

CHAPTER 1

GENERAL INTRODUCTION

1.1. A Brief Introduction to Nanotechnology and Nanomaterials:

Nano is derived from the Greek word 'nano' which means dwarf. This prefix is used in the metric system to mean 10^{-9} meter or one billionth of a meter. It is the unit of length that is most appropriate for describing the size of a single molecule. Nanometer objects are too small to be seen with naked eye. To indicate the smallness of any object, we often compare it with the human hair in which the diameter of it is estimated to be about 50,000 - 1,00,000 nanometers [1], a red blood cell which is approximately 7,000 nm wide and water molecule which is almost 0.3 nm across. The comparative size of a nanometer is the same as the size of a marble to that of the earth [2]. The smallest things that the unaided human eye can resolve are 10,000 nm across. In the nanoscale, common materials are exhibiting unusual properties. Some of these properties include lower melting points, faster chemical reactions and remarkably lower resistance to electricity.



Figure 1.1: SEM images of human hair, red blood cells, water molecule

There are two terms related to nano and these are nanoscience and nanotechnology. Nanoscience is an emerging area of science which concerns itself the study of materials that have very small dimensions i.e. in the range of nano scale. The word itself is a combination of nano and science which means dwarf and knowledge [3]. Thus, nanoscience is the study of phenomenon and manipulation of materials at atomic,

molecular and macromolecular scales where properties differ significantly from those at a larger scale. It involves an interdisciplinary of sciences such as material science, physics, chemistry, biology, engineering, computer science and more. In contrast, the term nanotechnology is defined as the study and use of structures between 1 - 100 nm in size. Thus, nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling the shape and size at nanometer scale. Structural features in the range 1 - 100 nm determine important changes as compared to the behaviour of bulk materials. So, while mentioning the word nanoscience and nanotechnology, it is necessary to know the term nanomaterials because nanomaterials are cornerstones of nanoscience and nanotechnology.

The term nanomaterials cover various types of nanostructured materials which possess at least one dimension in the nanometer range. When dimension of a material is continuously reduced from macroscopic size to nanometers, the physical and chemical properties drastically change. Depending on the dimension of a material, one can classify nanomaterials into three categories namely quantum well, quantum wire and quantum dot.

Quantum well: Quantum wells are those structures where one dimension is reduced to nanometer range i.e. < 100 nm so that the size is comparable to the de-Broglie wavelength of the exciton while the other two dimensions remain large. Example: Thin films, layers and coatings.

Quantum wire: Quantum wires are those structures where two dimensions are reduced to nanometer range i.e. < 100 nm and one remain large. Example: Nanotubes, fibres, nanowires.

Quantum dot: Quantum dots are those structures where all the dimensions are reduced to nanometer range i.e. < 100 nm. Example: Nanoparticles, quantum dots, nanoshells, nanorings, microcapsules.

