CHAPTER 1

INTRODUCTION

1 Background

In the recent years Nanoparticles are of current interest due to their potential applications in engineering, sciences and medical fields. This further opens a new era of research. Because of an emerging understanding of their possible effects on human health and environmental sustainability which increase due to increasing output of man-made nanoparticles into the environment intensive research on nano is continuously increasing. Nanoparticles are used in many applications in engineering and medical sciences. Ever since Richard Feynman, An American theoretical Physicist most remembered lecture “There is a plenty of room at the bottom” in APS meeting at Caltech 1959 and then Eric Drexler book “Engine of Creations’ in which he the term “Nanotechnology” the science of small particle have become one of the most dynamically fields of research [1,2]. Nanotechnology is the technology that has started a new and exciting era of interdisciplinary research among solid state Physicists, Chemists and Biologists. Smaller, faster, highly efficient, low cost and environmental friendly synthesis are the major issues concerned with excising technologies, used for electronics devices, Pharmaceutics, biomedical imaging, implant devices that led to rapid development of nano science [3-6].

1.1 Growth of Nano Research

Now Government of various countries realizing the importance of nanoscience for future of any Nation. US Govt. sanctioned $ 500 million in 2001 and then $1.4 billion in 2016 [7]. The Govt. of India allotted huge budget in start-up India for nano based projects in various fields [8].

Since invention of STM (Nobel award 1986) [9] by Binnig and Heinrich Rohrer and AFM, the research gained the pace. Discovery of CNT and graphene are considered as microscopic wonder. They are ready to redefine electrical and mechanical applications[10]. Tagging of nanoparticle with DNA is again a new area of research [11]. In spite of lot of work has been reported the research is still infancy stage. Water
solubility of nanoparticle is still challenging. Optimization of synthesis technique techniques is still to be done [12-14]. Research form Physics, Chemistry, Material science. Biology are working continuously to create new science with huge technology possibilities.

1.2 Solids

Solids are one of the four fundamental state of mater (others are liquid, gas and plasma) and characterized by structural rigidity. Atoms in any solids are tightly bound to each a regular geometrical lattice or imaginary.

1.2.1 Classification of solids

On the basis of electrical conductivity and band theory solid materials can be classified into three categories [15]:

1. **Conductor**: Materials offers very low resistance for the flow of electric current. Example copper (Cu), zinc (Zn) silver (Ag) and sodium (Na). All have fully filled innermost valance bands and partially filled outermost conduction band. Electrons in valance band are free to move on applications of electric field.

2. **Semiconductor**: Such materials offers high resistance to the flow of electric current. In these material all the electrons are present in the valence band and the conduction band is empty. Band gaps in such materials are very small or falls in the range of optical spectra so such energy can be obtain from optical excitation. A semiconductor shows some resistance to the flow of electric current in between insulators and conductors. Their electrical conductivity is sensitive to temperature, illumination and magnetic field.

3. **Insulator** Such Materials offer very high resistance to the flow of electric current. In these material all the electrons are present in the valence band and the conduction band is fully empty. Due to a large band gap it is very difficult to raise an electron from the valence band to the conduction band. The classification of inorganic solids on the basis of resistivity, energy gap and carrier density are given in Table 1
### Table 1.1 Classification of materials based on Resistivity, Energy gap (Eg) and Carrier density (n) at room temperature.

<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>Resistivity (Ohm-Cm)</th>
<th>Band Gap (eV)</th>
<th>Charge Carrier concentration</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductor</td>
<td>$10^{-5}$ to $10^{-6}$</td>
<td>-</td>
<td>1022</td>
<td>Gold, Silver, Copper, Aluminum</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>$10^{-2}$ to $10^{10}$</td>
<td>0 to 4 eV</td>
<td>&lt; 1017</td>
<td>CdS, Si, Ge</td>
</tr>
<tr>
<td>Insulator</td>
<td>$10^{12}$ to $10^{122}$</td>
<td>&gt; 4 eV</td>
<td>&lt; 1</td>
<td>Rubber, wood</td>
</tr>
</tbody>
</table>

**Fig. 1.1** Band representations of Conductor, Insulator and Semiconductor.

#### 1.2.2 Semiconductors

Semiconductors exhibit electrical conductivity between conductor and insulator. Semiconductors have smaller band gap which ultimately dictates electrical properties. Due to which a variety of applications have been designed in electronics devices [16]. The band gap is lies between 0.3 and 3.8 eV. At OK temperature semiconductors behave as insulator due to absence of free electrons. But as the temperature increases electrons in the valence band gain energy and move to the higher-energy conduction band leaving a positive ‘hole’ in the valence band [17].

Semiconductors have two types.
1.2.3 Intrinsic and Extrinsic Semiconductors

**Intrinsic Semiconductors**

Also called pure semiconductor *e.g.* silicon, germanium characterized by an equal number of charge carriers’ *i.e.* the number of excited electrons and number of holes are equal.

