Chapter I

Introduction

This chapter provides an introduction to the thesis and the motivation behind the work presented. It gives an explanation to the size relations between quantum chemistry, nanoparticles and solid state physics. It discusses the classes of nanostructured materials and the approaches used for their fabrication. It also focuses on the various factors that influence the physical, chemical, optical and electronic properties. An insight into the atomic rearrangement at the nano- scale that influences the surface effects has also been addressed. The various factors that affect the physicochemical properties of semiconductor nanoparticles have been dealt with. The potential applications of these semiconductor nanoparticles and the relevant change they can make in the electronics industry are also highlighted. This is an attempt to explore the various mechanisms of synthesizing the semiconductor nanoparticles having novel opto-electronic properties.

1.1 Introduction to Nanoscience and Nanotechnology

Nanoscience and nanotechnology refers to the control and manipulation of matter at nanometer dimensions [1].

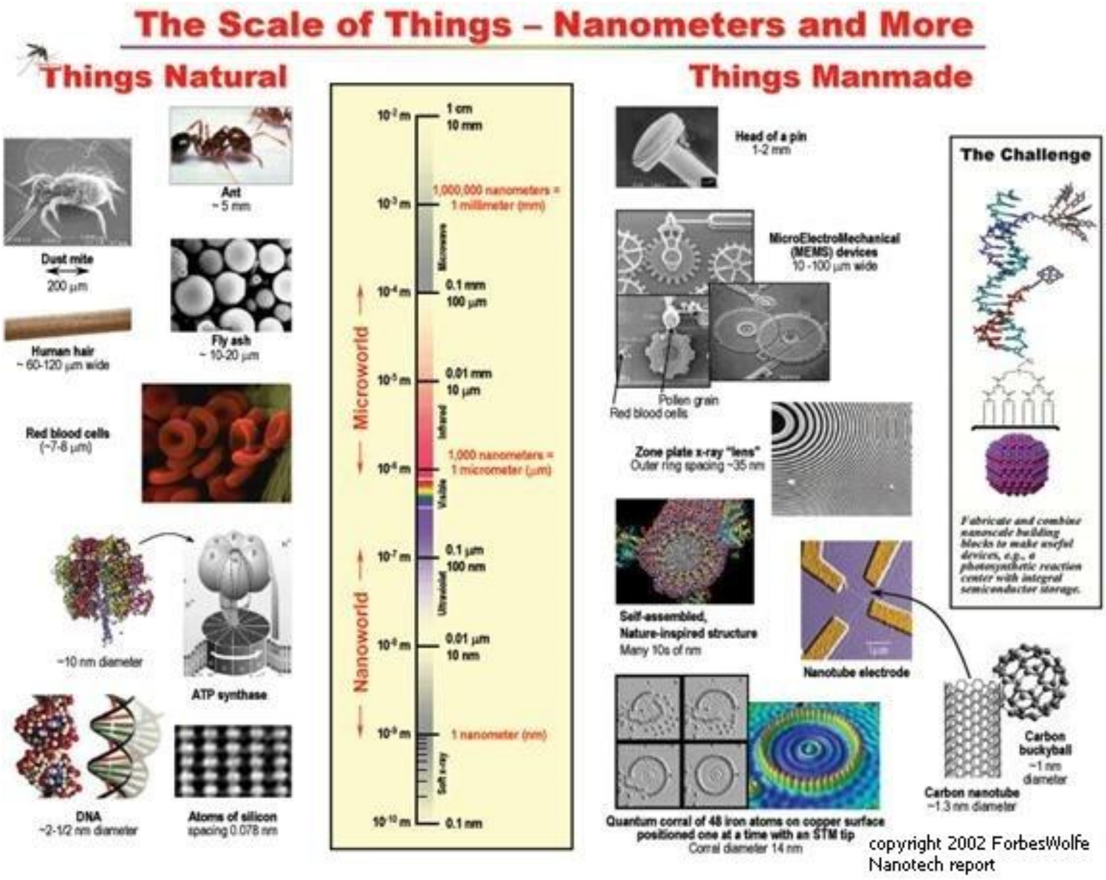

Fig. 1.1 ***Cartoon representing the relative sizes of various naturally occurring objects / species and man-made materials (courtesy: Josh Wolfe's report on Nanotechnology; http://www.forbeswolfe.com)***

