CHAPTER 1

OVERVIEW OF SEMICONDUCTOR NANOCRYSTALS
AND NANOSTRUCTURES

1.1 INTRODUCTION OF NANOMATERIALS

Nanotechnology is an important initiative in science and technology in the 21st century. The nanometer world is a particular domain, in which the dimensions of the materials reach the nanometer regime, where their behavior, characteristics and physico-chemical properties change drastically from those of bulk materials approaching the molecular features. It neither possesses the bulk properties nor those of the molecules. The term nanotechnology is employed to describe the creation and exploitation of materials with structural features in between those of atoms and bulk materials, with at least one dimension in the nanometer range (1 nm = 10^{-9} m). Table 1.1 lists typical nanomaterials of different dimensions.

All mainstreaming aside, nanotechnology has become a dominant player in the scientific arena. This field explores materials and their properties when at least one dimension is in the range of one to one hundred nanometers in length, a size regime referred to as the nanoscale. Materials at this scale may consist only of a few atoms or molecules clustered together. At the nanoscale, quantum confinement effects begin to dictate materials properties. These materials can exhibit significantly enhanced and altered properties as they experience quantum confinement in one, two or three dimensions.
Table 1.1 Examples of Nanomaterials

<table>
<thead>
<tr>
<th>Size (approx.)</th>
<th>Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanocrystals and clusters (quantum dots)</td>
<td>dia. 1–10 nm</td>
</tr>
<tr>
<td>Nanocomposites</td>
<td>dia. 1–100 nm</td>
</tr>
<tr>
<td>Nanowires</td>
<td>dia. 1–100 nm</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>dia. 1–100 nm</td>
</tr>
<tr>
<td>Nanoporous solids</td>
<td>pore dia. 0.5–10 nm</td>
</tr>
<tr>
<td>2-Dimensional arrays (of nanoparticles)</td>
<td>several nm²–mm²</td>
</tr>
<tr>
<td>Surfaces and thin films</td>
<td>thickness 1–1000 nm</td>
</tr>
<tr>
<td>3-Dimensional structures (superlattices)</td>
<td>Several nm in the three dimensions</td>
</tr>
</tbody>
</table>

The small size results in new quantum phenomena that yield some extraordinary benefits. Material properties change dramatically because quantum effects arise from the confinement of "electrons" and "holes" in the material. Size changes, other properties such as the electrical and nonlinear optical properties of a material, making them very different from those of the materials in bulk form. If a dot is excited, the smaller the dot, the higher the energy and intensity of its emitted light. Hence, these very small semiconducting quantum dots are gateways to an enormous array of possible applications and new technologies.
The following list enumerates some examples of materials, which can be produced in the nanometer range, giving rise to nanoparticles:

- **Metals:** Gold, Silver, Palladium, Platinum, Cobalt.
- **Oxides:** ZnO, TiO$_2$, SnO$_2$, CdO.
- **Semiconductors:** Silicon, II-VI (CdS, CdSe, CdTe, ZnS, ZnSe), III-V (GaAs, GaP, GaN, InAs, InP) and the IV-VI group (PbS, PbSe, PbTe).

The ability to work with atoms at the nanoscale and with atomic precision, promises to open new areas of technological development. The size-dependent luminescent properties of quantum dots and ultra-high strength of carbon nanotubes are just two of the nanomaterial properties that have gained notoriety over the past decade. However, this does not begin to break the surface of the vast and interesting structures and properties that nanoscience has discovered. This field is envisioned to change almost everything about how we manufacture and approach technology. Nanomaterials research has already garnered interest in field effect transistors (FET’s) for smaller, lighter and faster electronic devices, biological labeling for early detection of cancer and even opened new fields like spintronics.

Several attempts have been focused on the synthesis of a specific group of II-VI semiconducting one-dimensional nanostructures. It was also focused on the non-oxide II-VI semiconductors such as CdS, ZnS, ZnSe, ZnTe, CdSe, and CdTe, etc. Each of the semiconductors in this group has a stable or metastable wurtzite crystal structure with an associated piezoelectric phenomenon. Size affects the structure of nanoparticles of materials such as CdS and CdSe and also their properties such as the melting point and the electronic absorption spectra (Alivisatos 1996).
One of the greatest aspects of nanotechnology is that changing the size of a material by only a few nanometers can have a significant impact on the properties of the material. Conversely, this is one of the greatest detriments to nanotechnology, as a deviation in size of a material by only a few nanometers can have a significant impact on the material’s properties. In this way, there is a direct correlation between dimensionality and physical properties. For example, variance in size of quantum dots of only a few nanometers can shift their luminescence from red to blue. One can imagine from this illustration that the precision required controlling dimensionality within a few nanometers or less has been, up to this point, an arduous – yet equally significant – task.

With the recent progress in materials science, the size of materials has reached the nano- or sub-nanometer scale. In these regions, the structure size is comparable with the Fermi wavelength of the conduction electrons. For example, metal has typically a Fermi wave vector of the order of $10^8 \text{ cm}^{-1}$ (Ashcroft and Mermin 1976). That is, the wavelength of the metal is approximately 0.6 nm. Semiconductors have smaller Fermi wave vectors of the order of $10^6 \text{ cm}^{-1}$ (Beenakker and Houten 1991). Thus, their Fermi wavelengths are approximately 60 nm. In state-of-the-art nanotechnology, materials can be scaled down to these Fermi wavelengths. In nanostructures of Fermi wavelength size and hence the quantum confinement of conduction electrons become significant. A small change in structure has a marked influence on the quantized electron states. This suggests the possibility of size control of nanomaterials via quantum confinement of the conduction electrons.