**Extrinsic Semiconductors**

Extrinsic Semiconductors are created by doping of external impurities. Electrical properties of pure semiconductors can be further modified by doping process. Impurity atom adds an electron or a hole which allows the free passage of charge.

Extrinsic Semiconductors can further be classified into two types.

1.2.4 *n* type and *p* type Semiconductors

**n-type Semiconductors** : Semiconductors with more electrons in the doping region are called *n*-type. Such semiconductor can be created by adding pentavalent impurities. In *n*-type semiconductor, the Fermi level lies close to the conduction band edge

**p-type Semiconductors** : The semiconductor with more holes in the doping region are called *p*-type semiconductor, In *p*-type semiconductor fermi level lies close to the valence band edge.

![Fig. 1.2 Intrinsic and Extrinsic semiconductors](image-url)
1.2.5 Direct and Indirect band gap semiconductors

Semiconductors can also be classified as direct band gap semiconductors and indirect band gap semiconductors on the basis of their band structures;

In direct band gap semiconductors the minimum energy of the conduction band lies directly above the maximum energy of the valence band in momentum space and so the transition from conduction band to valence band involves no change in momentum. Hence, for direct band gap materials, the excess energy of the electron-hole recombination released as heat or photon of light.

In indirect band gap semiconductors the electron goes from the bottom of the conduction band to the top of the valence band. It also undergoes a significant change in momentum (Figure 1.3). So Indirect band gap semiconductors are inefficient to emit light [18-19].

![E-K Diagrams for direct and indirect band gap semiconductors](image)

1.3 Nanostructures

The word "nano" means a billionth \(10^{-9}\) part of a unit

\[1 \text{ nm} = 10^{-9} \text{ m} = 10^{-3} \mu\text{m} = 10 \text{ Å}\]

*Nanostructure* materials refer to materials having length in the range of ~ 1-100 nm in at least one of its dimension. Due to pronounced quantum nature electrons are confined in
the nanoscale dimension(s), but are free to move in other dimension(s). Nanostructures are unique as compared with both individual atoms/molecules at a smaller scale and the macroscopic bulk materials. On the basis of confinement of nanostructures can be classified as [20].

1.3.1 Quantum dots, Quantum wires Quantum well

**Quantum well:** In Quantum well electrons are confined in one dimension (1D), free in other 2D. It can be realized by sandwiching a narrow-bandgap semiconductor layer between the wide-gap ones. A quantum well is often called a 2D electronic system. System includes thin films.

**Quantum wires:** In Quantum wires electrons are confined in two dimensions, free in 1D (so it is called a 1D electronic system). Real quantum wires include polymer chains, nanowires and nanotubes.

**Quantum dots:** In Quantum dots electrons are confined in all dimensions, as in clusters and nano-crystallites

![Fig. 1.4 Behavior of Quantum well, quantum wire and quantum dot](image_url)
1.3.2 What makes nanostructures unique and interesting?

Bulk materials have their intrinsic physical properties, such as density, conductivity and chemical reactivity, are independent of their sizes. However significant property changes occurs when the size goes down to the nanoscales. The following phenomena critically affect the properties of nanostructural materials:

Quantum confinement: The confinement of electrons in the nanoscale dimensions results in quantization of energy and momentum, and with reduced dimensionality of electronic states. Electrons quantization leads to formation of discrete energy levels depending on the size of the structures. Quantum confinement effects are mainly associated with quantum dots. Properties of these quantum dots (QDs) lie between bulk semiconductor and discrete molecule. The size dependent optical and electronic properties of the QDs are associated with the “quantum confinement effects”. The quantum confinement effect is observed when the size of the particle is too small to be comparable to the wavelength of the electron. If the size of the quantum dot is smaller than that of the Bohr radius then confinement occurs leading to a transition from continuous to discrete energy levels [21].

![Fig. 1.5 Change in transition from discrete to continuum with size of particle.](image-url)
Optical properties of nanostructures

Optical properties strongly depend on size of the particles. Increase in the band gap results in shift in the absorption edge to smaller wavelength. Semiconductor and metallic nanomaterials and nanocomposites possess interesting linear absorption, photoluminescence emission, and nonlinear optical properties [22].

Surface/interface effects:

Significant number of (even the majority) of atoms in nanostructure is located at and near the surfaces or interfaces. Due to which the mechanic, thermodynamic, electronic, magnetic, optical and chemical states of these atoms can be quite different than those interior atoms [23].

Both the crystalline (bulk) states and the surface/interface states cannot be ignored in nanoscale structures. The different mixture of atomic/molecular, mesoscopic and macroscopic characters make the properties of nanostructures vary dramatically. Their detailed atomic configuration depends sensitively on the kinetic processes in which they are fabricated. Therefore, the properties of nanostructures can be widely adjustable by changing their size, shape and processing conditions.

