CHAPTER 1

Existing Literature
Survey on Undoped and Doped CdS Nanoparticles
1.1 Introduction to Nanotechnology

The prefix “nano” is began to use by researchers more than thirty years ago, but its use has spread to practically just from last ten years in every field of science and technology. Nanotechnology is the technology which uses phenomena and structures that can only occur at the nanometer scale, which is the scale of single atoms and small molecules. In the nanoscale, which is normally seen as going from 100 nm and down to just a few nanometers, the materials have properties that can be very different from those at a larger scale. Nanotechnology is the term used to cover the design, construction and utilization of structures with at least one characteristic dimension measured in nanometres. Today, it is used as much for fashion as it is for scientific classification and we have reached the point where it is possible to manipulate materials at the molecular level that can be used for particular applications. Such materials can be designed to exhibit significantly improved physical, chemical and biological properties, by controlling shape and size of their constituent particles at the nanoscale. The objects at nanoscale may display physical attributes significantly different from those displayed by either atoms or bulk materials. Ultimately, this can lead to new technological opportunities as well as new challenges. Nanotechnology term broadly refers to such fields as biology, physics or chemistry, any scientific field really, or a combination thereof, that deals with the deliberate and controlled manufacturing of nanostructures. Quantum effects can be responsible for the dominating behaviour of matter at the nanoscale. The goal of evolutionary nanotechnology is to improve existing processes, materials and applications by scaling down into the nano realm and ultimately fully exploit the unique quantum and surface phenomena that matter exhibits at the nanoscale.

The number of atoms or molecules on the surface of nanoparticle is comparable to that inside the particles, therefore nanoparticles can be used to develop materials with unique properties [1]. It is reported that to meet the technological demands in the areas such as electronics, catalysis, ceramics, magnetic data storage, structural components etc, the size of the materials should be reduced to the nanometer scale. Recently, the synthesis of nanoparticles has become very important. Nanoparticles synthesized using different
methods may have different internal structures that affect the properties of materials consolidated from them. One of the most critical characteristics of nanoparticles is their very high surface to volume ratio, i.e. large fractions of surface atoms. The large fractions of surface atoms together with ultra fine size and shape effects make nanoparticles exhibit distinctly different properties from the bulk [2]. The percentage of surface atoms increases as the size of the nanoparticles is decreased. Controlling the size, shape and structure of nanoparticles is technologically important because of strong correlation between these parameters and optical, electrical, magnetic and catalytic properties [3, 4].

1.2 Quantum Confinement

Nanotechnology has yielded a number of unique structures that are not found anywhere in nature. Most demonstrate an essential quality of quantum mechanics known as quantum confinement. The idea behind confinement is all about keeping electrons trapped in a small area. The sizes for confinement have to be less than 30 nm for effective confinement. Quantum confinement comes in several flavors. 2−D confinement is only restricted in one dimension, and the result is a quantum well (or plane). These are what most lasers are currently built from. 1−D confinement is restricted in two dimension, confinement occurs in nanowires. 0−D confinement is restricted in all three dimensions, confinement is found only in the quantum dot as shown in fig. 1.1. Confinement is important as it leads to new electronic properties that are not present in bulk semiconductor devices. The typical quantum dot is anywhere between 3−60 nm in diameter. That is still 30 to 600 times the size of a typical atom. Quantum dots are large enough to be manipulated by magnetic fields and can even be moved around with an STM or AFM. Many important atomistic characteristics can be deduced from a quantum dot that would otherwise be impossible to research in an atom.
Quantum confinement is responsible for the increase of energy difference between energy states and band gap as shown in fig. 1.2. A phenomenon tightly related with the optical and electronic properties of the materials. The quantum confinement effect can be observed once the diameter of the particle is of the magnitude as the wavelength of electron wave function \[5\]. When the materials are so small, their electronic and optical properties deviate substantially from those of bulk materials \[6\].

A particle behaves as if it were free when the confining dimension is large compared to the wavelength of the particle. During this state, bandgap remains at its original energy due to continuous energy state. However, as the confining dimension decreases and reaches a certain limit, typically in nanoscale, the energy spectrum turns to discrete. As a result, bandgap becomes size dependent. This ultimately results a blue shift in optical illumination as the size of the particles decreases. Specifically, the effect describes the phenomenon results from electrons and electron holes being squeezed into a dimension that approaches a critical quantum measurement, called the exciton Bohr
radius. Nanocrystals lie in between the atomic and the molecular limit of discrete density of electronic states and the extended crystalline limit of continuous band [7].

Fig. 1.2 Illustrating that quantum confinement is responsible for the increase of energy difference between energy states and band gap.

1.3 Exciton

An exciton is a bound state of an electron and hole which are attracted to each other by the electrostatic Coulomb force. It is an electrically neutral quasiparticle that exists in insulators, semiconductors and in some liquids. The exciton is regarded as an elementary excitation of condensed matter that can transport energy without transporting net electric charge.

A vivid picture of exciton formation is as follows: a photon enters a semiconductor, exciting an electron from the valence band into the conduction band. The missing electron in the valence band leaves a hole behind, of opposite electric charge, to which it is attracted by the Coulomb’s force. Exciton results from the binding of the electron with its hole; as a result, the exciton has slightly less energy than the unbound electron and hole. The wave function of the bound state is hydrogenic i.e. an "exotic
atom" state like to that of a hydrogen atom. However, the binding energy is much smaller and the size much bigger than a hydrogen atom because of the effects of screening and the effective mass of the constituents in the material. Excitons are thus, the main mechanism for light emission in semiconductors at low temperatures being less than the exciton binding energy, replacing the free electron–hole recombination at higher temperatures.

1.4 Unique Properties at Nanoscale

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

- Gravitational forces become negligible and electromagnetic forces dominate.
- Quantum mechanics model is used to describe motion and energy instead of the classical mechanics model.
- Greater surface area to volume ratio.
- Random molecular motion becomes more important.

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

1.4.1 Optical Properties

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

1.4.2 Chemical Reactivity

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

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

1.4.4 Melting Point

Melting Point is the temperature at which the atoms, ions or molecules in a substance have enough energy to overcome the intermolecular forces that hold them in a fixed position in a solid. At nanoscale, surface atoms require less energy to move because they are in contact with fewer atoms of the substance as shown in fig. 1.3.

![Fig. 1.3 At nanoscale, surface atoms are in contact with fewer atoms as compared to inner atoms.](image)

1.4.5 Magnetic Properties

Magnetic nanomaterials are those whose property can be affected using magnetic field as shown in fig. 1.4. They usually contain magnetic elements like iron, nickel, cobalt etc. and show a variety of unusual magnetic behaviour when compared to the bulk
materials, mostly due to surface or interface effects, including symmetry breaking, electronic environment or charge transfer and magnetic interactions. The physical and chemical properties of magnetic nanomaterials mainly depend upon the chemical structure and method of synthesis. For example, bulk gold and platinum are non–magnetic, but at the nano size they are magnetic. Nanocomposite magnets have high coercivity and high value of remanence. Magnetic studies in nanostructured materials have been focused on the interaction between electron charges and magnetic spins which led to discoveries of new and unique phenomena that are neither observable in traditional bulk materials nor explainable using classical theories [8].

![Diagram of magnetic properties](image)

**Fig. 1.4** Magnetic properties of nanostructured materials.

### 1.4.6 Thermal Properties

Effect of temperature on the fluctuation of energy difference between the bottom of conduction band and the top of valence band is weaker for the discrete states of the semiconductor nanomaterials than the continuous states in bulk semiconductors. Therefore, the nanomaterials has some advantages on the thermal stability over bulk materials. The thermal conductivity of nanomaterials are very high and is due to the vibration of covalent bonds. Its thermal conductivity is 10 times greater than the bulk material. The very high thermal conductivity of nanomaterial is also due to minimum defects in the structure [9].
1.5 Magnetism

The origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another. The best way to introduce the different types of magnetism is to describe how materials respond to magnetic fields. This may be surprising to some, but all matter is magnetic. It's just that some materials are much more magnetic than others. The main distinction is that in some materials there is no collective interaction of atomic magnetic moments, whereas in other materials there is a very strong interaction between atomic moments.

The magnetic behavior of materials can be classified into the following five major groups:

1. Diamagnetism
2. Paramagnetism
3. Ferromagnetism
4. Ferrimagnetism
5. Antiferromagnetism

Materials in the first two groups are those that exhibit no collective magnetic interactions and are not magnetically ordered. Materials in the last three groups exhibit long range magnetic order below a certain critical temperature. Ferromagnetic and ferrimagnetic materials are usually what we consider as being magnetic (ie, behaving like iron). The remaining three are so weakly magnetic that they are usually thought of as "nonmagnetic".