The ultimate goal is to understand what role each of the synthesis parameters plays in impacting the morphology and structure/property relation of the nanostructures. To reduce the variability of the size and morphology
within a given run, a series of systematic studies were carried out in order to investigate the impact on specific synthesis parameters, namely pressure and temperature on the nanomaterials. If successful, the ramifications of fully understanding and exerting precise control over these nanomaterials will allow a higher level of selectivity, more control over dimensionality and type of morphology, easier manipulation, and hopefully, the eventually implementation of these structures into a device.

1.2 QUANTUM DOTS

Nanocrystalline semiconductor colloids, also called quantum dots, belong to a state of matter that is intermediate between molecules and solids. Their size-dependent physical and chemical properties, i.e. 'quantum size effects', are currently investigated in various fields of science. Some experimental evidence for the existence of quantum size effect was published before 1980 (Berry 1967 and Dingle et al 1974). However, a fast development of the research on colloidal nanocrystals started in 1982 (Rossetti and Brus 1982). Quantum dots (QDs) are semiconductors that have all three dimensions in the nanoscale and for this reason they are referred to as zero-dimensional (0D) structures. Discovered in the late 1980’s, these nanostructures demonstrated a physical property phenomenon that had never before been observed, scientists could modify the luminescent and electronic properties by simply changing the size of the QD. The energy band structure for various solids directly affects the electronic and optical properties of a material. These properties are inherent to the bulk material and can only be altered by adding constituents to the system. The phenomenon that garnered quantum dots so much attention within the scientific community was how the optical and electronic properties could be precisely tuned not by adding dopants but by merely changing the size of the dots. An important step forward was made in 1993, when Murray, Norris and Bawendi (Murray et al
1993) published a very powerful wet-chemical synthesis route to prepare high-quality monodisperse CdS, CdTe and CdSe nanocrystals.

Quantum dots are particularly significant for optical applications due to their theoretically high quantum yield. Because the quantum dot has discrete energy levels, much like an atom, they are sometimes called "artificial atoms". The energy levels can be controlled by changing the size and shape of the quantum dot, and the depth of the potential. More specifically, as the size of the quantum dot approaches the bulk exciton Bohr radius, the motion of electrons within the solid becomes confined. This confinement reconfigures the band structure, giving way to discrete energy levels instead of energy bands shown in Figure 1.1 (Norris and Bawendi 1995). It is at this point that the electronic and optical properties become size dependent. As the size decreases upto a few nanometers, a shift in the energy levels to higher values is resulted (Alivisatos 1996). While the material which makes up a quantum dot more significant in terms of coloration is the size. The larger the dot, the fluorescence is more towards the red end of the spectrum. The smaller the dot, it moves towards the blue end of the spectrum. The coloration is directly related to the energy levels of the quantum dot. Larger quantum dots have more energy levels which are more closely spaced. This allows the quantum dot to absorb photons containing less energy, i.e. those closer to the red end of the spectrum. The ability to tune the size of quantum dots is advantageous, as the larger and more red-shifted the quantum dots is, the less the quantum properties are. The small size of the quantum dot allows to take advantage of these quantum properties. In large numbers, quantum dots may also be synthesized by means of a colloidal synthesis. By far the cheapest, colloidal synthesis has the advantage of being able to occur at benchtop conditions and is acknowledged to be the least toxic of all the different forms of synthesis.
Quantum dots possess a “size-tunable” bandgap, these diminutive particles have potential applications as transducers which inter-convert light and electricity in detectors (Erley et al 1998), light-emitting diodes (Greenham x et al 1996), electroluminescent devices (Dabbousi et al 1995), and lasers (Shoji et al 1995). Quantum dots are one of the most hopeful candidates for solid-state quantum computation. Another cutting edge application of quantum dots is also being researched as potential artificial fluorophore for intra-operative detection of tumors using fluorescence spectroscopy. Quantum dots offer the advantages of being significantly brighter and vastly more resistant to photobleaching than the organic dyes, which are currently being used for biological labeling (Smith et al 2004). Meanwhile, in the root of so-called bottom-up nanotechnology, a structure of 1 nm size or less can be easily fabricated. Therefore, the nanostructure by the bottom-up process is more realistic for versatile nanotech devices which operate at room temperature.
The color of the emitted light depends on the size of the dots: the larger the dot, the redder the light. As the dots shrink in size, the emitted light becomes shorter in wavelength, moving toward the blue. A rainbow of colors can be emitted from a single material simply by changing the dot size. With all these different colors, it's now possible to make light-emitting diodes (LEDs) from quantum dots. Quantum dots are also possible materials for making ultrafast, all-optical switches and logic gates. Quantum dots provide a remarkable million fold improvement in speed. Other possible applications are all-optical demultiplexers (for separating various multiplexed signals in an optical fiber), all-optical computing, and encryption.

Replacement of fluorescent organic dye(s) by fluorescing semiconductor quantum dots makes it more interesting because of the possibility of tuning their size, shape, optical, fluorescence and electronic properties, and obtaining relatively higher photostability (Neretina et al 2008, Kumar and Chaudhary 2007). QDs are also becoming popular as replacements for fluorescent dyes in biological fluorescence imaging because of their superior resistance to photobleaching and continuous absorption spectra (Wu et al 2003).