1.4 Semiconductor nanostructures

Over the past three decade nanoparticles of semiconductor materials have been given considerable attention for their applications in device technologies [24]. The surface properties have significant effects on their structural and optical properties because of the high surface-to-volume ratio of nanoparticles. Some common properties of semiconductors are given in Table 1.2.
Fig. 1.6 Bulk semiconductors to nano semiconductors

Table 1.2 Properties of Semiconductors

<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>Band gap</th>
<th>Type</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.66</td>
<td>Indirect</td>
<td>Cubic</td>
</tr>
<tr>
<td>Si</td>
<td>1.12</td>
<td>Indirect</td>
<td>Cubic</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.68</td>
<td>Direct</td>
<td>Cubic , Hexagonal</td>
</tr>
<tr>
<td>CdS</td>
<td>2.42</td>
<td>Direct</td>
<td>Cubic , Hexagonal</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.70</td>
<td>Direct</td>
<td>Cubic , Hexagonal</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.70</td>
<td>Direct</td>
<td>Cubic , Hexagonal</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.56</td>
<td>Direct</td>
<td>Cubic</td>
</tr>
<tr>
<td>GaP</td>
<td>2.26</td>
<td>Indirect</td>
<td>Cubic</td>
</tr>
<tr>
<td>Ga As</td>
<td>1.42</td>
<td>Direct</td>
<td>Cubic</td>
</tr>
<tr>
<td>InP</td>
<td>1.35</td>
<td>Direct</td>
<td>Cubic</td>
</tr>
<tr>
<td>InAs</td>
<td>0.36</td>
<td>Direct</td>
<td>Cubic</td>
</tr>
<tr>
<td>AlAs</td>
<td>2.16</td>
<td>Indirect</td>
<td>Cubic</td>
</tr>
</tbody>
</table>
1.5 Cadmium and Zinc Chalcogenide

Chalcogenide compounds consist of at least one chalcogen anion and at least one more electropositive element. Although all group 16 elements of the periodic table are defined as chalcogens, the term chalcogenide is more commonly reserved for sulfides, selenides, and tellurides, rather than oxides.

Cadmium sulfide is the yellow inorganic compound with the formula CdS [25]. It occurs in nature with two different crystal structures as the rare minerals greenockite and hawleyite, but is more prevalent as an impurity substituent in the similarly structured zinc ores sphalerite and wurtzite. It is the principal source of cadmium for all commercial applications. Cadmium sulfide has, like zinc sulfide, two crystal forms. The more stable hexagonal wurtzite structure (found in the mineral Greenockite) and the cubic zinc blende structure (found in the mineral Hawleyite). Cadmium sulfide is a direct band gap semiconductor (gap 2.42 eV) [26]. The magnitude of its band gap means that it appears coloured. The conductivity increases when irradiated with light (leading to uses as a photoresistor). When combined with a p-type semiconductor it forms the core component of a photovoltaic (solar) cell and a CdS/Cu$_2$S solar cell was one of the first efficient cells to be reported (1954) [27]. CdS luminesces under electron beam excitation (cathodoluminescence) or visible light excitation and is used as phosphor CdS crystal can act as a solid state laser [28].

**Zinc Sulphide** is an inorganic compound with the chemical formula of ZnS. This is the main form of zinc found in nature, where it mainly occurs as the mineral sphalerite. Although this mineral is usually black because of various impurities, the pure material is white, and widely used as a pigment. In its dense synthetic form, zinc sulfide can be transparent, and used as a window for visible optics and infrared optics. ZnS exists in two main crystalline forms. In each form, the coordination geometry at Zn and S is tetrahedral. The more stable cubic form is known also as zinc blende or sphalerite. The hexagonal form is known as the wurtzite [29]. The transition from the sphalerite form to the wurtzite form occurs at around 1020 Celsius.

1.6 Applications of Semiconductors

The elemental semiconductor (Si, Ge) are used for the production of transistors and integrated circuits, while the compound semiconductors used for solar cells, light
emitting diodes (LED), optical detectors, thermal imaging device, environmental sensors[30]. The main applications of semiconductors are summarized in Fig 1.7.

Fig. 1.7 Applications of Semiconductors

1.7 Optoelectronic applications of Chalcogenide semiconductors

Chalcogenide nanoparticles have their potential applications in optoelectronic devices due to their bandgap lie in visible or UV region. The electron can be excited using UV, Vis or IR radiations. Size dependent properties make them suitable for various high efficient and high functional devices. Many application have been designed or modified using such nanostructures [31].