Nature has evolved numerous incredibly functional assemblages of proteins, nucleic acids and other macromolecules to perform complicated tasks that are still daunting for us to emulate in our laboratories. One such task, which has been of great interest to material scientists, is the creation of the most efficient miniaturized functional materials by nature through ingenious ways. The interest towards nanoscience and nanotechnology is due to the relentless attempts to create functional miniaturized structures following nature's way.

Manufactured products are made from atoms. The properties of those products depend on how these atoms are arranged. The idea of manipulating and positioning individual atoms and molecules is still new. In a classic talk Prof. Richard Feynman gave on December 29th 1959 at the annual meeting of the American Physical Society at Caltech entitled 'There's Plenty of Room at the Bottom' [2], Prof. Feynman said, "The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big." We need to apply at the molecular scale the concept that has demonstrated its effectiveness at the macroscopic scale: making parts go where we want by putting them where we want. What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? In the future, nanotechnology will help to assemble these atoms or these building blocks to give new products. We'll be able to snap together the fundamental building blocks of nature easily, inexpensively and in most of the ways permitted by the laws of physics. In attempts to create miniaturized structures, significant achievements have been obtained and the structures of micron and nano-dimensions can now be routinely fabricated.

Chemistry deals with atoms and molecules, matter having dimensions typically few tens of angstrom units. Condensed matter physics deals with solids of essentially an infinite array of bound atoms or molecules of dimensions greater than 100 nm. A significant gap exists between these regimes which are illustrated below:

Atoms / Molecules	**Nanoscale Particles**		**Condensed Matter**	
1	125	70,000	$6x10^{6}$	∞ N^{0} Atoms
	1	10	100	∞ Diameter (nm)
Quantum Chemistry	**?**		**Solid State Physics**	

Fig. 1.2 ***Size relationships of chemistry, nanoparticles and condensed matter physics.***

This gap of 1-100 nm size particles having $10\text{-}10^{3}$ atoms or molecules per particle is a nanoparticle. In this nanoscale, neither quantum chemistry nor classical laws of physics hold [3]. In materials where strong chemical bonding is present, delocalization of valence electrons can be extensive. The extent of delocalization can vary with the size of the system. This effect, coupled with structural changes with size variation can lead to different physical and chemical properties, depending on size. Magnetic properties, optical properties, melting points, surface reactivity are some of the properties which are size dependent [4].

The most important aspect of these nanosize particles are synthesis, physical properties and chemical properties.

1.2 Quantum Dots

Quantum dots (QD) are nanometer scale “boxes” for selectively holding or releasing electrons. Quantum dots are small devices that contain free electrons. They are fabricated in semiconductor materials and have typical dimensions of a few nanometers . The size and shape of these structures and therefore the number of electrons they contain can be precisely controlled.

QDs are semiconductor structures in which electron wave function is confined to all three dimensions by the potential energy barriers that form the QD's boundaries, QD's size, shape and composition can all be tailored to create a variety of desired properties. The energy levels in a quantum dot become quantized due to the confinement of electrons.

Semiconductor quantum dots signify a class of materials in which quantum confinement effects are investigated in detail. They are also referred to as "semiconductor nanocrystals". Quantum dots refer to semiconductor particles and nanocrystal can be any inorganic entity in which there is a crystalline arrangement of constituent atoms / ions. In a macroscopic semiconductor crystal, the energy level form bands. The valence band is filled and the conduction band is completely empty at 0° K. The bands are separated with a specific energy gap E_g. When an electron gets excited due to thermal excitations, an electron hole pair is created. The electron in the conduction band and the hole in the valence band can be bound when they approach each other at a finite distance. This bound pair is called "exciton" which is delocalized throughout the crystal.