1.2.1 Quantum Size Effect

In semiconductor materials, the electric current is carried by electrons and holes (Schroter 2000). Figure 1.2 (a) shows the Schematic illustration of the density of states in metal and semiconductor clusters according to Alivisatos (Alivisatos 1996) and Figure 1.2 (b) shows the density of states of a semiconductor. 3D represents the bulk, 2D quantum films, 1D quantum wires or fibers and 0D the quantum dots. There is an energy gap or band gap (Figure 1.2a) between the allowed energies of the electrons in the material that separates the normally filled energy levels of the valence band (where missing electrons behave like positively charged current carriers called
“holes”) and the conduction band (where electrons behave like a gas of free negatively charged carriers). For semiconductors, the dashed lines show the increasing band gap separations for bulk toward molecule, between valence band (VB) and conduction band (CB). The band gap width in between the two bands depends on the nature of the material, but also on temperature and pressure. The absorption of energy can elevate electrons to the conduction band leaving a hole in the valence band. At low temperature, these two charge carriers form a weak coupled pair, which is called exciton. The energy of the exciton lies below the energy of the band gap of the semiconductor crystal because of the electrostatic Coulomb interaction.

Quantization depends on spatial confinement and can be classified in three different regimes: confinement in one, two or three dimensions. Confinement in one dimension produces quantum films, in two dimensions quantum wires and confinement in three dimensions produces quantum particles, often referred to as quantum dots, nanoparticles (NPs) or nanocrystals (NCs). Fundamental differences exist between the three different quantization regimes, for example the density of states (DOS) as a function of the energy is quite different for each quantum system (Figure 1.2b). For quantum films the DOS is a step function while for the quantum dots it is a series of discrete values resembling that of a molecule or an atom. Quantum wires have a DOS distribution that is intermediate between the quantum films and the quantum dots. The great interest in these materials is mostly due to the optical, electrical and photoredox properties of the semiconductor which can be tuned and manipulated in many ways, just by controlling the shape and dimensionality of the material. Quantum confinement increases the gap as size (r) decreases more steeply with a smaller ‘r’ (variation with $1/r^2$). This gives bandgap energy ($E_g$) for nanocrystals of different semiconductors from macroscopic solid parameters shown in Figure 1.3 (a) and the variation of the band gap calculated for different semiconductors, zinc oxide, zinc selenide,
cadmium sulfide, cadmium selenide and gallium arsenide in Figure 1.3 (b). HOMO and LUMO represent respectively the highest occupied molecular orbital and lowest unoccupied molecular orbital. With appropriate light excitation, nanocrystals can re-emit by fluorescence, photons of energy equal to the bandgap value. With different semiconductors, a broad spectrum of gap energies is therefore covered, spanning a complete spectral range from near infrared to near ultraviolet.

Figure 1.2  a) Schematic illustration of the density of states in metal and semiconductor clusters, b) Density of states in one band of a semiconductor as a function of the dimensional freedom.
Because of the finite number of atoms and the quantum confinement, the energy bands of a nanocrystal are split into discrete levels, which widen as the radius ‘$r$’ of the nanocrystal decreases. To a first approximation, the gap ‘$E_g$’ of the spherical nanocrystals is given by the formula in the Equation 1.1.

$$E_g = E_{g}^{\text{Solid}} + \frac{\hbar^2 \pi^2}{2r^2} \left\{ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right\} - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0} \frac{1}{r}$$  (1.1)

In this equation, the first term ‘$E_{g}^{\text{Solid}}$’ corresponds to the gap of the macroscopic crystal. The second $1/r^2$ term, called quantum confinement (spherical nanocrystal) which are confined, an electron and a hole of respective effective masses ‘$m_e^*$’ and ‘$m_h^*$’. The effective mass is a corrective factor applied to the mass of the free electron of the valence and conduction bands.
bands near the energy gap. ‘$m_e$’ represents the mass of the electron ($m_e = 9.1 \times 10^{-31}$ kg) and ‘h’ the quantum of angular moment ($h = h/2\pi = 1.0546 \times 10^{-34}$ Js).

The last term accounts for the coulomb attraction between the electron and the hole. ‘$\varepsilon$’ is the static dielectric permittivity of the material relative to that of a vacuum $\varepsilon_0 = (\varepsilon_0 = 8.854$ pF/m). ‘e’ is the electric charge of the electron ($e = 1.602 \times 10^{-19}$ C).

1.3 SEMICONDUCTOR NANOCRYSTALS

Semiconductor nanocrystals are made of materials from periodic groups II – VI, III – V, or IV – VI. Electrons in bulk semiconductor material have energy levels that are so close together that they behave as if the levels were the same. This characteristic sets the band gap energy at a fixed amount. Semiconductor quantum dots behave differently.

In II-VI and III-V semiconductors, excitons are considered to be similar to a hydrogen atom and can be well described by hydrogen like model incorporating the effective mass and the screening described by the dielectric constant. Brus (1984) considered that unlike in bulk materials, where the electron-hole pair is free to move, in small quantum dots they can become physically confined. Strong confinement leads to a rising of the electronic energy in the same way as would be expected from the simple particle-in-a-box model of quantum mechanics. An exciton is defined as an excited electron–hole pair. The average distance between an excited electron and a hole is called the Exciton Bohr Radius.