1.7.1 LED

A light-emitting diode (LED) is a semiconductor p–n junction diode, which emits light when activated light source [32]. When a suitable voltage is applied, electrons recombine with holes within the device, releasing energy in the form of photons. This effect is called electroluminescence, and the color of the light is determined by the energy band gap of the semiconductor. The first high-brightness blue LED was demonstrated by Shuji Nakamura of Nichia Corporation in 1994 and was based on InGaN [33-34]. Tenability of nanoparticles allows quantum dot LEDs to create almost any color. This provides more
color options and better color rendering than white LEDs since the emission spectrum is much narrower, characteristic of quantum confined states [35-36].

1.7.2 Photocatalytic

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst [37]. In catalysed photolysis, light is absorbed by an adsorbed substrate. The photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals (e.g. hydroxyl radicals: •OH) able to undergo secondary reactions. Nanocrystalline photocatalysts are ultrasmall semiconductor particles which are a few nanometres in size. During the past decade, the photochemistry of nano semiconductor particles has been one of the fastest growing research areas in physical chemistry (Henglein, 1997) [38]. The interest in these small semiconductor particles originates from their unique photophysical and photocatalytic properties (Bahnemann, 1993) [39].

1.7.3 Solar cells

A solar cell also known as photovoltaic cell is an electrical device that converts the energy of light directly into electricity. It is a device whose current, voltage, or resistance, vary when exposed to light [40]. Quantum dot based photovoltaic cells based on dye-sensitized colloidal TiO₂ films were investigated in 1991 and were found to exhibit promising efficiency of converting incident light energy to electrical energy, and also due to the low cost of materials used [42].

1.7.4 Other Applications

Optoelectronics is based on the quantum mechanical effects of light on electronic materials, especially semiconductors, other nano semiconductors applications are Phototransistors, Photomultipliers, Optoisolators, Integrated optical circuit (IOC) elements, Photoconductive camera tubes, Charge-coupled imaging devices, Stimulated emission, Injection laser diodes, Quantum cascade lasers, Optocoupler, Optical fiber communications[43-45].
1.8 Schiff bases

**General Introduction of Schiff bases**

The synthesis of Nitrogen – Sulphur containing ligands and their metal complexes is the most important area of research in inorganic and bioinorganic chemistry in view of their presence in many biologically significant systems. The synthesis and study of Nitrogen – Sulphur containing ligands have undergone tremendous growth in recent years and their complexation behaviour with a wide variety of metal ions has been extensively studied. A Schiff base is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by C=N-R group [46-48]. It is usually formed by condensation of an aldehyde or ketone with a primary amine according to the following scheme:

![Schiff base formation](image)

**Fig.1.8 Condensation reaction**

Where R, may be an alkyl or an aryl group. Schiff bases that contain aryl substituents are substantially more stable and more readily synthesized, while those which contain alkyl substituents are relatively unstable. Schiff bases of aliphatic aldehydes are relatively unstable and readily polymerizable while those of aromatic aldehydes having effective conjugation are more stable [48-49]. The formation of a Schiff base from an aldehydes or ketones is a reversible reaction and generally takes place under acid or base catalysis, or upon heating (Fig. 1.8).
Fig. 1.9 Formation of a Schiff base from an aldehydes or ketones

The formation is generally driven to the completion by separation of the product or removal of water, or both. Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base. The mechanism of Schiff base formation is another variation on the theme of neucleophilic addition to the carbonyl group. In this case, the neucleophile is the amine. In the first part of the mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called carbinolamine. The carbinolamine loses water by either acid or base catalyzed pathways. Since the carbinolamine is an alcohol, it undergoes acid catalyzed dehydration.

Typically the dehydration of the carbinolamine is the rate-determining step of Schiff base formation and that is why the reaction is catalyzed by acids. Yet the acid concentration cannot be too high because amines are basic compounds. If the amine is protonated and becomes non-neucleophilic, equilibrium is pulled to the left and carbinolamine formation cannot occur. Therefore, many Schiff bases synthesis are best carried out at mildly acidic pH.
The dehydration of carbinolamines is also catalyzed by base. This reaction is somewhat analogous to the E2 elimination of alkyl halides except that it is not a concerted reaction. It proceeds in two steps through an anionic intermediate.

The Schiff base formation is really a sequence of two types of reactions, i.e. addition followed by elimination.

Dithiocarbazic acid, \( \text{NH}_2\text{NHCSSH} \) and its derivatives have been synthesized and investigated over past few decades[49-53]. Dithiocarbazic acid and the Schiff bases derived from S-alkyl and S-benzyl ester form an interesting series of ligands. Researchers in this area have synthesized a large number of nitrogen – sulphur donor ligands through Schiff base condensation with various aldehydes and ketones. The properties of these ligands can be greatly modified by introduction of organic substituents. The different ligands of this series show greater variation in biological properties although they slightly differ in their molecular structures. The synthesis of transition metal complexes is interesting because of their specific coordination behaviour and potential therapeutic use. They also find applications in health and skin care products.