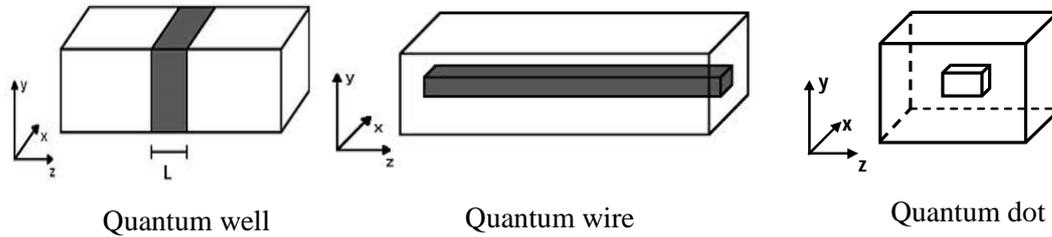


Figure 1.2: Schematic illustration of the three types of nanomaterials

The word quantum is associated with these three types of nanostructure materials because the change in properties arises from quantum mechanical nature of physics in ultra small domain. The physical and chemical properties of materials changes when the bulk becomes nanosize. At this stage, they show a very different properties compared to what they exhibit on a macro scale, enabling unique applications. For instance, copper which is opaque at micro scale becomes transparent; silicon insulators become conductors and gold which is solid, inert and yellow in room temperature at micro scale becomes liquid and red in colour in nano scale at room temperature. This indicates that the optical properties of the gold particles are changed when their size become nanosize. Thus, the study on nanostructured materials is one of the thrust areas during the last decades because of their novel properties. Nowadays, a number of sophisticated instruments are developed for characterization and study of nanoparticles. Among them X-ray diffractometer (XRD), Atomic force microscope (AFM), Transmission electron microscope (TEM), High resolution transmission electron microscope (HRTEM), Scanning electron microscope (SEM), UV-vis spectrophotometer, Photoluminescence (PL) and Fourier transform infrared (FTIR) spectroscopy are very important tools for the study of these small particles. With these sophisticated instruments, one can easily determine the structure of the materials, the surface morphologies and exact size of the particles. For the last two decades, extensive study on synthesis, characterization and studies on properties of nanoparticles have increased tremendously. Study on

nanoparticles have a number of advantages over the study of bulk materials as these types of materials have potential applications in physics, chemistry, material science and biological sciences. Thus study on nanoparticles will lead to the development of new devices and technologies for future industries.

Although the term nanotechnology got its definition in 1974, the actual concept was introduced way back in 1867, when James Clerk Maxwell proposed minuscule entity called Maxwell's Demon that was capable of handling individual molecules. The big step forward in nanoparticle research was made by Michael Faraday approximately 150 years ago. As a matter of fact, his systematic studies on the interaction of light with metal nanoparticles can be regarded as the beginning of modern colloid chemistry and the emergence of nanoscience and nanotechnology [4]. Richard Adolf Zsigmondy was the first person to observe and measure the dimensions of nanoparticles. He was the first person to use nanometer for characterizing the size of the nanoparticles unambiguously. He determined that 1 nm was 1/ 1,000,000 millimeter and also developed the first classification system which was based on the size of the particle that range in nanometer. In the 20th century, several developments took place that help in characterizing nanomaterials. Like in 1920, Irving Langmuir introduced the concept of monolayer, where a layer of material is just one molecule thick and he had received a Nobel Prize for that concept. The first use of the concept found in "nanotechnology" was in "There is Plenty of Room at the Bottom", a legendary talk delivered by American physicist Richard P. Feynman in the Annual general body meeting of the American Physical Society on 29th of December 1959 at California Institute of Technology [5]. In that talk he discussed about the ideas of manipulating and controlling things at the atomic scale. He is regarded as the father of nanotechnology. But the term nanotechnology was first used in 1974 by Japanese Scientist Prof. Norio Taniguchi at the Tokyo Science University and his paper stated that "Nanotechnology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or by one molecule". In the 1980s the basic idea of this definition was explored in much more depth by Dr. K. Eric

Drexler, an American Engineer and the founder of Foresight Nanotech Institute, who promoted the technological significance of nanoscale phenomena and devices through speeches and his book entitled “Engines of Creation, the Coming Age of Nanotechnology” [6]. The era of nanotechnology and nanoscience got started in the early 1980s with two major developments, the birth of cluster science and the invention of the Scanning tunnelling microscope (STM). This development led to the discovery of fullerenes in 1985 and carbon nanotubes a few years later. In another development, the synthesis and properties of semiconductor nanocrystals was studied; this led to a fast increasing number of metal and metal oxide nanoparticles and quantum dots [7].

1.2. Properties of Nanomaterials:

1.2.1. Structural properties:

Nanomaterials have the structural features in between atoms and that of the bulk materials. While most microstructural materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulk materials. This is mainly due to the nanometer size of the materials which render them (i) large fraction of surface atoms (ii) high surface energy (iii) spatial confinement and (iv) reduced imperfections, which do not exist in the corresponding bulk materials [8].