![Figure 1.4 The Exciton Bohr Radius in relation to semiconductor crystals](image-url)
In bulk material, this radius is much smaller than the semiconductor crystal. But nanocrystal diameters are smaller than this Bohr radius (Figure 1.4). Because of this, the “continuous band” of electron energy levels no longer can be viewed as continuous. The energy levels become discrete, and quantum confinement is seen to operate. The difference of a few atoms between two quantum dots alters the band gap boundaries. Small nanocrystals absorb shorter wavelengths or bluer light, whereas larger nanocrystals absorb longer wavelengths or redder light as shown in Figure 1.5. Changing the shape of the dot also changes the band gap energy level. Tunable band gaps which increase the range of sunlight captured, and less expensive materials and processing are areas of active research. As exciting as these advances are, they represent only part of the challenge of efficient solar energy conversion. Once these electrons are excited, they must be prevented from recombining with holes, and they must be transported to electrodes.

Semiconductor nanocrystals or quantum dots have the potential for photonic device applications such as tunable lasers, light-emitting diodes, and displays. Much effort has been devoted to control the wavelength and intensities of the photoluminescence (PL) by controlling the size of QDs, doping of transition metal ions, or surface capping. In smaller QDs, due to the high surface to volume ratio, surface states play a major role in optical properties. Nanosized materials, whose electronic properties are size-tunable, enable the application of a larger range of semiconductors as candidates for viable photocatalytic processes in renewable energy as well as other fields such as environmental remediation. Hybrid nanocrystals (NCs) based on semiconductor materials would be useful for optoelectronic and photovoltaic applications. Adjacent domains of semiconductors having different band gaps and appropriately chosen band offsets could either trap electron–hole pairs in specific regions of the NCs, thus forcing them to recombine therein with high efficiency, or separate electrons from holes (Milliron et al 2004).
1.4 BASIC PROPERTIES OF CdS

Recently II-VI semiconducting chalcogenides nanoparticles, especially sulfides and selenides have been investigated extensively, owing to their interesting optoelectronic properties (Hullavarad et al 2008). Cadmium sulfide is the inorganic compound semiconductor which occurs in nature with two different crystal structures, the more stable hexagonal wurtzite structure (found in the mineral Greenockite) and the cubic zinc blende structure (found in the mineral Hawleyite). In both these forms, cadmium and sulfur atoms are four coordinate (Wells 1984).

In the quantum confined regime, the control of particle size allows the band gap to be “tuned” to give the desired electronic and optical properties. For cadmium sulfide (CdS) particle diameters below 60 Å, the absorption spectrum is “blue shifted” from the bulk (2.42 eV), and correlations have been made between the absorption threshold and the size of the particles, using both theoretical calculations (Lippens and Lannoo 1989) and experimental measurements (Spanhel 1987). It receives a wide range of research interest because of their unique properties and their wide variety of potential applications, for instance, for laser light-emitting diodes, solar cells, non linear optical, optoelectronic and electronic devices. The most important properties of CdS are shown in Table.1.2.
In the last decade, the main efforts have focused on the preparation of different sized binary II–VI group semiconductor nanocrystals to obtain different color-emitting luminescence. However, the tuning of physical and chemical properties by changing the particle size could cause problems in many applications, in particular if unstable small particles are used. Recent advances have led to the exploration of tunable optical properties by changing their constituent stoichiometries in ternary alloy nanocrystals. Although bulk or thin-film semiconductor alloys have been extensively investigated due to their wide application in optoelectronics, before the realization of alloy nanocrystals under high temperature, only a limited number of studies have been reported for the preparation of alloy or composite nanocrystals by co-precipitation or slow diffusion of their constituents via wet chemistry routes (Petrov et al 2002).

### Table 1.2 Properties of Cadmium Sulfide

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>4.82 g/cm³</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Hexagonal, Cubic</td>
</tr>
<tr>
<td>Molar mass</td>
<td>144.48 g mol⁻¹</td>
</tr>
<tr>
<td>Lattice parameters at 300K</td>
<td>( a_0 = 0.4135 \text{ nm} ) ( c_0 = 0.6749 \text{ nm} )</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.47 J/gK</td>
</tr>
<tr>
<td>Melting point</td>
<td>1750 °C, 2023 K, 3182 °F (10 MPa)</td>
</tr>
<tr>
<td>Boiling point</td>
<td>980 °C, 1253 K, 1796 °F (subl.)</td>
</tr>
<tr>
<td>Thermal conductivity (at 25°C)</td>
<td>0.2 W/cmK</td>
</tr>
<tr>
<td>Coef. of Thermal expansion (500 K):</td>
<td>( \alpha_1 = 6.26 \times 10^{-6}/K; ) ( \alpha_3 = 3.5 \times 10^{-6}/K )</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.9</td>
</tr>
<tr>
<td>Refractive index ( (n_D) )</td>
<td>2.51</td>
</tr>
<tr>
<td>Energy gap</td>
<td>2.42 eV, direct</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>28 meV</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K for low n-type conductivity</td>
<td>340 cm²/V.s</td>
</tr>
<tr>
<td>Hole effective mass</td>
<td>0.80</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.21</td>
</tr>
<tr>
<td>Hole Hall mobility at 300 K for low p-type conductivity</td>
<td>340 cm²/V.s</td>
</tr>
</tbody>
</table>
Because of its wide band gap CdS has been used as a window material together with other semiconductors such as CdTe, Cu$_2$S and CuInSe$_2$. Also the interest in CdS thin films stems from its piezoelectric properties and potential laser applications (Zhang et al 2003).

Previously CdS-based materials have not received much attention as other II-VI materials, like ZnSe, and ZnO, partially due to the unavailability of suitable substrates for high quality epitaxial growth. Such a picture has been totally changed in recent years with the advances in the fabrication of low dimensional semiconductor nanostructures which lead to various optical devices such as lasers, detectors, waveguides, etc., for future integrated photonics. CdS, being a photoconductive material, is supposedly to show also the light soaking effect, which can be a promising candidate for high current field emitter of flat panel displays and high brightness electron sources.