**Carbazic acid and its derivatives**

In Fig. 1.10 (a) Dithiocarbazic acid (b) mono dithiocarboxyl (CSSH) derivatives of hydrazine (a), (c) Free dithiocarbazic acid, (d) hydrazinium salts salts have long been known and shown here.

Dithiocarbazic acid is soluble in polar solvents such as water and DMSO but insoluble in common organic solvents. The solubility behavior of dithiocarbazic acid has been taken as evidence in favour of its dipolar structure (Fig: 1.10 (e)).
Fig. 1.10 (a) Dithiocarbazic acid (b) mono dithiocarboxyl (CSSH) derivatives of hydrazine (a), (c) Free dithiocarbazic acid, (d) hydrazinium salts (e) solubility behavior of dithiocarbazic acid.

Conclusive proof in favour of dipolar structure was forthcoming from IR spectral analysis of this acid and its N-substituted derivatives. The N-H stretching bands occurring in 2000-3500 cm\(^{-1}\) region were of two types, those belonging to the \(\text{NH}\) grouping and other belonging to N-H grouping. The later give rise to absorption in the region 3000-3100 cm\(^{-1}\) in the free dithio acid. This frequency range is below that normal N-H stretching vibrations. This shifting developed due to the inductive effect of the positive charge on neighboring nitrogen atom. The N-H stretching vibrations due to the \(\text{NH}\) grouping were only observed in the free dithiocarbazic acid which confirms its dipolar structure as stated above. The identity of the absorption in question was confirmed by its deuteration.

U. Anthony has compared the IR spectra of the dithiocarbazic acid with selenium analogue (Fig: 1.11( a)) and assigned symmetric \(\text{CSS}^-\) and \(\text{CSeSe}^-\) vibrations ca. 680–691 cm\(^{-1}\) and 581-623 cm\(^{-1}\) respectively.
Fig. 1.11 (a) dithiocarbazic acid, (b) N-substituted free dithiocarbazics acids, (c) S-alkyl esters of dithiocarbazic acid and S-alkyl/benzyl dithiocarbazate.

The hydrazinium salt of dithiocarbazic acid is obtained as a white crystalline solid when carbon disulphide is added to an alcoholic solution of hydrazine hydrate. The ammonium salt is however precipitated out as a white crystalline solid when carbon disulphide is passed through an aqueous solution of hydrazine hydrate and ammonium hydroxide. A pure form of salt is obtained by crystallization from ethanol. The N-substituted free dithiocarbazics acids (Fig: 1.11 (b)) are prepared by adding 6N HCl to the saturated aqueous solutions of the respective hydrazinium salt of the acid cooled below -5 °C) in an efficient cooling mixture.

The free dithiocarbazic acid was found to separate instantly as gleaming white crystals which rapidly developed a yellowish tinge. The free acids are stable for several months at temperature below -4 °C. The stability of these acids has been attributed to their dipolar structure. Since the dipolar structure may also be attained by free dithiocarbazic acid has prepared the potassium salt of the acid by reacting carbon disulphide with a mixture of hydrazine hydrate and potassium hydroxide in dioxane medium at 0 °C.

A number of S-alkyl esters of dithiocarbazic acid (Fig: 1.11(c)) are also known now. All these esters are stable crystalline substances and condense readily with carbonyl compounds of both aliphatic and aromatic series yielding their respective well defined Schiff bases [56]. These esters are generally prepared by treating potassium salt of the
dithiocarbazic acid with appropriate alkyl halide in aqueous and alcoholic medium following the method reported by Busch [58].

Luigi Aurelio et al [59] have isolated a number of S-methyl esters of mono N-alkyl (Primary or secondary or phenyl) substituted dithiocarbazic acid without isolating potassium dithiocarbazate. S-methyl dithiocarbazate can also be prepared by the methylation of ammonium salt of the acid with methyl iodide in aqueous solution.

The preparations of a number of S-alkyl/benzyl esters of dithiocarbazic acid and their reactions with aliphatic and aromatic aldehydes and ketones have been reported. A large number of S-alkyl/benzyl dithiocarbazate (Fig: 1.11(d)) have been studies by many authors.

1.8.1 Applications of Schiff bases

Schiff bases have a large number of synthetic uses in organic chemistry. Acylation of Schiff bases by acid anhydrides, acid chlorides and acyl cyanides is initiated by attack at the nitrogen atom and leads to net addition of the acylating agent to the carbon-nitrogen double bond. Reactions of this type have been put to good use in natural product synthesis.

Schiff bases appear to be an important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate. In this respect pyridoxal Schiff bases derived from pyridoxal and amino acids have been prepared and studied from the biological point of view [60-62]. Transition metal complexes of such ligands are important enzyme models. The rapid development of these ligands resulted in an enhance research activity in the field of coordination chemistry leading to very interesting conclusions.