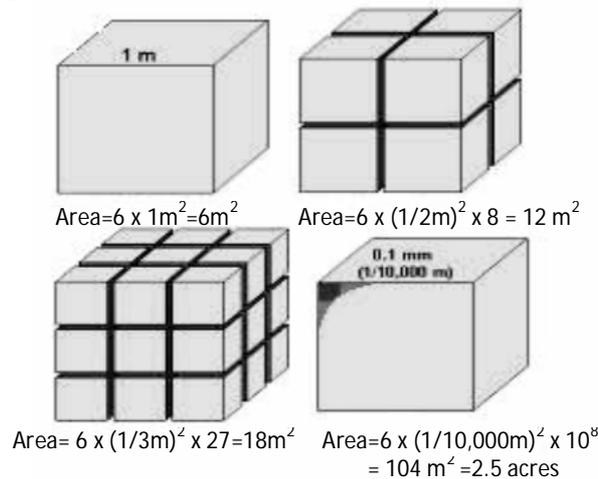


Figure 1.3: Schematic diagram of large surface-to-volume ratio

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio. For example, the surface area increases when a cube is cut into smaller pieces. This results in the increase of surface area to volume ratio and greater amount of a substance comes in contact with surrounding materials (Figure 1.3.). The large surface area to volume ratio makes a large fraction of atoms of the materials to be on the surface or interfacial atoms, resulting in more surface dependent material properties. Especially when the sizes of nanomaterials are comparable to length, the entire material will be affected by the surface properties of nanomaterials [9, 10]. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials which bring the quantum effects.

1.2.2. Optical properties:

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photoelectrochemistry and biomedicine.

The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics and other variables including doping and interaction with the surrounding environment or other nanostructures. Likewise, shape can have dramatic influence on optical properties of nanomaterials. Another interesting property of nanomaterial is that their interaction with light differs from that of a bulk. When the particle diameter is decreased, the band gap (E_g) is blue shifted due to quantum confinement effect. Cadmium selenide (CdSe) quantum dot nanoparticles are an example of this phenomenon. Their emission colour differs depending on their particle size.

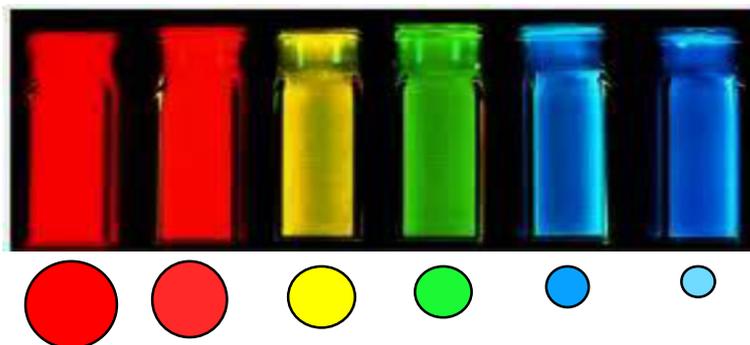


Figure 1.4: Difference in emission colour with respect to the increase in particle size

The quantum size effect is most pronounced for semiconductor nanoparticles, where the band gap increases with a decreasing particle size, resulting in the interband transition shifting to higher frequencies [11, 12]. In a semiconductor, the energy separation i.e. the energy difference between the completely filled valence band and the empty conduction band is of the order of a few electron volts and increases rapidly with a decreasing particle size [12]. Quantum confinement produces a blue shift in the band gap as well as appearance of discrete subbands corresponding to quantization along the direction of confinement. The optical properties of nanostructured semiconductors are highly size dependent and thus can be modified by varying the size alone, keeping the chemical composition intact. The luminescent emission from the semiconductor nanostructures can be tuned by varying the size of the nanoparticles. Surface plasmon resonance is the coherent collective excitation of all the free electrons within the conduction band, leading to an in-phase oscillation [13, 14]. When the size of a metal nanocrystal is smaller than the wavelength of incident radiation, a surface plasmon resonance is generated [15]. The energy of the surface plasmon resonance depends on both the free electron density and the dielectric medium surrounding the nanoparticles. The width of the resonance varies with the characteristic time before electron scattering. For larger nanoparticles, the resonance sharpens as the scattering length increases. Noble metals have the resonance frequency in the visible range of electromagnetic spectrum.