1. Diamagnetism

Diamagnetism appears in all materials, and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. However, in a material with paramagnetic properties (that is, with a tendency to enhance an external magnetic field), the paramagnetic behavior dominates. Thus, despite its universal occurrence, diamagnetic behavior is observed only in a purely diamagnetic material. In a
diamagnetic material, there are no unpaired electrons, so the intrinsic electron magnetic moments cannot produce any bulk effect. However, when exposed to a field, a negative magnetization is produced and thus the susceptibility is negative.

2. Paramagnetism

In a paramagnetic material there are unpaired electrons, i.e. atomic or molecular orbitals with exactly one electron in them. While paired electrons are required by the Pauli exclusion principle to have their intrinsic (spin) magnetic moments pointing in opposite directions, causing their magnetic fields to cancel out, an unpaired electron is free to align its magnetic moment in any direction. When an external magnetic field is applied, these magnetic moments will tend to align themselves in the same direction as the applied field, thus reinforcing it, resulting in a net positive magnetization and positive susceptibility.

3. Ferromagnetism

A ferromagnet, like a paramagnetic substance, has unpaired electrons. However, in addition to the electrons intrinsic magnetic moment's tendency to be parallel to an applied field, there is also in these materials a tendency for these magnetic moments to orient parallel to each other to maintain a lowered energy state. Thus, even when the applied field is removed, the electrons in the material maintain a parallel orientation.

4. Ferrimagnetism

Like ferromagnetism, ferrimagnets retain their magnetization in the absence of a field. However, like antiferromagnets, neighboring pairs of electron spins like to point in opposite directions. These two properties are not contradictory, because in the optimal geometrical arrangement, there is more magnetic moment from the sublattice of electrons that point in one direction, than from the sublattice that point in the opposite direction.
5. Antiferromagnetism

In an antiferromagnet, unlike a ferromagnet, there is a tendency for the intrinsic magnetic moments of neighboring valence electrons to point in opposite directions. When all atoms are arranged in a substance so that each neighbor is 'anti aligned', the substance is antiferromagnetic. Antiferromagnets have a zero net magnetic moment, meaning no field is produced by them. Antiferromagnets are less common compared to the other types of behaviors, and are mostly observed at low temperatures. In varying temperatures, antiferromagnets can be seen to exhibit diamagnetic and ferrimagnetic properties.

1.6 Dilute Magnetic Semiconductor (DMS)

The material joining both the characteristics of semiconductor as well as magnetic material are known as dilute magnetic semiconductor or semimagnetic semiconductor. The DMS are semiconducting materials in which a fraction of the host cations can be substitutionally replaced by magnetic ions (Fe, Co, Ni etc.) or appropriate rare earth elements [10] as shown in fig. 1.5.

![Diagram of DMS](image_url)

**Fig. 1.5** Schematic showing (a) nonmagnetic semiconductor, which contains no magnetic ions; (b) diluted magnetic semiconductor (DMS), i.e., a cross between a nonmagnetic semiconductor and a magnetic transition metal (TM) element, in a paramagnetic state; (c) DMS with ferromagnetic order mediated by charge carriers (holes).
1.7 Applications of DMS

Diluted magnetic semiconductors (DMSs) are promising materials for applications as well as interesting from the basic physics point of view. Possible application exist in spin electronics (spintronics) [11, 12], which employ the spin degree of freedom of electrons in addition to their charge. This may allow the incorporation of ferromagnetic elements into semiconductor devices, and thus the integration of data processing and magnetic storage on a single chip. Since the electronic spin is a quantum mechanical degree of freedom, quantum interference effects could be exploited in devices, eventually leading to the design of quantum computers [13].

Medical diagnostics and treatments

Magnetic nanoparticles are used in an experimental cancer treatment called magnetic hyperthermia [14] in which the fact that nanoparticles heat when they are placed in an alternative magnetic field. Another potential treatment of cancer includes attaching magnetic nanoparticles to free floating cancer cells, allowing them to be captured and carried out of the body. The treatment has been tested in the laboratory on mice and will be looked at in survival studies [15, 16].

Magnetic nanoparticles can be used for the detection of cancer. Blood can be inserted onto a microfluidic chip with magnetic nanoparticles in it. These magnetic nanoparticles are trapped inside due to an externally applied magnetic field as the blood is free to flow through. The magnetic nanoparticles are coated with antibodies targeting cancer cells or proteins. The magnetic nanoparticles can be recovered and the attached cancer associated molecules can be assayed to test for their existence. Magnetic nanoparticles can be conjugated with carbohydrates and used for detection of bacteria. Iron oxide particles have been used for the detection of Gram negative bacteria like Escherichia Coli and for detection of Gram positive bacteria like Streptococcus Suis [17, 18].
Magnetic immunoassay

Magnetic immunoassay [19] (MIA) is a novel type of diagnostic immunoassay utilizing magnetic beads as labels in lieu of conventional, enzymes, radioisotopes or fluorescent moieties. This assay involves the specific binding of an antibody to its antigen, where a magnetic label is conjugated to one element of the pair. The presence of magnetic beads is then detected by a magnetic reader (magnetometer) which measures the magnetic field change induced by the beads. The signal measured by the magnetometer is proportional to the analyte (virus, toxin, bacteria, cardiac marker, etc.) quantity in the initial sample.

Waste water treatment

Thanks to the easy separation by applying a magnetic field and the very large surface to volume ratio, magnetic nanoparticles have a good potential for treatment of contaminated water [20]. In this method, attachment of EDTA–like chelators to carbon coated metal nanomagnets results in a magnetic reagent for the rapid removal of heavy metals from solutions or contaminated water by three orders of magnitude to concentrations as low as micrograms per litre.

Chemistry

Magnetic nanoparticles are being used or have the potential use as a catalyst or catalyst supports [21]. In chemistry, a catalyst support is the material, usually a solid with a high surface area, to which a catalyst is affixed. The reactivity of heterogeneous catalysts occurs at the surface atoms. Consequently great effort is made to maximize the surface area of a catalyst by distributing it over the support. The support may be inert or participate in the catalytic reactions. Typical supports include various kinds of carbon, alumina, and silica.
Biomedical imaging

There are many applications for iro oxide based nanoparticles in concert with magnetic resonance imaging [22]. Magnetic CoPt nanoparticles are being used as an MRI contrast agent for transplanted neural stem cell detection [23].

Information storage

Research is going into the use of using magnetic nanoparticles (MNPs) for magnetic recording media. The most promising candidates for high density storage is the face centered tetragonal phase FePt alloy. Grain sizes can be as small as 3 nanometers. If it is possible to modify the MNPs at this small scale, the information density that can be achieved with this media could easily surpass 1 Terabyte per square inch [24].

Genetic engineering

Magnetic nanoparticles can be used for a variety of genetics applications. One application is the isolation of mRNA. This can be done quickly usually within 15 minutes. In this particular application, the magnetic bead is attached to a poly T tail. When mixed with mRNA, the poly A tail of the mRNA will attach to the bead's poly T tail and the isolation takes place simply by placing a magnet on the side of the tube and pouring out the liquid. Magnetic beads have also been used in plasmid assembly. Rapid genetic circuit construction has been achieved by the sequential addition of genes onto a growing genetic chain, using nanobeads as an anchor. This method has been shown to be much faster than previous methods, taking less than an hour to create functional multi−gene constructs in vitro [25].

1.8 Methods of Fabrication

In general, there are two philosophically distinct approaches for making nanostructures, which can be characterized as top−down and bottom−up.
Top to down

Top–down approach begins with larger starting materials and, in a more or less controlled fashion, removes the material until the desired structure is achieved. It is inherently simpler and relies either on the removal or division of bulk material, or on the miniaturization of bulk fabrication processes to produce the desired structure with the appropriate properties as shown in fig. 1.6. Small features are patterned in bulk materials by a combination of lithography, etching and deposition to form functional devices. Most microfabrication techniques for inorganic materials such as lithography and milling fit this description. Production processes by using top–down approaches are:

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

Bottom to up

In this approach atoms, molecules and even nanoparticles themselves can be used as the building blocks for the creation of complex nanostructures; the useful size of the building blocks depends on the properties to be engineered as shown in fig.1.6.