1.9 Single source precursor

Although so many methods have been developed for the synthesis of fine-quality nanoparticles, toxicity quality, repeatability have been a problem related to such methods. single source precursors, is a method to avoid the use of hazardous compounds. The use of single-source precursors for the synthesis of semiconductor nanoparticles was first reported by Steigerwald et al. [63] where [Cd(Se(C6H5))]2 or
[Cd(SePh)2][Et2PCH2CH2PEt2] were used as a single-source precursors to prepare CdSe nanoparticles in refluxing pyridine. These single-molecular precursors contain both metal and non-metal (chalcogenide) elements within the same molecule[63-64].

1.9.1 Advantages of Synthesis of nanoparticles with single source precursors

They have many advantages for the one-step synthesis of nanoparticles The use of single-source precursors has a following advantages over other [65].

- The synthesis using single source routes, avoid the need for volatile, toxic precursors. The uses of the single source precursors minimize the exclusion of toxic gases and also the pre-reactions may be limited.

- Due to air sensitive nature of group II-VI nanoparticles synthesis is carried out under inert conditions.

- In single source routes only one in volatile precursor is involved. So purification of this precursor is easier. Since only one volatile precursor is used in single source precursor. Very less chance of introduction of impurities into the nanoparticles.

- It is easy to maintain the stoichiometries of metal and ligand compositions by using single source precursor.

- Control of the coordination numbers at the metal by the formation of adducts or aggregates decrease the sensitivity towards the air and moisture.

- It is also easy to control the decomposition temperature by designing the precursor.

1.10 How Microwave is useful for nanoparticle synthesis

Nanomaterials have size dependent properties. So based on the area of application, it is required to have exact size distribution in nanoparticles. Recently microwave-assisted synthesis has been reported itself as a new way to produce different nano materials.

Using microwave irradiation it is possible to control size shape and ultimately properties of nanoparticles can be controlled. The application for such nanoparticles ranges from
medical (drug delivery systems, formulations) to many industries, (vehicle manufacturing: coatings, windshields, energy storage, cosmetics (sun protection, shampoo, toothpaste), textile production (outdoor clothing, shoes) and electronics (circuit boards, solar cells, LEDs, touchscreens). Prof. Kappe et al form Christian Doppler Laboratory for Microwave Chemistry at the Karl-Franzens University of Graz investigated the influence of the size distribution of the quantum dots in the range from 0.5 nm to 4 nm via the chosen cadmium complexes and the time at which the oleic acid was added. Microwave irradiation synthesis provides very short reaction times Microwave reactors allow easy access to high temperatures and pressures which are only obtained in special, difficult to handle autoclaves over a long period of time due to controlled system parameters is delivers reproducible results.

1.11 Computational methods

Computational chemistry is one of today's most rapidly expanding and exciting areas of scientific research. Recent low cost computer technologies have made availability of computational resources less expensive than most other major chemical instrumentations. A researcher can perform an extensive computational study in much lesser time than is required for the rest experimental counterpart without consumption of chemicals. Computational chemistry often becomes a cost-effective alternative and companion to conventional chemistry. The result obtained by any other scientific method may be compared by computational chemistry with certain limitations. However, the computational data so obtained help to prepare new derivatives of immense medicinal and chemical utility etc.

Computational chemistry finds some most important applications in the support of experimental inferences. There are many types of data that can be directly measured experimentally and can also be computed as well. For example the vibrational spectra (IR and Raman) the detailed descriptions of vibrational motions and frequency predictions are sometimes critical for explaining spectra in complicated experimental situations, such as a mixture of conformers. Extensive calculations can be performed on the specific conformers of a particular compound which provides information to compare dipole moment of a particular conformer and works out other conformers. Band assignment can be facilitated by the ability to subtract calculated spectra from
experimental one and the assignment based on the computational description support particular motions in spectral bands.

Calculation of electron density on specific atoms is one of the most important parameter. Such Information can be used to predict relative reactivities of different substrates as well as sites of reaction. The electronic bond orders are also available from this study. The bond orders are measures of the net bonding character between pairs of atoms. Many qualitative assessments of specie’s bonding patterns can be made using bond orders. Such information can also be correlated with other observed data like bond lengths and vibrational frequencies.

Electronic structure methods can also be used to study reaction mechanisms. This is particularly true for the semiempirical techniques. Because of their fast computational speed, they can be used to extensively examine reaction potential surfaces. These calculations can then rapidly differentiate between a set of mechanisms postulated from the available experimental data. In short, the application of computational methods is a supportive and corroborative technique.

There are two broad areas within computational chemistry related to the structure of molecules and their reactivity: molecular mechanics and electronic structure theory. They perform the same basic types of calculations:

1) Computing the energy of a particular molecular structure. The properties related to the energy may also be predicted by some methods

2) Performing geometry optimizations, which is modest attempt to locate the lowest energy molecular conformation

3) Computing the vibrational frequencies of molecules resulting from interatomic motions within the molecule.