Cadmium sulfide is valued for their good thermal stability in many polymers, for example in engineering plastics. Cadmium sulfide has useful properties for optoelectronics, being used in both photosensitive and photovoltaic devices. During the past decades, various methods have been applied to fabricate cadmium sulfide nanocrystals, such as electrochemically induced deposition, thermal decomposition, laser-assisted catalytic growth method, ultrasound irradiation, solvothermal method, and hydrothermal method (Bostick et al 2000).

Hyperbranched nanocrystals are grown in the II-VI class of semiconductors, such as CdSe and CdTe, which have an intermediate fractional ionicity of bonds that poises them between two possible crystal structures. The basic branch point consists of a pyramidally shaped cubic zinc blende unit with hexagonal wurtzite arms projecting outward at the tetrahedral angle. The branch is possible because the two crystal structures are close in
energy and can occur at the same temperature and pressure (polytypism) (Ito 1998). Switching between the two structures can be driven kinetically; increased relative growth rate favors the cubic phase, while slower rates favor the hexagonal (Ito 1998).

Nanocrystals synthesized by chemical route gives the chance to control their size, distribution and the most important is to improve the crystallinity by altering the concentration of the reagents and their mixing rate at different temperature (Rossetti 1985). These small-size nanostructures have a large surface to volume ratio, which plays a dominant role in optical properties of the nanostructures. For good quality nanomaterials, various kinds of capping agents and inorganic shell are used to passivate the undesired sites, which result in the enhancement of luminescence intensity. Doping different activator ions (acts as a recombination center) in these stabilized nanostructures not only gives the chance to obtain required emission color, but it also reduces the self quenching by intrinsic defects in the nanocrystals (Xiao and Xiao 2008).

1.4.1 Crystallographic Structure of II-VI Semiconductors

In the broadest sense, II-VI semiconductors include all compounds formed from elements of the group II and group VI of the periodic table. By definition this encompasses the oxides, sulfides, selenides, and tellurides of beryllium, magnesium, zinc, cadmium, and mercury etc. However there has been a significantly less amount of research conducted on the chalcogenides of beryllium, magnesium, cadmium and mercury. Therefore, the focus is narrowed to the sulfides, selenides, and tellurides of zinc and cadmium. This is a natural cutoff within the II-VI compounds since all of the compounds in this restricted II-VI group takes one of two crystal structures in the bulk material, zinc blende or wurtzite. CdS of cubic structure is more effective than hexagonal structure as a photocatalyst (Walter and Joachim 1997).
Despite the zinc blende crystal structure being cubic and the wurtzite crystal structure being hexagonal, the two structures do share some commonalities. The combination of the group II elements with the group VI elements give as an average of four valence electrons per atom. If there is a preference for the electrons to be shared rather than transferred between atoms, then II-VI atoms within the compound will tend to form tetrahedral coordination (Ray 1969). A tetrahedral lattice site in a compound AB is one where each ‘A’ atom is surrounded symmetrically by four nearest neighboring ‘B’ atoms. In order for this to occur, the ‘B’ atoms must sit on the corners of the tetrahedron with the ‘A’ atom placed in the center of the geometric figure. Within the AB compound the ‘A’ and ‘B’ sites are identical in relation to their tetrahedral nature.

![Figure 1.6](image1.png)  
(a)       (b)  

**Figure 1.6** Tetrahedral configurations for the II-VI compounds corresponding to the (a) hexagonal wurtzite and (b) Cubic zinc blende crystal structures.

There are two possible combinations for forming the tetrahedral sites that are relevant to II-VI compounds. The first possible formation, illustrated in Figure 1.6 (a), configures the two tetrahedra interpenetrating each other with the base triangles parallel and lined normal to one another. This configuration corresponds to the hexagonal wurtzite crystal structure.
Figure 1.6 (b) depicts a similar configuration, but rotates the bases 60°, while still keeping the bases parallel. This yields the cubic zinc blende crystal structure.

1.5 PREPARATION OF SEMICONDUCTOR NANOCRYSTALS

Metal nanocrystals are generally obtained by the controlled reduction of metal salts, while nanocrystals of metal chalcogenides and oxides are prepared by arrested precipitation or thermal decomposition (Rao et al 2002). Metal chalcogenides such as CdS films can be deposited by a number of methods, including metal organic chemical vapor deposition (MOCVD), chemical bath deposition (CBD), sputtering, vapor transport deposition (VTD), spray pyrolysis, electrodeposition (ED), laser ablation, and screen printing and the synthesis of CdSe NCs have been reported, including routes such as the single molecule precursor route (Crouch et al 2003), the solvothermal route (Gautam et al 2001), the sonochemical route (Ge et al 2002), the microwave irradiation route (Zhu et al 2000), the organometallic precursor route (Hambrock et al 2001), and the non-organometallic precursor route (Nair et al 2004).

Traditional material processing techniques usually involves taking a big chunk of the material and with cutting, grinding, polishing, either physically, chemically or using sophisticated techniques like ion beam etching and mechanical milling to get the desired shape and size. This is also called the ‘Top-Down’ approach. Complementary to the ‘Top-down’ approach is a process ubiquitous in nature, involving building up materials right from the molecular levels, to form macrosized shapes and structures. Just like laying bricks together to form an everlasting structure, it is possible to engineer materials into any forms and sizes by building them up using small clusters of molecules or even molecules as basic building blocks. This approach is dubbed as the ‘Bottom-Up’ approach.
The emerging field of nanotechnology will require tailor made building blocks for the bottom-up construction of advanced materials and devices. The availability of colloidal particles with unique and tailored functional properties like optical, mechanical and electrical properties has made colloidal synthesis the favored method for obtaining nanoparticles (Caruso 2002).

