atoms, which can be neglected for a bulk solid material, play a major role in determining the electronic properties. For example, while the melting point of bulk CdS is ~1600°C, a typical 2.5nm CdS crystallite melts at a temperature of about 400°C [23]. Such a depression in the melting point is due to a higher surface energy of the nanoparticles compared to the bulk. The high aspect ratio along with the ability to tune the band gap means that nanodispersed ZnS or CdS can be used as sensitizers and catalysts in photochemical reactions [24].

C. Applications:

ZnS and CdS nanoparticles are used chiefly for optoelectronic applications. They are also utilized for energy conversion and storage, catalytic and chemical sensors. With their bright, photostable fluorescence these QDs show promise as alternatives to organic dyes for fluorescent biological labelling (for example to trace a biological molecule) which use both the small particle size and tunable energy levels [25]. While the ZnS nanoparticles are widely used as phosphors and infrared windows, nanoparticles of CdS are mainly used in photovoltaic cells.
1.3.3 Growth of ZnS and CdS Nanoparticles

ZnS and CdS nanoparticles can be fabricated using a number of technologies, differing in the environment in which nanoparticles appear, growth conditions, size range, and size distribution, as well as physical and chemical stability and reliability.

These crystallites can be developed in an organic environment using a variety of techniques based on organometallic and polymer chemistry [26, 27]. ZnS and CdS nanoparticles can be grown in inorganic matrices. A diffusion-controlled process in a glass matrix is successfully used to fabricate nanocrystals of II-VI semiconductors [12]. Okuyama et al. prepared ZnS and CdS fine particle sizes by an ultrasonic spray pyrolysis method [28].

Several successful attempts have been reported of fabrication of ZnS and CdS nanoparticles embedded in a sol-gel matrix. Mathieu et al. have managed to get a rather large set of CdS nanoparticles ranging from 2.1 to 9.2nm, that is, covering both weak and strong confinement cases for the same crystallite porous glass matrix system [29].

Synthesis and organization of nanoscale ZnS and CdS semiconductor materials is performed by using the evolved peptide specificity and viral capsid assembly [10]. Recently researchers have engineered a particular type of long, narrow virus to contain a peptide with an affinity for ZnS nanocrystals, and showed that under the right conditions a mixture of virus and crystals will build itself into a liquid crystal film [10].

A synopsis of the ZnS and CdS nanoparticles fabricated by various techniques is given in the table 1.1 as follows:

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Synthesis Method</th>
<th>Particle size range (nm)</th>
<th>References</th>
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<tr>
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<td>2-4</td>
<td>30</td>
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<tr>
<td></td>
<td>2. Arrested precipitation in aqueous and methanolic solutions.</td>
<td>&lt;2</td>
<td>31</td>
</tr>
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<td></td>
<td>3. Photodegradation of 3nm particles or precipitation in phosphate containing solutions.</td>
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<td></td>
<td>4. Treatment of zinc containing copolymers with H$_2$S.</td>
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<td></td>
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|     | 2. Formation within polymer matrices using ionomers. | 1.8-2.3 | 37 |
|     | 3. Treatment of Xerogel matrix (polysilsesquioxane) with C and S². | 6-9 | 38 |
|     | 4. Hydrolysis of P₂S₅ in an ethanol solution of Cd(NO₃)₂·4H₂O. | <6 | 39 |
|     | 5. Arrested precipitation in aqueous and methanolic media. | 3 | 15 |
|     | 6. CdSO₄·(NH₄)S in aqueous/acetonitrile solutions using copolymers as stabilizers. | 2.1-7.5 | 40 |
|     | 7. Arrested precipitation within surfactant vesicles. | 2.2-5 | 41 |
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1.4 Motivation

At present, research in nanoscience and nanotechnology faces four main challenges [1]:
(a) Synthesis of structurally controlled nanomaterials, with well defined atomic-scale structure, high purity and large yield.
(b) Characterization of the structure and their properties; especially the properties of individual nanostructures.
(c) Device fabrication, nanomanipulation and inter-device interconnection.
(d) System integration and large-scale manufacturing.

While a & b fall in the realm of scientific investigations, an expertise in technology is a prerequisite to face the challenges in c & d. A huge wealth of literature is available on the synthesis and characterization of nanostructured materials. However, the
research on the synthesis and characterization of nanomaterials remains unabated primarily due to following reasons:

(a) Many new properties, unforeseen phenomena are being observed in the already investigated nanostructured materials. The emergence of new properties or the change in known characteristics appears due to change in synthesis and characterization procedures.

(b) Although numerous methods for the preparation of nanomaterials have been established, there is still a need of suitable methods to overcome the problems of size distribution, agglomeration, extraction from precursors and yield of these materials so as to utilize them for device fabrication.

Semiconductor nanomaterials in general and ZnS and CdS nanoparticles in particular are technologically important substances due to their optoelectronic, chemical and catalytic properties. Recently the findings of structural transformation in wet ZnS nanoparticles suggest a route for post-synthesis control of nanoparticle structure and the potential use of the nanoparticle structural state as an environmental sensor [45].

Furthermore, the results imply that the structure and reactivity of nanoparticles at planetary surfaces, in interplanetary dust [46] and in the biosphere [47, 48] will depend on both particle size and the nature of the surrounding molecules.

Early research in last two decades has been tremendously focused on the investigation of various physicochemical properties of ZnS & CdS nanoparticles prepared by a number of physical, chemical and biological routes [refer section 1.3]. Though the nanomaterial prepared by these methods have provided a wealth of information about ZnS and CdS nanoparticles, most of these methods are not suitable for device application due to above-mentioned reasons.

In this thesis we have proposed novel methods to synthesize ZnS and CdS nanomaterials. The structural, optical and electronic properties of thus prepared material were investigated with the help of various characterization techniques. The fundamental motivation behind this work was to device facile and economically viable procedures for the synthesis of ZnS and CdS nanoparticles so that these nanomaterials can be produced in large quantities. Fulfillment of this aim will lead the way to apply these nanomaterials directly for industrial applications.
References

www.its.caltech.edu/~feynman/plenty.html