1.2.3. Chemical properties:

When particle size is reduced to nanoscale, the ratio of surface area to volume increased dramatically. Since many important chemical reactions including those involving catalysts occur at surfaces, it is not too surprising that very small particles are staggeringly reactive. This is one of the reasons that chemists are very excited about nanoscience that is if they can make more surface area, they get more catalytic action. Therefore nanoparticles are used as reaction catalysts. The application potential of nanoparticles in catalysis ranges from fuel cell to catalytic converters and photocatalytic devices. Catalysis is also important for the production of chemicals. Catalysis represents a major success story both in the use of oxide - supported, highly dispersed metal catalysts and in the use of crystalline materials as highly selective catalysts.

On the macroscale, gold is considered to be much less catalytic active than other transition metals. However, nanoscale particles of gold that are less than 8 nm in diameter can act as catalysts to enhance the rate of some chemical reactions. One possible application for these particles is in the catalytic converter where harmful pollutants produced by automobiles such as carbon monoxide react to form carbon dioxide and water. Automobiles generate most of their pollution within the first five minutes after starting up. Therefore at this time, majority of the harmful pollutants are generated as the catalytic converter is ineffective due to the low temperature of the exhaust. The use of nanoscale gold particles for this application may help significantly reduce automobile - related air pollution since gold particles catalyzed the reaction even at the sub-zero temperature [16].

1.2.4. Electrical properties:

At the nanoscale, electrical properties are not necessarily the same as they are on the macroscale. Electrical properties of nanoparticles discuss about fundamentals of electrical conductivity. So, materials that are conductors on the macroscale may lose their

conductivity at the nanoscale and vice versa. For instance, when an insulator becomes thin enough, it can be rendered conductive through a process called quantum tunneling, a non-classical effect that is generally only observed at the nanoscale or smaller [17]. The important point here is that with decreasing diameter of the wire (insulator), the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well defined quantized steps [18]

Carbon in the form of graphite is soft and malleable but at the nanoscale carbon can be stronger than steel and six times lighter. Nanotubes are long, thin cylinders of carbon. They are 100 times stronger than steel, very flexible and have unique electrical properties. Their electrical properties change with diameter and number of walls. They can be either conducting or semiconducting in their electrical behaviour [19].

1.2.5. Magnetic properties:

Bulk gold and platinum are non-magnetic but at the nano size, they are magnetic. Surface atoms are not only different to bulk atoms but they can also be modified by interaction with other chemical species that is capping the nanoparticles. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping them with appropriate molecules. Actually, it should be possible that non-ferromagnetic bulk materials exhibit ferromagnetic like behaviour when prepared in nano range. One can obtain magnetic nanoparticles of platinum, palladium and the surprising case of gold from non-magnetic bulk materials. In the case of platinum and palladium, the ferromagnetism arises from the structural changes associated with size effects. However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules, the charge localized at the particle surface gives rise to ferromagnetic like behaviour [18].

1.3. Applications of Nanomaterials:

From the last decade, major thrust is given in the field of ‘nanoscience and technology’. Nanotechnology seems to become the other big growth area of the century after genetic engineering. Products which are better and cheaper can be made using nanosystem rather than by using conventional materials. We can find many applications of nanomaterials in various fields. Some of the applications are described as follows:

- (i) **Fuel cell:** A fuel cell is an electrochemical energy conversion device that converts the chemical energy from fuel and oxidant directly into electricity. The heart of fuel cell is the electrodes. The performance of a fuel cell electrode can be optimized in two ways i.e. by improving the physical structure and by using more active electro catalyst. One of the suggested solutions for the future fuel crisis is generating electric energy from fuel cells especially for vehicles. Hydrogen is used as the immediate fuel in fuel cells which can be generated from hydrocarbons by catalytic reforming. The potential use of nano-engineered membrane to intensify catalytic processes could enable higher efficiency, small scale fuel cells. One of the major practical concerns with regard to fuel cells is storing hydrogen in a portable manner. Research is being conducted to use nano materials such as fullerenes as a hydrogen storage media [20].