In the synthesis of colloidal NCs, several experimental conditions come into play in the manipulation of their size and morphology, such as the choice of suitable precursors, catalysts, templates, and stabilizer molecules that control their growth, the adjustment of their relative concentration ratio in the liquid phase, and temperature modulation (Kumar and Nann 2006). Spheres, cubes, rods, stars, disks, wires, multi-branches, and other unusually shaped structures can now be prepared for a variety of materials on the gram-scale with relatively inexpensive equipment.

1.5.1 Role of Surfactants

For the synthesis of colloidal NCs, the key strategy stands within the use of specific molecules, which act as terminating or stabilizing agents, ensuring slow growth rate, preventing inter-particle agglomeration, and conferring stability and further process ability to the resulting NCs (Ozin and Arsenault 2005). Often, such molecules are chosen among various classes of surfactants. Surfactants are molecules composed of a polar head group and one or more hydrocarbon chains with hydrophobic character.

Surface active agents (surfactants) are a larger class of molecules which have a significant technological and biological importance. Generally these molecules consist of a hydrophilic (water soluble) and a hydrophobic (water insoluble) part shown in Figure 1.7. This amphiphilic nature of surfactants is responsible for their association behaviour in solution (micelles,
bilayers, vesicles, etc.) and their accumulation at interfaces (air/water or oil/water). The hydrophobic part usually consists of hydrocarbon or fluorocarbon chains, while the hydrophilic part consists of a polar group (-OH, -COOH, -NH$_3^+$, -PO$_4^-$(CH$_2$)$_2$NH$_3^+$ etc.). The association behaviour of surfactants in solution and their affinity for interfaces is determined by the physical and chemical properties of the hydrophobic and hydrophilic groups, respectively. The size and shape of the hydrocarbon moiety and the size, charge and hydration of the hydrophilic head group are of utmost importance in this respect.

![Surfactant micelle and polyvinyl pyrrolidone structure](image)

**Figure 1.7** (a) Surfactant micelle in aqueous media (b) Comonomer structure of polyvinyl pyrrolidone (PVP).

More effective surface passivation has been an important process to reduce the detrimental effects of surface states on luminescent properties, which will lead to efficient and photostable luminescence. Inorganically passivated nanocrystals have been developed and shown to have dramatically enhanced luminescence properties (Peng et al 1997).

During the synthesis, the surfactants play a key role in tuning the reactivity of the monomers, and in regulating the temporal evolution of the nanocrystal size over time in a controlled way, as they are continuously adsorbing and desorbing from the surface of the NCs through their polar head groups. The combination of specific surfactants and of high temperatures
facilitates the formation of NCs with narrow size distributions, with fewer internal defects and with a more uniform surface reconstruction, hence having well defined physical properties (for instance, strong plasmon absorption or luminescence in a relatively narrow interval of energies from metal and semiconductor materials, respectively). Most of the physical or chemical properties exhibited by nanoparticles are due to these crystallites in the nano regime. Further growth in size is due to a few such crystallites agglomerating to form primary particles. This growth is controlled by adding capping agents for steric hindrance, or when the adsorption of ions on these particles is enough to cause electrostatic stabilization.

Among all the useful polymeric materials, polyvinyl pyrrolidone (PVP) belongs to a neutral charged polymeric dispersant and has outstanding colloidal and complexing properties (Du and Ilegbusi 2004). PVP has been widely used as the protecting agent or stabilizer for synthesizing nanoparticles (Pattabi et al 2007). The co-monomer structure of PVP is shown in Figure 1.7 (b). PVP was used as the dispersant that adsorbs the single colloidal particle to form a molecular folium to prevent the particle from reuniting. The complexing agents (PVP) that capped the particle surface to prevent the colloidal particle from agglomeration play an important role in the formation of the nanoparticles.

1.6 DOPED SEMICONDUCTOR NANOCRYSTALS

Doped II–VI chalcogenide semiconductor nanostructures have recently attracted a lot of attention due to their application in various modern era devices. Cadmium sulfide is used for a long time for the construction of photosensitive devices. The photoelectric properties of undoped CdS crystals are not very interesting from the technical viewpoint. The photoelectric efficiency and sensitivity in the region of 600–900 nm are considerably increased by the introduction of donors and acceptors. Dopants are introduced
into CdS grains during the activation. Undoped cadmium sulfide exhibits a band gap 2.42 eV, which corresponds to absorption edge 510 nm. Dopants create new energy levels which are responsible for the optical absorption at longer wavelength (Bube 1960).

Besides, the growth of reduced dimension structures of ternary II–VI semiconductor compounds presents an increasing interest for applications in solar cells, resistors, colour displays, batteries, etc. (Petruska et al 2003). The formation of II–VI ternary alloys and other un-sulphured binary semiconductor, like ZnO, are also explored because of its wide band gap for optoelectronic and high speed electronics applications (Look 2001).

Synthesis of these doped nanocrystals has become a major interdisciplinary field of research during the past decades. The ability to tune the band gap by doping the impurity is another important factor to suit any specific application. Light emission from these nanocrystals is possible through a radiative recombination process of charge carriers generated by higher energy photon absorption. The color of emission can be tailored by changing the crystalline size and appropriate doping (Seigel 1996).