By altering the size of the building blocks, controlling their surface and internal chemistry, and then controlling their organization and assembly, it is possible to engineer properties and functionalities of the overall nanostructures solid or system. These processes follow the highly controlled and complex chemical synthesis procedure. Production processes by using bottom–up approach are:

- Crystallization
- Sol–gel
- Chemical vapour deposition
- Solvothermal/Hydrothermal
- Micelle and micro emulsion synthesis
- Spray pyrolysis
- Template Synthesis: Electrochemical and Electroless

1.9 Brief Overview of CdS Characteristics

Cadmium sulfide is a II–VI semiconductor material with the formula CdS. It is a yellow colored semiconductor [26], existing as two different minerals, the more stable hexagonal wurtzite structure (found in the mineral Greenockite) and the cubic zinc blende structure (found in the mineral Hawleyite) [27]. It is a direct band gap semiconductor (2.42 eV) [28]. For bulk CdS, the excitonic binding energy is around 28 meV. Consequently, the excitons are stable only at a low temperature [29]. In recent years, nanocrystalline CdS attracted much attention because of their properties in the nanoforms differ significantly from those of their bulk counterparts [30]. Nanoparticles of CdS are by far the most studied system among all the semiconducting nanoparticles [31]. The typical Bohr exciton diameter of CdS is around 5.8 nm; consequently, CdS nanoparticles in the size range of 1–6 nm show sizable quantum confinement effects [32]. On the other hand, when crystallite radius becomes comparable to or less than the Bohr...
exciton radius, there is a considerable enhancement of the exciton binding energy \[33\]. It used for different applications in optoelectronics such as nonlinear optics, flat panel displays, light emitting diodes, lasers, thin film transistors, etc.\[34\text{–}40\]. It forms thermally stable pigments and with the addition of materials like CdTe and HgS, colors ranging from deep red to yellow are formed \[41\]. It also finds wide application as a commercial photovoltaic material, such as the window material in heterojunction solar cells \[42, 43\].

1.10 Properties of CdS

1.10.1 Structural Properties

Cadmium sulfide can crystallize in four different crystalline structures; the hexagonal structure (wurtzite), the cubic structure (zinc blende), the cubic rock salt structure and the distorted rocksalt structure. Among these four crystalline structures, the wurtzite, which can be found in nature as rare Greenockite mineral is the thermodynamically most stable and thus the most common. CdS with zinc–blende modification is a metastable structure \[44\], found in nature as rare mineral Hawleyite. The rock salt modification can exist only under high pressure condition, i.e. subjecting the hexagonal CdS to pressures ranging from 2.6 to 4.2 GPa. At this pressure the two modifications coexist \[45\]. At higher pressure, the rock salt structure transforms into the KCN–like distorted rock salt structure having Pmmm symmetry. These two last modifications coexist in a hydrostatic pressure ranging from 60 to 68 GPa \[46\]. The two most important crystalline structures, i.e. the wurtzite and the zinc blende structures are shown in the fig. 1.7. The values of lattice parameters and space group for each of these structures are shown in table 1.1.
Table 1.1 Space groups in international crystallographic notation (Hermann–Mauguin) and Schönies notation relative to the four lattice modifications. The crystallographic parameters are taken from [46, 47] (X–ray diffraction data).

<table>
<thead>
<tr>
<th>Modification</th>
<th>Space group</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wurtzite</td>
<td>P63mc</td>
<td>a = 4.1348, c = 6.7490</td>
</tr>
<tr>
<td>Zinc blende</td>
<td>F43m</td>
<td>a = 5.818</td>
</tr>
<tr>
<td>Rock salt</td>
<td>Fm3m</td>
<td>a = 5.32</td>
</tr>
<tr>
<td>Dist. rock salt</td>
<td>Pmmn</td>
<td>a = 3.471, b = 4.873, c = 3.399</td>
</tr>
</tbody>
</table>

Fig. 1.7 Crystal structure of CdS.

1.10.2 Chemical Properties

1. Cadmium sulfide can be prepared by the precipitation from soluble cadmium (II) salts with sulfide ion and this has been used in the past for the gravimetric analysis of cadmium.

\[
\text{Cd}^{2+} + \text{NH}_3 \rightarrow [\text{Cd} (\text{NH}_3)_4]^{2+} \tag{1}
\]

Pigment production usually involves the precipitation of CdS, the washing of the precipitate to remove soluble cadmium salts followed by calcination (roasting) to convert it to the hexagonal form followed by milling to produce a powder. The preparative route and the subsequent treatment of the product, affects the
polymorphic form that is produced. It has been asserted in the past that chemical precipitation methods produce the cubic zinc blende form however there are more recent examples where the hexagonal form is produced [48].

2. Cadmium sulfide is soluble in acids and this has been investigated as a method of extracting the pigment from waste polymers e.g. HDPE pipes: [49]

\[
\text{CdS} + 2\text{HCl} \rightarrow \text{CdCl}_2 + \text{H}_2\text{S}
\]  

(2)

3. When sulfide solutions containing dispersed CdS particles are irradiated with light hydrogen gas is generated: [50]

\[
\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S} \Delta\text{H}_f = +9.4 \text{ kcal/mol}
\]  

(3)

The reaction mechanism proposed involves the electron/hole pairs created when incident light is absorbed by the cadmium sulfide followed by these reacting with water and sulfide [51].

Production of an electron hole pair

\[
\text{CdS} + h\nu \rightarrow e^- + \text{hole}^+
\]  

(4)

Reaction of electron

\[
2e^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^-
\]  

(5)

Reaction of hole

\[
2\text{hole}^+ + \text{S}^{2-} \rightarrow \text{S}
\]  

(6)

1.10.3 Electrical Properties

Cadmium sulfide either in hexagonal (wurtzite) or cubic structure (zinc blende) is a direct band gap semiconductor with the smallest band gap at the center of the Brillouin zone \(\Gamma\), see fig. 1.8 and fig. 1.9. In the hexagonal allotropic modification, the topmost valence band \(\Gamma_5 + \Gamma_1\) due to crystal field perturbation and spin–orbit coupling is split into three spin–degenerate states \(\Gamma_9, \Gamma_7\) and \(\Gamma_7\) [52, 53]. Therefore there are three possible optical transitions at \(E_{g0}, \Gamma_9\rightarrow \Gamma_7C\ (2.5537 \text{ eV}), \Gamma_7C \rightarrow \Gamma_7V\ (2.5686 \text{ eV}), \Gamma_7C \rightarrow \Gamma_7V\ (2.632 \text{ eV})\). In the cubic modification, the effect due to crystal field perturbation is much less relevant. Neglecting the spin orbit interaction, at \(\Gamma\) point the conduction band is constituted by the non degenerated state \(\Gamma_{1c}\), while the valence band by a two
fold degenerated state $\Gamma_{5v}$ and a non degenerate state $\Gamma_{1v}$. Such levels give rise to a single optical transition $\Gamma_{1C} \rightarrow \Gamma_{15C}$ [54]. Including the spin orbit interaction, the six fold degenerated valence band is split into four fold degenerated states with $J = 3/2$ ($\Gamma_8$) and other two fold degenerated states with $J = 1/2$ ($\Gamma_7$). The two levels are separated by the spin orbit split $\Delta$ [55]. In hexagonal CdS, the main band gap relative to the transition between the critical points $\Gamma_{9V} \rightarrow \Gamma_{7C}$ is of 2.4812 eV. This value has been obtained by optical ellipsometry measurements [53]. By density functional theory calculations, in the local density approximation, using self interaction corrected pseudopotentials [53], a band gap value of 2.5 eV is obtained. Measurements performed on cubic CdS give, for the main band gap (transition $\Gamma_{1V} \rightarrow \Gamma_{15C}$) a value of 2.48 eV at 1.8 K [54], while always from the same kind of LDA calculation used for hexagonal CdS [56], the calculated band gap is of 2.4 eV. Even though the physical properties of the CdS in cubic modification are interesting from the physical point of view, they will not be dealt hence forth and the interest will be focused exclusively on the hexagonal CdS.

**Fig. 1.8** Zinc blend CdS electronic band structure calculated by Band structure from a first principles OPW calculation [57]. The calculated does not include the spin orbit interaction.
Fig. 1.9 Wurtzite CdS electronic band structure calculated by density function theory (DFT) in the self interaction corrected local density approximation (LDA). Notice that critical points of the smallest band gap $E_{g0}$ are indicated by $\Gamma_1$ and $\Gamma_5$ since the spin orbit interaction is here neglected.

1.10.4 Optical Properties

The band gap energy of thin films is one of the most important parameters of solar cell window layers. CdS polycrystalline films possess a direct band gap of 2.42–2.45 eV at room temperature. High optical transparency is one of the first requirements for solar cell applications. It depends on the band gap energy value and the thickness measured on the films, and shows a strong dependence on the film preparation procedure. The optical properties related to the deposition techniques are discussed by several authors [58–60]. In spite of this, the optical properties of both structures (cubic and hexagonal) are broadly similar [61, 62].

For instance in chemical bath deposition (CBD) grown CdS, it has been shown that the higher the temperature at which the samples were prepared, the lower their band gap energy [63]. Also, samples subjected to annealing treatments present lower band gap energy than those in the same as grown conditions [63]. This trend should be correlated
to the structural properties of the samples to find the origin of the band gap shifting. It can be due to film thickness [59], grain size [64, 65] or even the presence of different phases [66, 67]. Although the difference of band gap in the two phases is only 30 meV (2.48 eV for hexagonal and 2.45 eV) [68], the phase changes therefore are unlikely to account for all of the band gap change so observed, other parameters affecting the band gap are strain, non-stoichiometric films and defects.