- (ii) **Electronics:** The microelectronics industry has been emphasizing miniaturization whereby the circuits such as transistors, resistors and capacitors are reduced in size. By achieving a significant reduction in their size, the microprocessors which contain these components can run faster thereby enabling computations at far greater speeds. However there are many limitations such as lack of the ultrafine precursors to manufacture these components, poor dissipation of tremendous amount of heat generated by these microprocessors due to faster speeds, short mean time to failures etc. Nanomaterials help the industry break these barriers down by providing the manufactures with nanocrystalline starting materials, ultra-

high purity materials, materials with better thermal conductivity and longer-lasting durable interconnections. So in the near future, we can also expect computers, controlled molecular machines, much smaller than a speck of dust that have the accuracy and precision of today's target drug molecules. Microelectronics industry will become the nanoelectronics industry with the next generation of chips having device features near and below 100 nanometers. All devices and computer chips will be nanodevices. Also nanoscale magnetic or optical memories will be available which will become extremely dense and cheap.

- (iii) **Catalysis:** Nano-catalysts tend to have exceptional surface activity with the availability of higher surface area with the nanomaterials counterparts. For example, reaction rate at nano-aluminium can go so high that it is utilized as a solid fuel in rocket propulsion whereas the bulk aluminium is widely used in utensils. Nano-aluminium becomes highly reactive and supplies the required thrust to send off pay loads in space. Similarly, catalysts assisting or retarding the reaction rates are dependent on the surface activity and can very well be utilized in manipulating the rate controlling step.
- (iv) **Phosphors for High Definition TV:** The resolution of a television or a computer monitor depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors" which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel or the phosphors. Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride synthesized by the sol-gel techniques are candidates for improving the resolutions of monitors. The use of nanophosphors is set to reduce the cost of these displays so as to render high definition television (HDTVs) and personal computer affordable.
- (v) **Elimination of pollutants:** Nanomaterials possess extremely large grain size boundaries relative to their grain size. Hence, they are very active in terms of their

chemical, physical and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with noxious and toxic gases such as carbon monoxide and nitrogen oxide generated by automobile and power generation equipment to prevent environmental pollution.

- (vi) **Health and Medicine:** Nanotechnology has also its application in the field of health and medicine called nanomedicine which imparts benefits to humanity. The approaches to nanomedicine range from the medical use of the nanomaterials, to nanoelectronic biosensors and even possible future applications of molecular nanotechnology [21]. Nanomedicine has the potential to enable early detection, prevention and essentially improve diagnosis, treatment and follow-up of diseases. Also, controlled surgery at the cellular and molecular levels will be possible and can be used to treat cancer and other diseases. Biological tests measuring the presence or activity of selected substances will become quicker, more sensitive and accurate when certain nano scale particles are put to work as tags and labels. Nanodevices can make gene sequencing more efficient. Nanotechnology can also help to reproduce or repair damaged tissue.
- (vii) **Sunscreen and cosmetics:** Prolonged ultra violet (UV) exposure causes skin burns and cancer. Nano-sized titanium dioxide and zinc oxide are currently used in some sunscreen as they absorb and reflect UV rays and yet are transparent to visible light and so are more appealing to the consumer. Nanosized iron oxide is used in some lipsticks as a pigment. However, there are a number of concerns regarding the use of nanoparticles in cosmetics.
- (viii) **Sensors:** Sensors rely on the highly active surface to initiate a response with minute change in the concentration of the species to be detected. Engineered monolayers on the sensor surface are exposed to the environment and the peculiar functionality is utilized in sensing.

1.4. Quantum Confinement Effect in Nanomaterials:

The quantum confinement effect can be observed once the diameter of the particle is of the same magnitude of the wavelength of electron wave function [22]. When materials are so small, their electronic and optical properties deviate substantially from those of bulk materials [23]. A particle behaves as if it is free when the confining dimension is large compared to the wavelength of the particle. During this state, the band gap 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, the band gap becomes size dependent. This ultimately results in a blue shift in optical illumination as the size of the particle decreases.