**Molecular mechanics**

Molecular mechanics simulations use the laws of classical physics to predict the structures and properties of molecules. They are many different molecular mechanics methods. Each one is characterized by a force field. A force field has the following components:
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i) A set of equations defining how the potential energy of a molecule varies with the locations of its component atoms.

ii) A series of atom types, defining the characteristics of an element within a specific chemical context. The atom type depends on hybridization, charge and the types of the neighbouring atoms to which an atom is bonded.

iii) One or more parameter sets that fit the equations and atom types to experimental data.

Molecular mechanics calculations do not explicitly treat the electrons in a molecular system. Instead, they perform computations based upon the interactions among nuclei.

This approximation makes molecular mechanics computations quite inexpensive in computation time and allows them to be used for very large systems containing thousands of atoms. However, it also carries several limitations:

i) Particular force fields achieve good results only for a limited class of molecules related to those for which it was parametrised. No force field can be generally used for all molecular systems.

ii) Neglect of electrons means that molecular mechanics methods cannot treat chemical problems where electronic effects predominate.

Electronic structure methods

\[ \mathbf{H} \psi = E \psi \]

For any but the smallest, totally symmetric systems, however, exact solutions to the Schrödinger equation are not practical. Electronic structure methods are characterized by their various mathematical approximations to its solution. There are two major classes of electronic structure methods:

Semi-empirical methods
These methods use parameter derived from experimental data to simplify the computation. They solve an approximate form of the Schrödinger equation that depends on having appropriate parameters available for the type of chemical system in question.

**Ab Initio methods**

Unlike either molecular mechanics or semi-empirical methods, these methods use no experimental parameters in their computations. Instead, their computations are based solely on the laws of quantum mechanics—the first principles referred to in the name *ab initio*—and on the values of a small number of physical constants:

i) The speed of light

ii) The masses and charges of electrons and nuclei

iii) Plank's constant

**Semi-empirical methods** use a simpler Hamiltonian than the correct molecular Hamiltonian and use parameters whose values are adjusted to fit experimental data. Because of the difficulties in applying ab-initio methods to medium and large molecules many semi-empirical methods were developed to treat such molecules. All the geometries were fully optimized without any symmetry constraints using AM1, PM3, MNDO and MINDO/3 methods and stationary points were obtained on the potential energy surfaces. The semi-empirical SCF procedures in general do not make use of symmetry in SCF cycles in economizing the CPU time.

Third version of the modified INDO called (MINDO/3)[68] has been parameterized for compounds containing C, H, O, N, B, F, Cl, Si, P, and S atoms. MINDO/3 is based on the INDO approximation and the average absolute errors in calculated properties are large.

MNDO method[69] is based on the far more justifiable NDDO approximation and give better results as compared with MINDO/3. The MNDO valence electron Hamiltonian $\hat{H}_{\text{val}}$ is given by equation (1) and the Fock matrix elements are given by equation (2),

$$
\hat{H}_{\text{val}} = \sum_{i=1}^{n_{\text{val}}} \hat{H}_{\text{val}}^{(i)} + \sum_{i=1}^{n_{\text{val}}} \sum_{j>i} \frac{1}{r_{ij}}
$$

(1)
Where $\hat{H}_{\text{val}}^{\text{core}}(i) = -\frac{1}{2} \mathbf{v}_{i}^2 + V(i)$

and $n_{\text{val}}$ is the number of valence electrons in the molecule, $V(i)$ is the potential energy of valence electron $i$ in the field of nuclei and inner-shell (core) electrons, $\hat{H}_{\text{val}}^{\text{core}}(i)$ is the one-electron part of $\hat{H}_{\text{val}}$.

$$F_{\text{val},rs} = H_{\text{val},rs}^{\text{core}} + \frac{1}{2} \sum_{[z]} \sum_{[\nu]} P_{ul}[\langle rs|tu \rangle - \frac{1}{2} \langle ru|ts \rangle]$$ (2)

In MNDO, the core-core repulsion term is given by equation (3)

$$V_{CC} = \sum_{B>A} \sum_{A} \left[ C_{A}C_{B}(s_{ASA}|s_{BSB}) + f_{AB} \right]$$ (3)

Where $(s_{ASA}|s_{BSB})$ is electron repulsion integral which involves the valence $s$ orbitals of atoms A and B (and is approximately proportional to $1/R_{AB}$), and $f_{AB}$ is a small term whose form differs in various theories. $f_{AB}$ is an empirical function of $R_{AB}$ that finetunes interatomic attractions and repulsions in the molecule, so as to improve agreement with experiment. For MNDO method $f_{AB}^{\text{MNDO}}$ is given by equation (4).

$$f_{AB}^{\text{MNDO}} = C_{A}C_{B} \left( s_{ASA}|s_{BSB} \right) e^{-\alpha_{A}R_{AB}} + e^{-\alpha_{B}R_{AB}}$$ (4)

Where $\alpha_{A}$ and $\alpha_{B}$ are parameters for atoms A and B.