Some other properties of CdS have been listed as follows:

1. The conductivity increases when irradiated with light (leading to uses as a photoresistor).
2. When combined with a p-type semiconductor it forms the core component of a photovoltaic (solar) cell and a CdS/Cu$_2$S solar cell was one of the first efficient cells to be reported [69, 70].
3. When doped with for example Cu$^+$ ("activator") and Al$^{3+}$ ("coactivator") CdS luminesces under electron beam excitation (cathodoluminescence) and is used as phosphor.
4. Both polymorphs are piezoelectric and the hexagonal is also pyroelectric.

Some physical properties of CdS are shown in table 1.2.

Table 1.2 Shows the basic physical properties of CdS.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>144.48 g mol$^{-1}$</td>
</tr>
<tr>
<td>Density</td>
<td>4.82 g/cm$^3$</td>
</tr>
<tr>
<td>Melting point ($^\circ$C)</td>
<td>1750 $^\circ$C, 2023 K, 3182 $^\circ$F (10 MPa)</td>
</tr>
<tr>
<td>Std enthalpy of formation $\Delta_H^{298}$</td>
<td>$-162$ kJ·mol$^{-1}$</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.529</td>
</tr>
<tr>
<td>Energy gap (eV)</td>
<td>2.42, direct</td>
</tr>
<tr>
<td>Boiling point</td>
<td>980 $^\circ$C, 1253 K, 1796 $^\circ$F</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>28 meV</td>
</tr>
<tr>
<td>Standard molar entropy $S_{^{298}}$</td>
<td>65 J·mol$^{-1}$·K$^{-1}$</td>
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1.11 Existing Literature on Synthesis of CdS Nanoparticles

1.11.1 Existing Literature on Synthesis of Undoped CdS Nanoparticles

1. λ-DNA was first diluted by distilled water to 2, 10, 20, and 40 ng μl⁻¹. 10 μl Cadmium acetate solution (50 mM) and 10 μl λ-DNA solution were mixed completely, and then a drop of mixed solution (about 10 μl) was placed onto the surface of freshly cleaved mica. After about 4 min, the mica was immersed in a heated thiourea solution for 100 min. Finally, the sample was taken out and dried in desiccators [71].

2. 0.5 mM Cadmium chloride (CdCl₂·5H₂O, AR) and 0.5 mM Sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O, AR) were dissolved in 30 ml distilled water under vigorously stirring for 15 min, then certain dosage of poly (N-vinyl-2-pyrrolidone) was introduced into the above solution under continuous stirring for 15 min, resulting in a clear and colorless solution. The solution and 20 ml distilled water were transferred into Teflon liner autoclave with 50 ml capacity. The autoclave was sealed and maintained at certain temperature for certain time, then cooled naturally to room temperature. Finally, the precipitates were dispersed in absolute ethanol [72].

3. CdCl₂ and Sodium sulfide (Na₂S) were used as starting materials. In a typical synthesis of nanocrystals, a Methanolic solution (50 ml) of Cd²⁺ ions (2.34×10⁻² M) and Thiophenol (5.75×10⁻² M) was prepared. To this solution, 0.5 ml alcoholic KOH solution (0.1 M) was added and argon was bubbled through the solution to remove dissolved oxygen. A saturated Methanolic solution of Na₂S was added to make the final molar ratio of Cd⁺² : Thiophenol : S⁻², 1:2.5:0.5. The solution thus obtained was centrifuged and the precipitate was washed in methanol for 4–5 times [73].

4. In a typical synthesis process, 10 mmol of CdCl₂, 5 mmol of CS (NH₂)₂ or 5 mmol of C₂H₅NS and 5 mmol of Sulfur powder were dissolved into 50 ml of Ethylene glycol (EG) and stirred at 333 K for 1 h. Then the system was purged for
20 min with Argon gas prior to switching on the microwave reactor. The resulting mixed solution was placed in a program controlled sonochemistry assisted microwave reactor with the microwave power set to 400 W and operated at 413 K for 45 min. In this process, a high intensity ultrasonic probe was directly immersed in the solution. The Ti horn was inserted to a depth of ~1 cm in the solution. Calorimetry was used to estimate the electro acoustic or energy transfer efficiency of the transducer to the solution. Based on the calorimetry measurements, the transfer efficiency of the ultrasonic energy from the transducer to the reactor solution was estimated as 30% (at 80% amplitude), with the assumption that all the ultrasonic energy was converted into heat in the reactor. Based on these calorimetry experiments, the power intensity of the system was calculated to be about 60 W/cm². After the reaction, the synthesized samples were separated by centrifugation, washed with absolute ethanol and doubly distilled water several times, and dried at 333 K in vacuum for 8 h [74].

5. Synthesis of CdS nanoparticles was performed at ambient temperature by addition of 5×10⁻³ M solution of Na₂S to the joint prepared solution of CdCl₂ (5×10⁻³ M) and pyridine (5×10⁻² M) under stirring. In case of chemical doping of CdS with In³⁺ (in fact with In₂S₃), the joint CdCl₂ pyridine solution contained also the necessary quantity of InCl₃. The calculated quantity of Na₂S solution was added to this solution to keep stoichiometric ratios of the elements and 10 or 20 % weight loading of In₂S₃ in the CdS nanoparticles. The reaction mixtures were kept in dark for 24 h to complete the nanoparticles formation. Then the yellow CdS nanodispersions were dialyzed against 5×10⁻² M water solution of pyridine through cellophane membrane [75].

6. Appropriate amount of analytically pure Cd(CH₃COO)₂·2H₂O was dissolved into a deaerated 35 mol% aqueous solution of Ethylenediamine (C₂H₈N₂) in a flask at room temperature. Then under vigorous stirring, analytical pure Na₂S was quickly added to this solution, and a milk white sol was formed soon. Next, the resultant milk white sol was heated to 100 °C, and kept on stirring at this temperature for about 6 hours until the milk white reaction mixture gradually turned to a yellow
colour. The final product was then collected and washed with distilled water and ethanol [76].

7. The CdS nanocrystals of various sizes were prepared by single source organometallic precursor in noncoordinating solvent ethanol. The precursor solution A was prepared by dissolving 36 mg Cadmium chloride (CdCl₂·2H₂O) and 12 mg of thiourea [(NH₂)₂CS] in 30 ml Ethanol at 60 °C in water bath under magnetic stirring. Another solution B was prepared by dissolving 10 mg Sodium hydroxide (NaOH) in 10 ml ethanol. Now the solution B was added into solution A. The mixed solution was kept at 60 °C under magnetic stirring. In the beginning a white solution was obtained, which gradually become transparent and the colour changed from white to green yellow. The solution samples were centrifuged and washed with ethanol and then with acetone, and dried to obtain nanocrystalline CdS powder [77].

8. CdS nanoparticles capped with poly (acrylic acid) (PAA) were prepared in aqueous solutions from Cd(NO₃)₂ and Na₂S. Cd(NO₃)₂·4H₂O (64.3 mg) was dissolved in 100 ml of water and transferred into a 500 mL, three necked round bottomed flask fitted with a mechanical stirrer. An appropriate amount of PAA (MW = 2100 g/mol) was dissolved in 150 mL of water, added to Cd solution, and deoxygenated with nitrogen for 10 min. For reactions run at pH 7.5, pH was adjusted with 10 M NaOH and/or 10 M HNO₃. Sulfide solution was prepared by dissolving 25 mg of Na₂S·3H₂O in 50 mL of water and injected into the reaction mixture. The reaction mixture was kept stirring at room temperature under nitrogen for an hour. pH usually increases by 0.5–1.0 units after Na₂S addition, and the reaction ends around pH 8.0–8.5 [78].

9. Aqueous solutions of 1M Cd(NO₃)₂ and (NH₄)₂S were prepared separately for the synthesis of uncapped CdS nanoparticlcs. Six co–precipitation chemical reactions were performed by mixing different volumes of the as prepared aqueous solutions. 200 mL of the 1M (NH₄)₂S aqueous solution was mixed with 30, 50, 100, 150, 170, and 200 mL of the 1M Cd(NO₃)₂ aqueous solution, at room
temperature and under mechanical stirring. The nominal Cd/S molar ratios of the mixed solutions were 0.15, 0.25, 0.50, 0.75, 0.85 and 1.0. After precipitation the samples were centrifuged, washed with deionized water, and dried in vacuum at $10^{-3}$ mbar [79].

10. At the synthesis of CdS nanoparticles, 4.41 mmol of cadmium acetate dihydrate, 6.24 mmol of thiourea and 5.48 mmol of 1–thioglycerol as a modifier were dissolved in 100 mL of DMF. The solution was refluxed for 4 h under argon flow. Then 20 ml of H$_2$O was added to the solution, which was refluxed again for 2 h. To the solution of thioglycerol modified nanoparticles, 5.48 mmol of 1–dodecanthiol as a secondary modifier was added and refluxed 1 h. During the reflux, CdS particles precipitated. The reaction mixture was centrifuged and the precipitate was collected by filtration. The CdS nanoparticles obtained as precipitates were washed three times with EtOH [80].