The Bohr radius of exciton is given as

$$a = \frac{h^2 \in}{4 \pi^2 e^2 [1/m_e + 1/m_h]}$$

Where $\in$ = dielectric constant

m_e = effective mass of electron

m_h = effective mass of hole

e = elementary charge

h = Planck's Constant

Quantum size effects are manifested when the length of nanocrystal made, d, is comparable to the exciton radius 'a'.

Some of the properties which change drastically as a function of size are the optical properties, including both the absorption and emission of light. These particles are called quantum dots as their electrons are confined to a point in space. They have no freedom in any dimension and electrons are said to be localized at a point, implying that a change in all directions changes the properties.

An ideal quantum dot is realizable only when the electronic states within the quantum dot face a discontinuity at the edge of the material. Due to this, the electron within the dot feels an insurmountable barrier at the edge. When a material is truncated at the surface, the surface atoms have unsatisfied valences. In order to reduce the surface energy, the surface reconstructs, which leads to energy levels in the forbidden gap of the semiconductor. The electrical and optical properties of material are degraded by these traps. In an ideal semiconductor nanocrystal, the surface atoms are bonded to other materials in such a way as to remove the defects. This is what is done when a quantum dot is covered with a material of larger band gap. In an ideal semiconductor quantum dot, when there are no defect sites for charges to get trapped, the quantum yield of luminescence will be very high, nearly 1. The emission will also be sharp. Better light emission occurs as the electrons and holes are confined spatially. This is achieved by chemically protecting the surface with protecting molecules called “capping agents”. Since surface of nanocrystal can be modified by various capping molecules, these materials can be adapted to suitable media, and quantum yield can be improved.

1.3 Nanostructured Materials

A study on nanostructured materials is the engineering of materials with improved properties through the controlled synthesis and assembly of material at nanoscale level. Using variety of synthesis methods, it is possible to produce nanostructured materials in the form of thin films, coatings, powders and as fillers for composite materials. The ability to control the nanostructure of the materials can result in enhanced properties in macroscopic levels like increased hardness, ductility, selective absorption showing more efficient optical and electronic behavior. The critical issues for nanostructure synthesis fall into two categories

1) Control of the size and composition of the nanocluster components, whether they are aerosol particles, powders or semiconductor quantum dots.
2) Control of the interfaces and distributions of the nanoparticles within the fully formed materials.

Classes of Nanostructured Materials

There are several different types of nanostructured materials. They range from zero dimensional atom clusters to 3D equiaxed grain structure. Each class has at least one dimension in the nanometer range.

Any multilayered material with layer thickness in nanometer range is classified as one dimensionally modulated. Layers in the nanometer thickness range consisting of ultrafine grains are 2D modulated. This includes coatings buried layers and thin films.

The last class is that consisting of 3D modulated microstructures or nanophase materials. To achieve this goal, researchers are trying to follow the “top-down” as well as “bottom-up” approaches. Among these, the top-down approach can be considered as the one with which the human race first learned to fabricate materials and in due course of time, perfected this art by being able to engineer structures at submicron levels.

Top down Fabrication

Top down approach is like sculpting from a block of stone. A piece of the base material is gradually eroded until the desired shape is achieved. That is, start at the top of the blank piece and work the way down removing material from where it is not required. Nanotechnology techniques for top down fabrication vary but can be split into mechanical and chemical fabrication techniques. The most top down fabrication technique is nanolithography. In this process, required material is protected by a mask and the exposed material is etched away. Depending upon the level of resolution required for features in the final product, etching of the base material can be done chemically using acids or mechanically using ultraviolet light, x-rays or electron beams. This is the technique applied to the manufacture of computer chips.