The fascinating optical changes observed by Berry [24, 25] and Brus [26] for the reduced sized semiconductor nanocrystals in colloidal dispersions can be related to an increase in band gap with decreasing particle size. When an electron in a semiconductor is transferred from the valence band to the conduction band through excitation, a hole in the valence band is created. This positive hole will form a bound state with the excited negative electron by Coulomb interaction. Such bound electron hole pair is known as an exciton (Mott-Wannier) and can be described in a similar way to the hydrogen - like bound state between the proton and the electron of the hydrogen atom. Thus, for bulk semiconductor, the dimension of the exciton can be theoretically calculated by exciton Bohr radius a_B [27, 28]

$$a_B = \frac{\hbar\epsilon}{\mu e^2} \dots\dots\dots (1.1)$$

where \hbar is defined as Planck's constant, ϵ is the dielectric constant, μ is the exciton reduced mass. However, if the radius of a semiconductor nanoparticle is reduced to less than its exciton Bohr radius, we can imagine that the exciton will be strongly confined in this limited volume and the electronic structure of the three dimensionally confined

electrons and holes will be drastically modified. Hence, the term quantum confinement describes this confinement of the exciton within the physical boundaries of the semiconductor. When the particle size approaches that of the exciton Bohr radius, the exciton wave function becomes confined by the spatial limitations of the crystal. The potential barrier at crystal surface forces the exciton wave function to go to zero at the crystal surface, confining the exciton wave function in the crystal. This will result in an increase in exciton energy with decreasing crystallite size, corresponding to a blue shift in both exciton absorbance and emission.

1.5. A Brief Note on Cadmium Sulphide (CdS) and Zinc Sulphide (ZnS):

Cadmium sulphide (CdS) and zinc sulphide (ZnS) belong to group II-VI semiconductor materials which also include cadmium oxide (CdO), cadmium selenide (CdSe), cadmium telluride (CdTe), zinc oxide (ZnO), zinc selenide (ZnSe) and zinc telluride (ZnTe). They are typically wide band gap materials. The synthesis of these materials at nano scale has attracted research in recent years due to their excellent perspective in catalysis, optical and magnetic functionality. Each of the II-VI semiconductors demonstrates some unique properties, making them useful for unique applications [29].

1.5.1. Crystal Structure of Cadmium Sulphide (CdS):

CdS is a chemical compound of II-VI semiconductor with many excellent physical and chemical properties. It is yellow in bulk and when it becomes nano, its colour changes to orange [30]. It exists in nature as two different crystal structures i.e. the more stable hexagonal wurtzite structure found in the mineral Greenockite and cubic zinc blende structure found in the mineral Hawleyite. CdS is a direct band gap semiconductor with a large band gap of 2.42 eV at room temperature. In both cubic and hexagonal forms the cadmium and sulphur atoms are four coordinate [31].

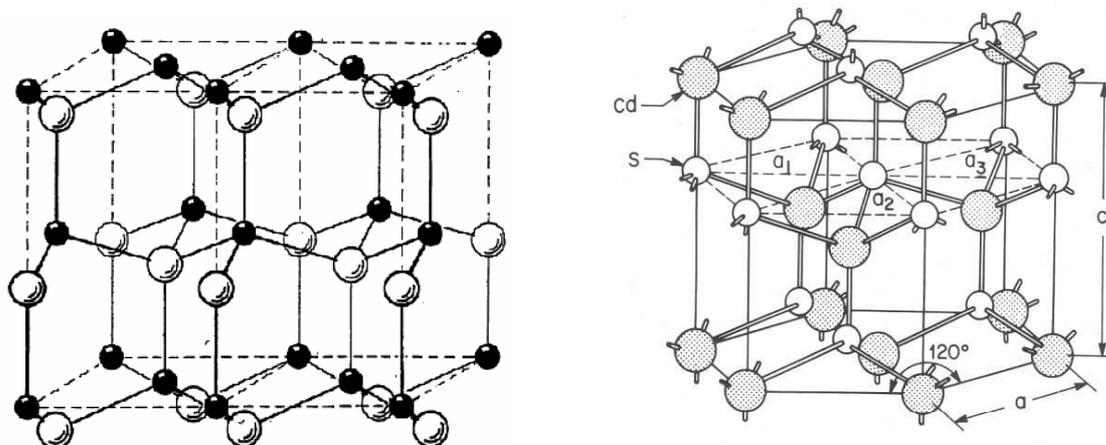


Figure 1.5: The cubic zinc blende and wurtzite structure of CdS.