11. For the synthesis of thiol capped CdS nanoparticles Cadmium chloride (2×10$^{-4}$ M) was dissolved in methanol. Thiophenol was added in appropriate proportions for preparing solutions with varying molar ratio of Cd$^{2+}$: Thiophenol. Argon gas of commercially pure grade was bubbled through the solutions before irradiation. All the chemicals were of highest purity available and were used as obtained. For $\gamma$–irradiation, a $^{60}$Co source at a dose rate of 60.6 Gray min$^{-1}$ (Gy min$^{-1}$) was used to generate 1.0×10$^{-5}$ M solvated electrons per minute. On irradiation of Cd$^{2+}$: Thiophenol mixture, a colloidal solution of CdS nanoparticles in Methanol was obtained. The solvent was removed from the solution by rotary evaporator and the nanoparticle powder thus obtained was washed with Acetone and Methanol 3–4 times each to get rid of the impurities. Finally, the product was dried and stored in vacuum desiccators [81].

12. CdCl 0.036 g was dissolved in 50 mL of Dimethyl sulfoxide (DMSO) previously purged for at least 30 min with N$_2$. When CdCl was completely dissolved under vigorous stirring, 0.016 g of Sodium 2–ethylhexanoate (Na(ethex)$_2$) were incorporated. Subsequently 0.12 g of Na$_2$S were dissolved in 5 mL of deionized
water bubbled with N$_2$ for 30 min. 0.1 mL of this solution was rapidly injected to the Cd$^{2+}$ solution. Finally, CdS Nps were prepared [82].

13. In a typical experiment, 11.25 mL of 0.15 M Cd$^{2+}$(aq) and S$^{2-}$(aq) were deposited into separate round bottom flasks each containing 239 mL of 0.5 M AOT in n–heptane. After stirring each mixture for 45 min, the S$^{2-}$(aq)/reverse micelle solution was cannulated into the Cd$^{2+}$(aq)/reverse micelle mixture and stirred for 2 h. Formation of CdS nanoparticles was indicated by the immediate color change, from colorless to yellow. To this transparent yellow solution, an excess of the complexing agent (4–fluorophenylthiol) was added (1.80 mL, 5 times the original Cadmium concentration) followed by the addition of triethylamine (2.24 mL, 5 times the original Cadmium concentration), resulting in precipitation. After stirring for 1 h, the capped CdS precipitate was isolated by centrifugation and washed three times with n–heptane. The wet precipitate was dispersed in Acetone to produce CdS nanoparticle sols of 0.1 and 0.5 M concentrations [83].

14. The CdS nanoparticles functionalized through the surface capping of cysteine were synthesized by 40 mL (0.01 M) Cadmium acetate aqueous solution was poured into a reaction flask. The solution was continuously stirred for 30min under nitrogen atmosphere and 20 mL newly prepared CH$_3$CSNH$_2$ solution (0.01 M) was slowly added into the flask. Then 1.2 mL 0.1 M Sodium hexametaphosphate was dropwise added into the flask while the solution was vigorous stirring. The pH value of the mixture was adjusted to ~ 9.5 with 0.1 M NaOH. A transparent yellow solution was obtained within minutes. The solution was continuously stirred for 1 h. And then 4 mL of 0.0185 M cysteamine aqueous solution was added into it. The reaction was maintained for 24 h with bubbling of nitrogen [84].

15. The starting materials for the synthesis of CdS nanoparticles were Cadmium chloride (Acros Organics) as Cadmium source, Sodium sulphide (R & M Chemical) and Thioacetamide (Sigma Aldrich) as Sulfur sources and distilled water as solvent. All chemicals were analytical grade products and used without
further purification. In a typical synthesis, 0.005 M of Cadmium chloride and 0.006 M of Sulfur source (Sodium sulphide for fcc structure or Thioacetamidne for hcp structure) were added into 100 ml glass beakers containing 20 ml of distilled water and stirred with 500 rpm for 30 min. The beakers were placed in a high power microwave oven (1100 W) operated using a pulse regime with 20% power for different irradiation time from 10 to 40 min. The precipitates were centrifuged (3500 rpm, 10 min) and washed several times with distilled water and absolute ethanol. The yellow products were dried in air at 60 °C for 24 h under control environment [85].

16. In this study, they used Cadmium nitrate Cd(NO₃)₂ as a Cd²⁺ ion source and Sodium sulphide Na₂S as a chalcogen ion S²⁻ source, respectively. For the synthesis of CdS nanoparticles, the 50 mL aqueous solution of (0.1 M) Cd(NO₃)₂ and 50 mL aqueous solution of (0.1 M) Na₂S were prepared. The freshly prepared aqueous solution of 0.1 M Na₂S was mixed drop by drop in the 0.1 M CdNO₃ solution using strong stirring. As the reaction started, the mixture gradually changed from transparent to pale yellow or cream coloured and after the completion of reaction this turned to dark yellow. The precipitates were washed several times with ethanol and centrifuge and were dried at 70 °C for four hours in vacuum. To remove any type of unreacted impurities, it was then washed three times with methanol and dried by evaporation method [86].

17. All chemicals were of analytical grade and used as received without further purification. CdS nanoparticles were prepared by the chemical precipitation method at room temperature. In this method aqueous solution of the reactants was prepared. 0.01 M CdCl₂ and 0.01 M Na₂S uses as the reactant materials. The reaction mixture was prepared by adding 4 mL CdCl₂ (0.01 M) and 4 mL Na₂S (0.01 M) into 40 mL deionized water. The solution turned to yellow color immediately due to the formation of CdS. The stirring was continued for some specific time in order to facilitate complete nanoparticle precipitation. The precipitate was then separated by centrifugation and washed with deionized water and ethanol repeatedly to get rid of unreacted species and by product. The sample
was dried at 35 °C for 6h and the free standing powder was collected and preserved in an airtight container. The same procedure was used to synthesize different nanoparticle size of CdS by varying the ratios of CdCl₂ to Na₂S in the mixture [87].

1.11.2 Existing Literature on Synthesis of Mn Doped CdS Nanoparticles

1. To grow CdS:Mn nanoparticles, 30 ml aqueous solution of CdSO₄, Mn(NO₃)₂ and Na₂S₂O₃ with concentrations of 1, 10 and 50 mmol l⁻¹ were prepared. Twenty milliliter aqueous solution of thioglycerol (C₃H₈O₂S, TG), with 0.5 mol l⁻¹ concentration, was prepared and added to the previous solution as the capping agent. The pH was adjusted to 8.0 using dilute solutions of NH₄OH and H₂SO₄. The sample was left in a dark place at room temperature for a few days and was continuously monitored for absorption, luminescence and pH [88].

2. All the reactants and solvents that are used for the wet synthesis process were of analytical grade. In a typical preparation process, 1.5 ml of 0.1 M Mn(NO₃)₂ and 0.05 g PVP was dissolved in 50 ml 0.1 M CdCl₂·5H₂O aqueous solution. Then 50 ml aqueous solution of 0.1 M Na₂S was added drop by drop in the above solution under vigorous stirring, resulting in the formation of CdS particles, via the following reaction at room temperature:

\[
\text{CdCl}_2\cdot\text{H}_2\text{O} + \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \rightarrow \text{CdS} + 2\text{NaCl} + 10\text{H}_2\text{O}
\]  

During the synthesis of CdS particles, it was observed that one deep yellow colloidal product was formed immediately upon mixing the two reactants. This phenomenon indicates that the rate of chemical reaction of the system is very fast which favored the formation of CdS nanoparticles. The obtained yellow solution was stored at room temperature [89].

3. To synthesize CdS nanoparticle the chemicals used were Cd(CH₃COO)₂·2H₂O, Mn(CH₃COO)₂·4H₂O, Polyvinylpyrrolidone (PVP), and Na₂S. All the chemicals were used as received (Merck & SD fine chemicals) without further purification. (4⁻y) mmol of Cd(CH₃COO)₂·2H₂O was taken into 20 ml DMSO and y = 0.12
mmol of Mn(CH₃COO)₂·4H₂O was taken into 20 ml of DMSO; 0.1 gm PVP dissolved in 20 ml DMSO was added to this solution. The reaction mixture was kept at a temperature of 55 °C in a beaker of 40 ml capacity under continuous stirring. Na₂S was added drop wise for 5 minutes. Two samples S₁ and S₂ of Mn²⁺ doped CdS (CdS:Mn) nanoparticles were collected after 3 h and 5 h stirring, respectively. The nonsolvent acetone was added in excess to reaction mixture to precipitate out nanoparticles. The solution was centrifuged and washed with methanol to get rid of any Mn²⁺ and other unreacted ions remaining outside the clusters [90].