1.6.1 Transition Metal Doped Semiconductor Nanocrystals

Recently, doped semiconducting nanocrystals have attracted considerable interest due to their interesting properties such as high luminescence quantum efficiency, short radiative lifetime, size dependent emission color tunability (Manzoor et al 2003), low voltage cathodoluminescence (Dinsmore et al 2000), multicolor electroluminescence (Manzoor et al 2004), etc. These materials are considered to be the luminophors for next generation displays, bio-labels, lasers, etc. (Shim et al 2001). The II-VI crystals doped with bivalent transition-metal ions are being extensively studied for the development of tunable IR lasers emitting in the range from 2 to 5 mm.
Interest in lasers based on such crystals is related to a broad scope of their applications in science and technology, for example, in spectroscopy, photochemistry, medicine, in devices for the environmental monitoring, etc.

Recently, attention has turned to the unusual optical, magnetic and photophysical phenomenon observed, when QDs are doped with paramagnetic impurities to form diluted magnetic semiconductor QDs (DMS-QDs) (Radovanovic and Gamelin 2001). Transition metal (TM) doped semiconductors, known as diluted magnetic semiconductors (DMS), have attracted widespread scientific attention due to their prospective applications. However, the usefulness of CdS for the futuristic devices resides in the ability to dope it with impurities so as to achieve the desired properties and to make them multifunctional. Transition metal (TM) such as Mn, Fe, Co, etc., doped with CdS has drawn considerable attention as it offers a great opportunity to integrate electrical, optical and magnetic properties into a single material, which makes it an ideal candidate for nonvolatile memory, magneto-optical and future spintronic devices (Oh et al 2008). Due to quantum confinement effects and rapid increase in surface-to-volume ratio as particle diameters are reduced to strong confinement regime, optical and magnetic properties are enhanced to large extent (Bhargava et al 1994).

Compounds containing transition metal ions, e.g., Zn_{1-x}Mn_xSe, Zn_{1-x}Co_xSe, and Cd_{1-x}Fe_xSe, are known as diluted magnetic semiconductors. The presence of magnetic ions leads to a number of unusual electronic and optical properties, which are due to the interaction of the magnetic ion with band electrons as well as to the exchange interaction between the magnetic ions themselves (Furdyna and Samarth 1987). The optical properties of Co(II) in II-VI compounds have been studied rather extensively in samples containing cobalt impurities (Uba and Baraowski 1978). In recent years, II–VI
semiconductors doped with transition-metal ions, such as Cr:ZnSe, Co:ZnSe, Co:ZnS and Co-CdSe have been explored as candidates for saturable-absorber Q-switches used with eye-safe lasers having output near 1.54 mm (Mierczyk et al 2006).

DMSs are II–VI, IV–VI, or III–V compounds in which fraction of nonmagnetic cations has been substituted by magnetic transition metal or rare-earth metal ions (Furdyna 1988). CdS-based DMS is a good candidate for such applications as magneto-optical devices (magnetic field sensors, isolators and magneto-optical switches), field-emission displays, solar cells and gas sensors. CdS based DMSs are very promising materials for spintronic devices operating at high temperature. The lattice constants and band parameters of these ternary DMS alloys can be modified by varying the concentration of the paramagnetic impurities. The presence of the paramagnetic ions can yield interesting magnetic properties (de Jonge and Swagten 1991 and Hamdani et al 1992).

1.6.2 Lanthanide Doped Semiconductor Nanoparticles

Lanthanide ions confer significant advantages to semiconductor nanoparticles that are important for fluorescence labeling. They are the potential candidate for multiple-color imaging with single wavelength excitation using different ions. As with all lanthanides up-conversion processes can be expected with excitation in NIR and the emission in the visible region. The NIR excitation offers deeper penetration into tissues and helps eliminate background luminescence. Additionally, up-conversion offers higher efficiency than the multiphoton excitation. The lanthanide ions have longer lifetime, useful for time resolved methods and the photobleaching which is important in fluorescent molecules. An appropriate choice of the semiconductor nanoparticles would then lead to excite the rare-earth ion by
nonradiative energy-transfer between the semiconductor nanoparticles and rare-earth ions through the matrix (Reisfeld et al 2000). Abundant research is focussed on different, either crystalline or amorphous wide bandgap compounds doped with various RE$^{3+}$ ions (Zanatta et al 2001). The rare earth ions would offer a possibility of obtaining three colors (blue, green and red) necessary for full colour devices. Thus, doping of II-VI compounds with trivalent cerium, terbium and europium has been extensively studied during recent years.

Confinement effects on electron-phonon interaction are primarily due to the discrete phonon density of states (PDOS) in a nanocrystal and the low-energy acoustic phonon modes, which are cut off. As a consequence of the PDOS confinement, luminescence dynamics of optical centers in nanoparticles, particularly, the nonradiative relaxations of ions from the electronically excited states are expected to behave differently from that of bulk materials. Therefore, controlling of optical excitation and luminescence dynamics such as vibronic transitions and phonon-assisted energy transfer may be achieved through modification of the PDOS in nanostructured materials. In this regard inorganic nanocrystals activated with rare earth or transition metal ions are of particular attraction because of their localized electronic states, in which phonon influence is very sensitive. There has been extensive research on spectroscopic studies on the luminescence dynamics of rare earth ions in nanocrystals (Meltzer and Hong 2000).