CdS is also known as cadmium yellow. One can obtain a range of colours, like pigment orange and pigment red by adding various amounts of selenium and selenide [32]. The synthetic cadmium pigments are valued for their good thermal stability, light and weather fastness, chemical resistance and high opacity. The conductivity of CdS increases when it is used as photoresistor [33]. When CdS is combined with a p-type semiconductor, it forms the core component of a photovoltaic cell. When fabricated into thin films, it can be used as a transistor [34, 35]. It also has properties of electroluminescence and cathodoluminescence [36]. Polymorph forms of CdS are piezoelectric while the hexagonal types are pyroelectric [37, 38].

CdS is also one of the important materials for application in electro-optic devices such as photoconducting cells, photosensors, transducers, laser materials, optical wave guides and non-linear integrated optical devices. It has been proved to be an ideal material for use as the window layer of heterojunction solar cells with cadmium telluride (CdTe) and copper indium diselenide (CuInSe₂) [39, 40].

1.5.2. Crystal Structure of Zinc Sulphide (ZnS):

Zinc sulphide is a well known II-VI compound semiconductor with the chemical formula ZnS. It is white in bulk and when it becomes nano, its colour changes to yellow.

ZnS is typically encountered in the more stable cubic form known as zinc blende or sphalerite. The hexagonal form is also known both as a synthetic material and as the mineral wurtzite. Both sphalerite and wurtzite are wide band gap semiconductors. The cubic zinc blende has a band gap of 3.54 eV at 300 K whereas the hexagonal form has a band gap of 3.91 eV [41]. The transition from the cubic zinc blende form to hexagon at wurtzite occurs at around 1020 °C.

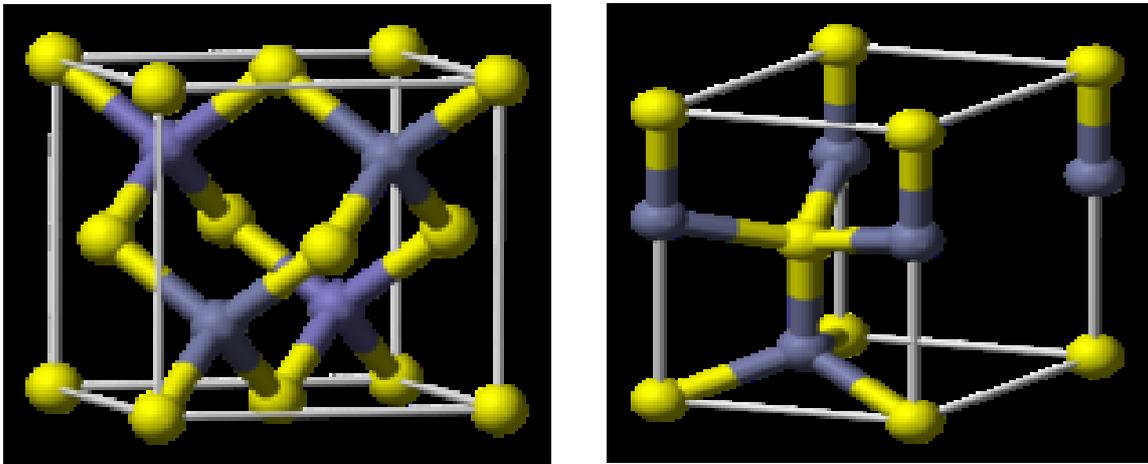


Figure 1.6: The cubic zinc blende and wurtzite structure of ZnS

ZnS displays a high refractive index of ~ 2.2 and having high transmittance of light in the visible region of the spectrum [42-44]. It also has relatively large (~ 40 meV) exciton binding energy. Owing to its wide band gap value, it can be used for many applications such as phosphors [45], electroluminescent devices [46], non-linear optics [47-49], thin film heterojunction and solar cells [50-53].

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