4. Mn²⁺ doped CdS NPs were prepared by simple co-precipitation method in aqueous medium. The chemicals, Cadmium acetate [Cd(CH₃COO)₂·2H₂O], Manganese acetate [Mn(CH₃COO)₂·4H₂O] and Sodium sulfide [Na₂S] were purchased from E. Merck Ltd., Mumbai, India. All the chemicals were of AR grade and used without further purification. For 5% Mn²⁺ doping, 10 ml of 1.0 M cadmium acetate and 5 ml of 0.1 M Manganese acetate solution were diluted with 75 ml double distilled water. This was followed by drop wise addition (1 drop per 10 s) of 10 ml of 1 M of Na₂S under vigorous stirring at 4000 rpm for 1 h at 60 °C. The pH value of the solution was 6.5. A yellow precipitate was obtained which was separated by centrifugation and washed several times with double distilled water and ethanol. The precipitate was dried under vacuum at 60 °C overnight to get the powdered sample. Using the same method 0%, 10% and 20% Mn²⁺ doped CdS NPs were also prepared. All the observations were taken at room temperature [91].

5. In a typical experiment, Cadmium acetate dehydrate (Cd(CH₃COOH)₂·2H₂O) is mixed in 50 ml of Ethanol. In the above 50 ml solution, aqueous solution of Sodium sulfide (Na₂S) is added drop wise to form CdS NPs. Manganese acetate (Mn(CH₃COO)₂·4H₂O) is used with Cadmium acetate (Cd(CH₃COOH)₂·2H₂O) to prepare Mn doped CdS NPs. Finally, the obtained product is washed with ethanol several times and is dried in vacuum oven at 40 °C for 4 h [92].
6. Synthesis of Mn (5, 10 and 15 wt%) doped CdS nanoparticles was carried out by wet chemical precipitation method at room temperature. The precursors, Cadmium acetate dihydrate (Cd(CH₃COO)₂·2H₂O), Manganese acetate dehydrate (Mn(CH₃COO)₂·2H₂O) and Sodium sulfide (Na₂S·2H₂O) were purchased from Merck of analytical reagent grade and were used as received. Absolute Ethanol was used as the solvent for all the stages of experiment. A mixture of Cadmium acetate dihydrate and Manganese acetate dihydrate were taken in weight proportionate and were dissolved in Ethanol under vigorous stirring. After 60 min of stirring, the pH of the mixture was adjusted to nine by adding liquid ammonia (25 N) and it was allowed to stir for 90 min. Under continuous vigorous stirring, the drop wise addition of Sodium sulfide into the mixture was carried out. The optimized ageing period for the nanoparticles was obtained by now allowing the mixture to stir further for 48 h. Then, nanoparticles (precipitate) were centrifuged and washed repeatedly with organic solvents (Ether, Acetone) to remove unreactants, and dried at 70 °C in a hot air oven for 4 h. The above stated process was followed to prepare 5, 10 and 15 wt% of Mn doped CdS nanoparticles. Through this preparation method, the product yield is nearly 90%. The products were allowed to cool and stored in a designator over anhydrous CaCl₂ and then subjected to characterization and material confirmation [93].

7. Here, Carbon disulfide was used as the Sulfur source and Ethylenediamine was used as the nucleophilic attack regents to release H₂S. Carbon disulfide can react with ethylenediamine as described by reaction (9):

\[
\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 + \text{CS}_2 \rightarrow \text{H}_2\text{NCH}_2\text{CH}_2\text{NHCSH}
\]  
(8)

The product will undergo polymerization accompanied by release of gaseous H₂S as described by reaction (10):

\[
n \left(\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCSH}\right) \rightarrow \left[\text{-HNCH}_2\text{CH}_2\text{NHCS-}\right]n + n\text{H}_2\text{S} \uparrow
\]  
(9)

Based on this strategy, the reaction route was designed to prepare CdS nano rods as follows. A 60 cm³ aqueous solution of final pH 7, which contains
Ethylenediamine (3 mmol), Cadmium chloride (1 mmol) and Manganese chloride was heated to 70 °C, Carbon disulfide (3 mmol) was rapidly injected into the warm solution. For changing the Manganese concentration in the host material, the concentration of Manganese chloride (0–5 at%) is changed. All the reagents are commercially available and analytical grades used without further purification. The mixture was maintained at this temperature under magnetic stirring for 4 h. Finally, the mixture became bright yellow. The precipitate was filtered off, washed with distilled water and absolute alcohol several times to remove the impurities, and then dried in vacuum at 70 °C for 8 h before further characterization [94].

8. The growth procedure was carried out in a horizontal tubular furnace via vapor transport and subsequent condensation. Typically, 2 g CdS powders (99.99%), loaded in a ceramic boat, were placed in the center of a quartz tube, and a p-type Si (100) wafer coated with Au film (~10 nm) was put downstream, 20 cm away from the ceramic boat. The quartz tube was pumped to ~10⁻² Torr and flushed several times by pure Ar (99.999%) to remove moisture and oxygen at first. Afterwards the center of the furnace was heated up to 925 °C at the rate of 10 °C/min under the Ar flow rate of 10 sccm and kept at this condition for 3 h. After the furnace was cooled naturally down to room temperature under Ar flow, the yellowish wool like products was formed on the surface of the Au coated Si substrate. To fabricate CdS:Mn NRs with the composition of Mn₀.₀₁₄₆Cd₀.₄₉₅₈S₀.₄₈₉₆, 2 g mixtures of CdS with MnC₂O₄·2H₂O powders (AR in purity) at the mass ratio of 24:1 were adopted respectively, then repeated the experiment process mentioned above [95].

9. Colloidal dispersions consisting of Cd₁−ₓMnₓS nanoparticles were prepared by mixing solution containing Cd(NO₃)₂ and MnSO₄ with solution containing Na₂S in the presence of surface active agent Sodium hexametaphosphate (NaPO₃)₆. The concentration of cations ([Cd²⁺] + [Mn²⁺]) was constant and equal to 2×10⁻³ M, while an “excess” of S²⁻ ions was used in the synthesis (2.4×10⁻³ M). The content of Mn²⁺ ions was varied up to x = 0.30. The concentration of (NaPO₃)₆ was
2×10^{-2} \text{ M}. The light and air were excluded during the preparation of colloidal dispersions. After precipitation of colloidal particles the solvent was removed by vacuum evaporation at room temperature. The obtained yellow powders could be re dissolved in water to give a colloid with the same structured absorption spectrum as the solution before evaporation of the solvent [96].

10. All the chemicals used in the present work were analytical grade and were used without any further purification. The major steps involved in this hydrothermal process were briefly described as follows. 1.14 g of \text{CdCl}_2\cdot5\text{H}_2\text{O} and various amounts of \text{MnCl}_2\cdot5\text{H}_2\text{O} were placed into four 50 ml Teflon lined stainless steel autoclaves, which had been filled with 30 g of distilled water and 20 g of ethylenediamine. The Manganese amount in the mixtures was counted to the required mole ratios corresponding to 0.0%, 2.5%, 5.0% and 7.5% doping respectively. In the next step, 0.4 g of (NH_4)_2\text{S} was injected dropwise into these four autoclaves with a syringe. Immediately, a clear yellow solution was obtained due to the reaction of Cd^{2+}, Mn^{2+} with S^{2−}. The autoclaves were sealed carefully and put into an oven maintained at 180 °C for 48h, then cooled down to room temperature gradually. The precipitates were separated from the aqueous solution and washed with distilled water repeatedly. The final products were dried in a vacuum at 80 °C for 4h and were collected for the further characterization [97].

11. \text{CdS: Mn} nanocrystals were prepared in aqueous medium as follows. Cadmium acetate (0.02 mol, \text{Cd(CH}_3\text{COO})_2), Manganese acetate (0–0.002 mol, \text{Mn(CH}_3\text{COO})_2) and appropriate Sodium polyphosphate (NaPP) were dissolved in 100 ml distilled water. Under Nitrogen flow, the above mixture was stirred at 60 °C for 30 min. Freshly prepared \text{Na}_2\text{S} solution was dropwise added to the precursor mixture, and kept strong stirring at 80 °C for 2 h. The molar ratio of S/Cd was chosen more than 1 to ensure that all metal ions were participated in the reaction. After cooled down to room temperature, the final precipitates were separated from solution by centrifugation at 6000 rpm, and then washed with distilled water and anhydrous ethanol several times, respectively. At last, the
samples were dried in vacuum at 50 °C for 12 h and collected for further characterization and treatment [98].

12. Thermochemically grown CdS:Mn nanoparticles were prepared using a 30 ml aqueous solution of analytical grade CdSO₄, Na₂S₂O₃ and Mn(NO₃)₂. The concentrations of CdSO₄ and Na₂S₂O₃ were 1 and 50 mmol l⁻¹, respectively. The Mn(NO₃)₂ concentration was adjusted to give a Mn:Cd ratio of 1% or 10%. A 20 ml aqueous solution of thioglycerol (C₃H₈O₂S, TG), with 0.5 mol l⁻¹ concentration, was prepared and added to the previous solution as the capping agent. Samples were then put in a water bath at a temperature of 96 °C, and they were continuously purged with argon. The color of the initial solution turned slightly green after the start of the heating process, showing the formation of the CdS nanoparticles [99].