The rare earth doped materials have drawn increasing attention as phosphor materials for use in optical display devices (Maqbool et al 2007). The electronic structure of rare earth ions differ from other elements because of incompletely filled 4f n shells. The 4f n electrons are shielded by 5s$^2$ and 5p$^6$ electron orbitals. Excitation of materials doped with such ions results in
sharp line emission due to intra 4f n shells transition of rare earth ion core (Koti et al 2005), which lies in a wide range covering UV, VIS, IR regions of the spectrum.

1.7 MESOPOROUS SEMICONDUCTOR NANOSTRUCTURES

The continuing development of mesoporous silica (Zhao et al 1998) has prompted increased research interest in host–guest nanomaterials. Due to its large specific surface area, narrow pore size distribution and tunable pore size in the range of 2–30 nm during synthesis, mesoporous silica is a perfect host material as a nanoreactor for the preparation of nanomaterials used as catalysts, optical components, sensors, optoelectronics and energy resources.

Mesoporous II–VI group semiconductors exhibit some novel properties. But it is rather difficult to fabricate such materials, and there have been very few reports in this area. Many methodologies have been developed to load nanoparticles into the pore channels of mesoporous powder materials, such as direct sorption (Chen et al 2000), covalent grafting (Hirai et al 1999), and ion exchange reaction (Zhang et al 2001). The introduction of semiconductors into mesoporous silica materials one can obtain various nanoparticles with well-controlled particle size and size distribution (Dimos et al 2006). For example, cadmium sulfide (CdS) is a typical and very attractive semiconductor material due to its unique optical properties and ease of preparation. Unless the advantages from the mesostructural ordering are demonstrated by the enhanced efficiency of practical devices, commercialization of such mesoporous materials has to face several challenging tasks. The simultaneous achievement of high crystallinity and high mesoscopic ordering is a major challenge (Crepaldi et al 2003). Because the properties and applications of the materials are dependent upon
microstructures, many attempts have been made to prepare the materials in different morphologies and structures (Barrelet et al 2003).

In order to study the optical properties of CdS nanoparticles, they have been incorporated into many different matrices, such as silica (Yu et al 1997) porous alumina (Routkevitch et al 1996), mesoporous silica MCM-41 (Hirai et al 1999), and others. SBA-15 is a kind of highly ordered mesoporous silica with two-dimensional hexagonal (P6mm) symmetry. It exhibits an extremely high surface area, from 600 to 1000 m$^2$/g, with pore diameters in the range of 4-30 nm and pore volumes of 0.6-1.3 cm$^3$/g (Wang et al 2002).

Figure 1.8  Schematic diagram illustrate the (a) mesoporous Silica SBA-15 template, (b) impregnation of precursors and (c) the ordered mesoporous material after the removal of SBA-15 template.

Three methodologies have been developed to transport precursor molecules or ions for assembly of nanoparticles inside the channels of such materials: (a) direct impregnation (Chen et al 2001), (b) modification of the surface walls followed by loading of precursors through affinity interaction (Wellmann et al 2001), and (c) ion-exchange reaction (Zhang et al 2001). Figure 1.8 represents the schematic diagram of the mesoporous material
synthesised using SBA-15 silica template. The synthesised well-patterned, 2D hexagonally ordered semiconducting metal sulfides nanoarrays with crystalline structures have great potential applications for the development of electronic, photonic and catalytic systems.

### 1.8 SCOPE OF THE THESIS

Considering the importance of luminescent materials in the interdisciplinary materials science for the future optoelectronics device applications, the present thesis is focused on the synthesis and optical property studies of PVP capped cadmium sulfide (CdS) and transition metal (cobalt) and rare earth (Eu, Ce, Sm) doped CdS nanoparticles and mesoporous CdS nanostructures. Overview of the present thesis was schematically illustrated below:

Cadmium sulfide with a direct bandgap of 2.42 eV at room temperature nanocrystals (NCs) has attracted extensive interest due to their potential application as key luminescent materials for blue and white LEDs. Tamborra et al (2004) reported a significant enhancement in the photoluminescence efficiency of CdS nanocrystals when embedded in polymeric matrices. In this work polyvinyl pyrrolidone (PVP) encapsulated
monodispersive CdS nanoparticles was synthesised by chemical co-precipitation method and their optical properties were studied. Recently, CdS based system motivated the research in DMS due to prediction of unexpected magnetism in Co doped CdS by Bogle et al (2008). With this motivation cobalt doped CdS nanocrystals were prepared by chemical co-precipitation method and their structural, optical and magnetic behaviour have been studied.

Okamoto et al (1988), Jayaraj and Vallabhan et al (1991) reported that rare earth doped luminescent II–VI materials have shown promising candidates for applications in optical memories and color thin film electroluminescence devices. Higher quantum efficiency and lifetime shortening of intrinsic and extrinsic semiconductor quantum structures due to quantum confinement effects motivated to synthesize and characterize rare earth ions (Eu, Ce, Sm) doped CdS nanocrystals. In this work, rare earth doped semiconductor nanoparticles were synthesised by chemical co-precipitation method and their structural, morphological and optical properties were discussed in detail.

It has attracted increasing interest in fabricating CdS nanostructures with desired morphology and to study the structural and optical properties. Here we discuss about the successful incorporation of large quantity of CdS nanoparticles inside the meso channels of silica (SBA-15) template with different pore diameters. Highly ordered two dimensional array of mesoporous cadmium sulfide, with high surface area compared to the previous methods were synthesised. Their structural, optical and textural properties were analysed. The photocatalytic activity of the synthesised CdS nanostructures was investigated by the degradation of Methylene violet-2B dye using visible light irradiation and the results are discussed.