There are six parameters to be optimized for each kind of atoms in MNDO. MNDO method has been parameterized for compounds containing H, Li, Be, B, C, N, O, F, Al, Si, Ge, Sn, Pb, P, S, Cl, Br, I, Zn and Hg atoms.

Austin Model 1 (AM1) [70,71] is an improved version of MNDO and it has been parameterized for H, B, Al, C, Si, Ge, Sn, N, O, F, P, S, Cl, I, Zn, and Hg atoms. The only differences between MNDO and AM1 are that the valence orbital exponents $\zeta_{s}$ and $\zeta_{p}$ on the same atom are allowed to differ and the core-core repulsion function in AM1 is given by equation (3) where $f_{AB}^{\text{AM1}}$ value is given by equation (5).
\[ f_{AB}^{AM1} = f_{AB}^{MNDO} + C_A C_B / R_{AB} / \sum_k a_{kA} \exp[-b_{kA}(R_{AB} - c_{kA})^2] + \sum_k a_{kB} \exp[-b_{kB}(R_{AB} - c_{kB})^2] \]

(5)

AM1 is re-parameterized to give the PM3 method [72] (Parametric method 3, 1 and 2 being MNDO and AM1). PM3 differs with AM1 in many ways. The one-center electron–repulsion integrals are taken as parameters to be optimized (rather than being found from atomic spectral data). The core-repulsion function contains only two Gaussian terms per atom. A different method was used to find the optimized PM3 parameters. PM3 has been parameterized for H, C, Si, Ge, Sn, Pb, N, P, As, Sb, Bi, O, S, Se, Te, F, Cl, Br, Al, Ga, In, Tl, Be, Mg, Zn, Cd and Hg atoms.

A major limitation of the original versions of the MNDO, AM1, and PM3 methods is that they use a basis set of s and p valence A.Os only, so they can’t be used with transition metal compounds (in Zn, Cd and Hg atoms the d electrons are not valence electrons). Moreover, for compounds containing such second-row elements as S, the contributions of d orbitals to MOs is significant, and these methods do not perform very well for such compounds.

MINDO/3 is an improved method [73] over MNDO. It uses a basis set which includes d-orbitals for many second-row and later elements. MINDO/3 does not add d-orbitals for first-row elements. Besides first-row elements MINDO/3 has been parameterized for Al, Si, P, S, Cl, Br, I, and for several transition metals. Semi-empirical methods are widely available in many programs/packages like MOPAC, Gaussian, Hyperchem, Chemoffice etc.

Moustafa M. Habeeb and Gamal A. Gohr have successfully utilized semi-empirical AM1 method to correlate the experimental FTIR data. They reported that AM1 method shows a reasonable consistency with experimental results [74]. Semi-empirical AM1, PM3, MNDO and MINDO/3 methods have been tested to find best auxiliary tool for FTIR identification of the compounds by V. A. Basiuk et. al. [75]. They reported that MINDO/3 method provides the best linearity between the calculated and experimental wave numbers.
D. Kumar, Rajeev Singh et al. [76] have used the Semi-empirical AM1, PM3, MNDO, MINDO/d methods to predict the bond length, bond angles, net atomic charge, atom electron densities, fundamental vibrational frequencies and thermodynamic parameters such as heat of formation, total energy, electronic energy, core-core repulsion energy, and ionization potential of Schiff bases derived from S-methyl/benzyl dithiocarbazate. They have also reported theoretical study on S-Benzyl-β-N-(2-furylmethylketone) dithiocarbazate Schiff base of S-benzyl dithiocarbazate and the performance of Semi-empirical AM1, PM3, MNDO, MINDO/d methods was tested to find the best auxiliary tool for the IR frequencies, geometry & electron densities. For bond length, the correlation coefficient obtained for AM1, PM3, MNDO, MINDO/d methods were 0.96, 0.990, 0.983 and 0.976 respectively. Out of the four Semi-empirical methods the most satisfactory correlation (cc = 0.996) was obtained by PM3 method. In case of bond angles, correlation coefficients were 0.836, 0.742, 0.706 and 0.685 for AM1, PM3, MNDO and MINDO-d methods respectively. The most satisfactory correlation coefficient (cc = 0.836) was given by AM1 method. For fundamental vibrational frequencies, the correlation coefficient obtained for AM1, PM3, MNDO and MINDO-d methods were 0.926, 0.967, 0.760, and 0.969 respectively. Out of the four semi-empirical methods MINDO/d gave the most satisfactory correlation (cc=0.969) between experimental and calculated fundamental vibrational frequencies. The computed coordination sites based on atom electron densities by PM3 were supported by experimental data.
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