13. Cadmium acetate (99%, Aldrich Chemical Co), Manganese acetate (99.1%, Fisher Scientific) and Na₂S·9H₂O (98%, Aldrich Chemical Co) as precursors, methanol (CH₃OH) as a solvent, Thiophenol (C₆H₅SH) as a template and double distilled water obtained from commercial source( analytical reagent, AR grade) were used for the chemical co-precipitation synthesis of CdS:Mn nanocomposite system. A microbalance (M/s SICO, India) was used to weigh the materials to 10 μg accuracy. Quartz tubes (M/s INFUSIL, India) were used to heat the samples in furnace which is run uninterruptedly using 10 KVA (M/s Kirloskar, India) generator. It has provision of high vacuum system (M/s Avac, India).

CdS:Mn powder samples were prepared by chemical route using their acetate salts. 2.6640 g of Cd(CH₃COO)₂ was completely dissolved in 100ml of Methanol to form 0.1 M solution and 2.9964 g of Mn(CH₃COO)₂ was completely dissolved in 100ml of Methanol to form 0.1 M solution. These two solutions were mixed in appropriate concentration to get the desired ratio of Cd:Mn and the solution was taken in a burette. Similarly 0.1 M solution of Na₂S with a few drops of Thiophenol was prepared and this solution was taken in a conical flask. Thiophenol was used as both reductant and surfactant. Now the solution in the
burette is added drop by drop into conical flask under continuous stirring for about 6 hours until fine precipitate of yellowish CdS:Mn was formed. Then the precipitate was filtered out separately and washed thoroughly with de-ionized water to remove the by product, Sodium acetate salt. Finally these samples were calcined at 300 °C for 2 h in vacuum to induce crystallinity, because the preliminary XRD studies on as prepared samples showed amorphous structure. A single step chemical reaction is given below for the precipitation of the Mn doped CdS nanoparticles [100].

\[(1-x) \text{CdCH}_3\text{COOH} + x \text{MnCH}_3\text{COOH} + \text{Na}_2\text{S} \rightarrow \text{CdS:Mn}↓ + 2\text{NaCH}_3\text{COOH}\]

14. CdS:Mn samples were prepared as follows. 5 ml of Mn(ClO$_4$)$_2$ (0.01 M) was added into 100 ml of aqueous solution of Cd(ClO$_4$)$_2$ (0.01 M), then 1 ml of mercapto acetate was added dropwise into the mixture and the pH was adjusted to 10 with 1 M NaOH aqueous solution. 10 ml of Na$_2$S solution was injected into the above solution under stirring and immediately a clear green yellow solution was obtained because of the formation of CdS:Mn nanoparticles. After the aqueous colloids were refluxed for several hours and cooled to room temperature, CdS:Mn nanoparticles were separated from aqueous solution by addition of 2−propanol and purified by precipitation and rinsing several times. The resulted powders were re−dispersed in water for optical and TEM measurements [101].

15. Chemicals used for synthesis of the nanoparticles were Cadmium sulphate hydrate [3CdSO$_4$·8H$_2$O], Sodium sulphide flakes [Na$_2$S], Manganese acetate tetrahydrate [Mn(CH$_3$COO)$_2$·4H$_2$O], 2 g of PVA and deionise water as dispersing solvent. CdS nanoparticles doped with different concentration of Mn$^{2+}$ were synthesized by chemical co−precipitation method using PVA as a capping agent at room temperature. 0.3 M of Cadmium sulphate hydrate [3CdSO$_4$·8H$_2$O] was dissolved in deionised water and stirred for 15 min. at room temperature to achieve complete dissolution. Manganese acetate tetrahydrate [Mn(CH$_3$COO)$_2$·4H$_2$O] of varying concentration and 0.3 M of sodium sulphide [Na$_2$S] were also dissolved in deionised water and stirred separately. Manganese acetate solution was mixed
with Cadmium sulphate solution to get the desired ratio of Cd:Mn and was stirred. Then 2 gm of PVA solution was added to the reaction medium to control the particle size and stirred for 1 h. Afterwards Na₂S solution was added drop by drop to the prepared solution maintained at a pH value of 6 and stirred continuously for 2 h. After the completion of the reaction, the yellow precipitate obtained was filtered using filter paper. To remove the last traces of adhered impurities, the precipitate was washed several times using deionised water and dried at 60 °C for 24 h. After sufficient drying, the precipitate was crushed into fine powder for further analysis [102].

1.1.3 Existing Literature on Synthesis of Ni Doped CdS Nanoparticles

1. In this work, DMS nanoparticles of CdS: Ni^{2+} was prepared by colloidal chemical co-precipitation method using Cadmium acetate, Sodium sulfide and Nickel acetate as starting compounds. Appropriate quantities of these were weighed in microbalance (M/s SICO, India) according to the stoichiometry to obtain 2, 4, 6, 8 & 10 at% target dopant concentrations and were dissolved in 100ml of methanol to make 0.1 M solutions. The stoichiometric solution was taken in a burette and was added in drops with continuous stirring to a mixture of Na₂S (0.1 M) + 50ml of H₂O + 1.1 ml of thiophenol + 100 ml of methanol until fine precipitate of CdS: Ni was formed. After complete, precipitation, the solution in conical flask was constantly stirred for about 20 h. A single step chemical reaction is given below for the precipitation of the Ni doped CdS nanoparticles. Then the precipitates were filtered out separately and washed thoroughly with deionized water. Finally these samples are subjected to sintering process. The green colored nanocrystalline CdS or CdS: Ni^{2+} powders were obtained. The samples were calcined at 300 °C/2 h vacuum [103].

2. The precursor materials purchased from the Merck were used as received. The Cadmium acetate dihydrate (Cd(CH₃COO)₂·2H₂O), Sodium sulfide (Na₂S·2H₂O) and Nickel acetate dihydrate (Ni(CH₃COO)₂·2H₂O) were used as Cadmium, Sulfur and dopant precursors respectively. Each 2 g of Cd and S precursors was
dissolved in ethanol in 200 ml beaker separately and added drop wise under vigorous stirring. Nickel precursor [10% (mol)] was added into this solution after 30 min of vigorous stirring. To this mixture, 120 ml of ethanol was further added and allowed for 6 h stirring. The pH varying agent liquid ammonia (25 N) was added to fix the pH values at 9.0, 10.0 and 11.0. The entire solution turned into deep green in color and further allowed to stir for 48 h which is the optimized ageing period of the growth process. The dark green final products were washed thoroughly with the organic solvents (acetone and ethanol) and dried at 160 ºC in a hot air oven and preserved in moisture free container [104].

3. The synthesis of PVP capped pure and Ni (2 at%) doped CdS nanoparticles have been prepared at room temperature by chemical co-precipitation. All chemicals were of analytical reagent grade and were used directly without further purification. The deionized water was used as solvent for all the solutions referred in the present work. First, a desired molar proportion of Cd(CH$_3$COO)$_2$·2H$_2$O and NiCl$_2$·6H$_2$O were dissolved in the deionized water. Then, an appropriate amount of PVP was added to the mixture as a capping agent. After stirring this solution for 60 min, the pH of the mixture was adjusted to 8.0, and then the thiourea solution was added dropwise with continuous vigorous stirring. Dried powders of CdS:Ni nanoparticles were obtained by precipitation and heating [105].

4. In the present study, Ni doped CdS quantum dots have been synthesized through chemical precipitation technique. Aqueous solution of Cadmium nitrate (Cd(NO$_3$)$_2$·4H$_2$O) and required amount of Nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O) were stirred for 1 h at room temperature. Aqueous solution of Sodium sulfide (Na$_2$S) was added drop wise to (Cadmium nitrate + Nickel nitrate) the solution and was stirred for 2 h. A precipitate with yellowish orange color was formed soon after the addition of the Na$_2$S. The nanoparticles were initially purified by precipitating the particles with excess double distilled water and the solution obtained was centrifuged at 4,000 rpm for 10 min. The sample was obtained as precipitate and after that the sample was dried at 80 ºC for 4 h [106].
1.11.4 Existing Literature on Synthesis of Co Doped CdS Nanoparticles

1. CdS and Co doped CdS nanoparticles have been synthesized through chemical precipitation technique. Aqueous solution of Cadmium nitrate (Cd(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O) and required amount of Cobalt (II) nitrate hexahydrate (Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O) were stirred for 1 hour at room temperature. Aqueous solution of Sodium sulfide (Na\textsubscript{2}S) was added drop wise to the solution (Cadmium nitrate + Cobalt nitrate) and was stirred for 2 h. A precipitate with orange green color was formed soon after the addition of Na\textsubscript{2}S. The nanoparticles were initially purified using excess double distilled water and the solution obtained was centrifuged at 4000 rpm for 10 min. The sample was obtained as a precipitate and after that the sample was dried at 100 °C for three hours [107].