Bottom up Fabrication

Bottom up fabrication is like building a brick house. Instead of placing bricks one at a time to produce a house, bottom up fabrication techniques place atoms or molecules one at a time to build the desired nanostructure. Such processes are time consuming and so self assembly techniques are employed where the atoms arrange themselves as required. Manufacturing quantum dots by self-assembly quantum dots has rendered the top down lithographic approach to semiconductor quantum dot fabrication virtually obsolete. In this thesis we have adopted the bottom up approach. The bottom up approach plays an important role in the fabrication and processing of nano structures. There are several reasons for this. When structures fall into a nanometer scale, there is a little chance for top down approach. Bottom up approach promises a better chance to obtain nano structures with less defects and more homogeneous chemical composition. On the contrary, top down approach most likely introduces internal stress, in addition to surface defects and contaminations

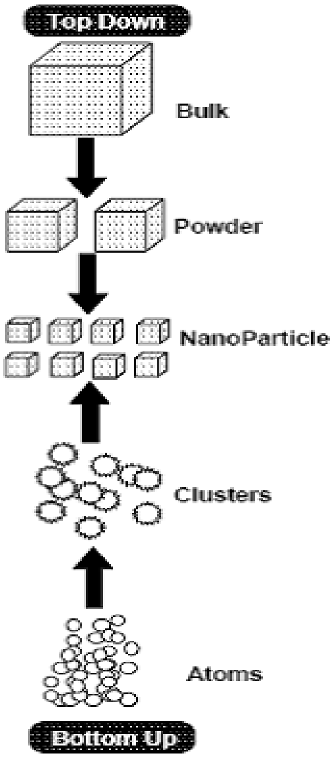

Fig1.3: ***Schematic representation of the building up of Nanostructures.***

It has been realized that materials in nano-dimensions exhibit properties that are very different from their bulk counterparts. These materials in nano-dimension will revolutionize our industries and our lives [4]. This is becoming more and more evident in the form of potential applications of nanoparticles which extend to a wide ranging areas such as catalysis [5-6], biosensors [7-10], diagnostics [11], cell labeling [12-14], solar cells [15-16], fuel cells [17], photonic band gap materials [18], single electron transistors [19,20], non-linear optical devices [21-24], information storage [25], refrigeration [26], chemical / optical computers [27], harder metals [28], self cleaning paints [29], improved national security [30,31]. The realization of various potential applications is only limited by our imagination [32-37].

A remarkable aspect of nanomaterials is that a number of factors can influence their physical, chemical, optical, electronic and magnetic properties. The factors that can strongly modulate their properties include their size [38-43], shape [44-46], surface composition [47-50], dielectric environment [51-54] and the inter-particle interactions [55-59]. Such remarkable variations in properties of nanomaterials are due to their dimensions being comparable to the de Broglie wavelength of the charge carriers, which modify their properties significantly. One of the readily perceptible properties in case of metal nanoparticles is their colour. The colour of metal nanoparticles originates due to surface plasmons i.e. the coherent charge density oscillations [60]. Surface plasmon is a special phenomenon, which is observed in metal nanomaterials at nanoscale. Similarly, when the size of other nanomaterials, leading to discreet energy levels in the conduction band and can be understood by making analogy with case of particle-in-a-box model [61,62]. The quantum size effects have been well studied in case of semiconducting nanoparticles and the energy level spacing for a spherical particle of radius R is predicted to be inversely proportional to R^2 [63].Thus, with decreasing size, the effective bandgap increases and the relevant absorption and emission spectra blue-shifts. As a consequence, the development which was initially concerned with metal nanoparticles led to realization that essentially all solid materials in nanoscale would be of interest.

1.4 Bandgap Engineering

Bandgap Engineering refers to the ability to tailor the electronic and chemical properties of semiconductor materials by varying the composition and impurity concentration throughout the body of a semiconductor device. With the development of modern epitaxial growth techniques like molecular beam epitaxy (MBE) and metal organic chemical vapour deposition (MOCVD), the composition of semiconductor layers can be controlled to a scale of one monolayer. It is possible to synthesize semiconductor devices by putting the crystal together one atomic layer at a time.