2. The preparation of Cd\textsubscript{1−x}Co\textsubscript{x}S thin films by the spray pyrolysis method. Aqueous solution of 0.1 M Cadmium acetate Cd(CH\textsubscript{3}COO)\textsubscript{2}·3H\textsubscript{2}O, 0.2 M Thiourea (NH\textsubscript{2}CSNH\textsubscript{2}) and 0.1 M Cobalt acetate Co(CH\textsubscript{3}COO)\textsubscript{2}·4H\textsubscript{2}O were taken as sources of Cd, S and Co. A considerable amount of (100 ml) solution was taken in the beaker ‘F’ fitted with the spray nozzle ‘A’. The clean substrate with a suitable mask was put on the susceptor of the heater ‘H’. The distance between the tip of the nozzle and the surface of the glass substrate was kept 25 cm. The substrate temperature was kept at 523 K and was measured by placing a copper constantan thermocouple on the substrate. When compressed air is passed through ‘P’ (at 0.50 bar pressure) and at the same time water based precursor solution is feed at the nozzle A, then the solution sprayed and was automatically carried to the reactor zone upto 5 minutes where film was deposited onto the heated substrate. In the hot zone, the atomized solution is dried and the constituent metal salts decompose and form intimate Cd\textsubscript{1−x}Co\textsubscript{x}S films [108].

3. All the chemicals and reagents used were purchased from Fisher Scientific having purity 99.5%. The chemicals were used without any further purification. In this synthesis, Copper acetate as source of Cu, Nickel acetate as source of Ni, Cadmium sulfate as source of Cd and Sodium sulfide as source of S were used.
To avoid any agglomeration between the synthesized nanoparticles, mercaptoethanol was used as capping agent. In a typical wet chemical process, 0.5 M solution of Cadmium sulfate, Copper acetate, Nickel chloride and sodium sulfide were prepared separately. Then, the solutions of Cadmium sulfate, Copper acetate and Nickel chloride were mixed, and sodium sulfide in appropriate stoichiometric proportions was added while stirring. About 2 ml capping agent mercaptoethanol was added dropwise. The mixture was stirred for 30 min at room temperature, and resultant particles were washed repeatedly with water and ethanol and dried in vacuum [109].

4. Typical synthesis of Cd$_{1-x}$Co$_x$S alloys is as follows: a suspension consisting of Cadmium dichloride (CdCl$_2$, 50 mM) in 20 ml of Triton X–100 (24 mM) is prepared. Aqueous solution of Thioacetamide in basic medium is added drop by drop to the above suspension under constant stirring at 80 °C in argon atmosphere. The desired amount of aqueous solution of Cobalt acetate (0.10 M, 0.2 M and 0.3 M) is injected into the resulting mixture and is refluxed for 12 h and left overnight. By taking in to account the reaction mechanism proposed for the synthesis of CdS nanoparticles [110], herein we propose a similar mechanism for the growth of Cd$_{1-x}$Co$_x$S nanoclusters as follows: [111]

\[
\text{CH}_3\text{CSNH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3(\text{NH}_2)\text{C(OH)} - \text{SH} \quad (11)
\]

\[
\text{CH}_3(\text{NH}_2)\text{C(OH)} - \text{SH} + \text{H}_2\text{O} \rightarrow \text{CH}_3(\text{NH}_2)\text{C(OH)}_2 + \text{H}_2\text{S} \quad (12)
\]

\[
\text{CH}_3(\text{NH}_2)\text{C(OH)}_2 \rightarrow \text{CH}_3(\text{NH}_2)\text{C} = \text{O} + \text{H}_2\text{O} \quad (13)
\]

\[
\begin{align*}
\text{Triton–X–100} \\
\text{H}_2\text{S} + \text{CdCl}_2 & \xrightarrow{\text{injection–of–Co}^{2+}} \text{Cd}_{1-x}\text{Co}_x\text{S} + 2\text{HCl} \quad (14)
\end{align*}
\]

5. Thin films of pure CdS and Co doped CdS were fabricated by thermal evaporation technique using an Edward coating unite at pressures of less than 7.5×10$^{-6}$ mbar on glass substrates at ambient temperature. CdS and Co Powders of 99.99% purity were supplied from Aldrich Company as the source materials.
The powders weighted in appropriate amounts (Cobalt percentage of $x = 0, 0.025, 0.05$) and were mixed after grinding in mortar perfectly. Then this powder was evaporated from a capped molybdenum boat to deposit the films. The deposition rate was measured and controlled in situ using thickness monitor in control panel of coating machine. The typical growth rate was 20 Å/s on average and also thickness of the films was chosen about 50 nm [112].

6. The samples of $\text{Cd}_{1-x}\text{Co}_x\text{S}$ nanoparticles with concentration $x = 0.0$ & 0.06 were prepared by co-precipitation route. The chemicals Cadmium acetate, Thioacetamide, Cobalt nitrate were dissolved in 50 ml of ethyl alcohol in separate beakers and stirred for 1 h with the help of magnetic stirrer. After 1 h the solution of Cobalt nitrate was added drop wise in the solution of Cadmium acetate and kept for 30 minutes. Then the solution of Thioacetamide was added into the mixture of Cadmium acetate and Cobalt nitrate. This solution again stirred for 1 h, filtered using a filter paper and then washed with ethanol to remove impurity present in it. The residue was collected and dried at room temperature. After that each sample is ground for 15 min. [113].

7. Cobalt doped CdS nanoparticles have been synthesized by the aqueous chemical precipitation method. 0.1 M aqueous solution of Cadmium acetate dihydrate (Cd(CH$_3$COO)$_2$·2H$_2$O) and Cobalt acetate tetrahydrate (Co(CH$_3$COO)$_2$·4H$_2$O)) was prepared with deionized water. These two solutions were mixed together and stirred magnetically at 80 °C until a homogeneous solution was obtained. The 0.1 M of Sodium sulfide (Na$_2$S) solution was also prepared with deionized water with the precursor ratio of 1:1. After an hour, aqueous solution of Na$_2$S was added dropwise into the mixed solution of Cadmium acetate and Cobalt acetate at room temperature, which resulted in an orange yellowish solution of Co:CdS. The solution was then refluxed with constant stirring at 120 °C for 30 min to attain saturation, which contains Co:CdS nanoparticles. The solution, after attaining the room temperature was added with small quantities of acetone with stirring to precipitate the nanoparticles. It was dried in hot air oven at 80 °C for 2 h. Co$^{2+}$ doped CdS nanoparticles with six different Co$^{2+}$ concentrations (1, 2, 3, 4, 5 and
10%) were prepared by the same procedure. In addition, for synthesis of surfactant (PVP) capped particles different amounts (0.5–2.5 g) of PVP were added in cadmium acetate solution before the addition of cobalt acetate [114].

1.12 Applications of CdS Nanostructures

1. CdS and cadmium selenide are used in manufacturing of photoresistors (light dependent resistors) sensitive to visible and near infrared light.

2. CdS thin film can be combined with other layers for use in certain types of solar cells [115].

3. CdS was also one of the first semiconductor materials to be used for thin film transistors (TFTs) [116].

4. Synthetic cadmium pigments based on cadmium sulfide are valued for their good thermal stability, light and weather fastness, chemical resistance and high opacity [117].

5. CdS is used as pigment in plastics [117].

6. The presence of cadmium in paints has been used to detect forgeries in paintings alleged to have been produced prior to the 19th century [118].

7. Cadmium sulfide is sometimes associated with sulfate reducing bacteria [119, 120].

8. CdS is an important material used in optoelectronics, such as nonlinear optics, light emitting diodes and lasers [121–126].

9. CdS based quantum dots are used as biomarkers in analysis of biological materials [127, 128].


11. Photodetector, laser, high density magnetic information storage and many others in semiconductor industries [133–137].
12. CdS thin film find applications in large area electronic devices like thin film field effect transistors [138] and solar cells [139].

13. It has great potential applications as nanoelectronics and photocatalytic materials [140, 141].

1.13 Aim of This Work

Among nanocrystalline semiconductors, studies on CdS have been done because its finds wide application in modern technology such as solar cell, light emitting diodes, biological labelling and optical devices based on the non linear optical properties [142]. Doping CdS has attracted a lot of attention as it is a convenient way to tailor its physical properties. Recently, spectroscopic studies of transition metal and rare earth doped nanocrystalline CdS have motivated to develop new and more efficient multicolor phosphor materials [143].

Therefore, main objective of this study was to see the effect of doping on the structural, magnetic, optical and thermal properties of cadmium sulfide with controlled morphology by chemical method and secondly to study the antibacterial behavior of undoped and doped CdS nanoparticles in different bacteria culture.
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