In comparison with bulk semiconductors, nanocrystals have a diverse and growing range of parameters that can modulate their electronic band gaps including size, shape and composition. Quantum confinement can shift the bandgap of most semiconductor by over 1*e*V, giving an enormous range of continuous tunability through size and shape for a single material composition. The use of quantum confined structures also allows the independent tuning of size and bandgap through the implementation of homogeneously alloyed materials such as $CdSe_yTe_{1-y}$ and $Cd_xZn_{1-x}S$ [64, 65].

A chemically related process to alloying is impurity doping, which creates an intraband electronic energy level that allows lower energy light emission from the defect state to the ground state. Doped nanocrystals can have interesting propertiess for bio-labeling and device application, such as large stokes shifts, paramagnetic propertiess and improved lasing. The synthesis of doped nanocrystals is a challenge due to the chemical dissimilarities between dopants and their crystalline matrices [66].

1.5 Atomic Rearrangement at Nanoscale

The percentage of surface atoms increases exponentially as we get into the nanometer scale. This situation leads to generation of phase of matter where properties are governed by the surface energies. Matter is composed of atoms which in turn contain tiny, heavy nuclei surrounded by a huge cloud of electrons which is thousands of times bigger in volume than the nucleus. Thus the size of electron cloud decides the volume of matter. The outer shell electrons form chemical bonds. In bulk state, there is more spatial freedom for movement of electron across atoms. However, in nanoparticles, large numbers of atoms are on the surface and their outer shell electrons are confined by small dimensions of the particles. This confinement occurs, when size reduces beyond Bohr radius and the effect is called as "Quantum

Confinement". Movement of the valence electrons may be restricted in one, two or three dimensions depending upon the shape of the nanoparticle viz layers, rods or particles respectively.

This confinement leads to electrons acquiring higher energy at nanoscale which increases the surface tension and the chemical potential on the surface. These high energy electrons decide the behaviour of nanoscale properties.

i) Atomic Restructuring

New type of bonds can be formed with the other atoms within the nanostructures thereby leading to a different crystal structure which is closely packed. This leads to relaxation of energy due to contraction and reduction in bond lengths. The defects in the crystals like vacancies and dislocations also get eliminated in nanocrystals. This changes the intrinsic properties of the material like chemical activity, conductivity, light absorption, catalytic activity and mechanical properties.

ii) Absorption

The high energy electrons may dissipate their energy by forming association with the surrounding medium through physical adsorption or chemisorption. This can lead to stabilization of the nanostructures in the continuous medium via electrostatic mechanisms. These nanostructures have extremely high interfacial area which will impact the extrinsic properties linking strength, colour, catalytic behaviour and some mechanical properties depending on the dimensions on nanoscale.

iii) Re-aggregation

High energy nanoparticles may again re-aggregate and form larger particles with low energy. This must be prevented so as to preserve nanophase and derive newer characteristics. Loose re-aggregation may occur without collapse of individual nanostructures.

1.6 Optical Activity of Quantum Dots

An electron in a quantum dot can be described by a quantum wave function that is similar to that used for an electron in a single atom, although the energy of the electron in quantum dot is spread coherently over the lattice of atomic nuclei. The electronic wave functions of quantum dots are often labeled with atomic notation but quantum dots are solid state nano structures that can be tailored into different shapes. Optical excitation of the semiconductor leads to the creation of a quasi – particle known as an “exciton” – a negatively charged electron bound together with a positively charged hole. Such dots remain electrically neutral on optical excitation. Absorption and emission spectra are studied to understand the behavior of these excitons. Quantum dots have great flexibility because their properties can be artificially engineered.

1.7 Chemistry of Semiconductor Nanoparticles

It is usually assumed that the properties of solid semiconductors are independent of their size. However, this assumption is valid for solids containing a macroscopic number of atoms. The electronic excitation of semiconductor crystal results in the formation of a loosely coupled electron-hole pair. In semiconductors, the size of the delocalization area of such a pair can be many times larger than lattice constant. The decrease in the size of a semiconductor crystal down to a size comparable with the delocalization area of the electron-hole pair affects the electronic characteristics [63].

The unusual physico-chemical properties of semiconductor nanoparticles mainly depend on three main factors.

1) The size of nanoparticles is comparable with molecular dimensions. This determines the difference between the kinetics of chemical transformations on the surface and the kinetics of chemical transformations in infinite space.
2) The surface atoms constitute a considerable proportion of the total number of atoms of a nanoparticle. This affects the thermodynamic characteristics of nanoparticles.
3) The non linear optical effects arise and the energies of excitonic transitions in nanoparticles become dependent on the size since it is comparable with the delocalization area of the charge carriers.

Light emitting diodes (LED) are semiconductor devices that emit incoherent monochromatic light when electrically biased in the forward direction. This is a type of electroluminescence. The colour emitted depends on the semiconductor materials used, and can be near ultraviolet, visible or infrared. If the emissive layer material of an LED is an organic compound, it is known as Organic LED (OLED). These OLEDs can be used for a wide spectrum of applications from being light sources to luminous cloth.

1.8 Work Described in the Thesis

In this thesis, we have tried to explore the various mechanisms of synthesizing the semiconductor nanoparticles having novel opto-electronic properties.

Chapter I of the thesis gives an introduction to the world of Nanoscience / Nanotechnology and the influence it will have in the industries. It emphasizes the effect of Nanoscience on semiconductor technology and how the properties of matter can be manipulated using this science.

Chapter II elucidates the use of various tools and techniques and gives an understanding of various equipments used for characterizing the synthesized samples.

Chapter III of the thesis discusses synthesis of Cadmium sulphide nanocrystals in aqueous foams with AOT as the surfactant. It also highlights the effect of doping cadmium sulphide with manganese at different compositions. It emphasizes the use of certain surfactant – stabilized aqueous foams providing an efficient and a simple chemical route for the synthesis of various nanomaterials with controllable structure, size and shape. The morphology variation is attributed to thr growth of CdS/ CdMnS nanoparticles in different regions of the foam contributing to varying topological structure.

Chapter IV focuses on the synthesis of Cadmium sulphide nanoparticles in chloroform. A simple method of synthesizing CdS, CdMnS and CdYS nanoparticles in organic phase at ambient room temperature is discussed. The prepared nanoparticles were rotavapped and then re-dispersed in other organic solvents like toluene and ethanol, and the fluorescence emission spectra were studied. Light emitting diodes is a semiconductor device that emits incoherent monochromatic light when biased in forward direction. This effect is a form of electroluminescence. Organic CdS / CdMnS / CdYS can be used for fabricating organic LEDs (OLED) and also in photovoltaic cells.

Chapter V discusses the synthesis of Zinc sulphide nanoparticles in chloroform. Synthesis of ZnS, ZnMnS and ZnYS nanoparticles has been discussed. The TEM and the XRD give the structural characterization. However, the UV – Vis Absorption spectrum , photoluminescence measurements and FTIR measurements were done to study the optical properties.

Chapter VI focuses the synthesis of mixed semiconductor nanoparticles. Mixed nanoparticles consisting of two semiconductors can be heterogeneously connected (Composite nanoparticles). They are coated particles with core-shell structure. Mixed semiconductor system offers potential advantages for solar energy utilization because of the possibilities presented by interparticle electron transfer and special properties. Reverse miscelles provide an ideal medium for the synthesis of stable, size selected semiconductor nanoparticles. The chapter emphasizes on the synthesis and characterization of ZnS coated CdS nanoparticles (CdS/ ZnS) and CdS coated ZnS nanoparticles (ZnS/ CdS) in organic phase.

Chapter 7 summarizes the work presented in the thesis. It also discusses the potential future developments for research in the area.

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