Recent Advances in the Synthesis and Characterization of Chalcogenide Nanoparticles

P.K. Bajpai[1,a], S. Yadav[1,b], A. Tiwari[2,c] and H.S. Virk[3d]

[1]Department of Pure & Applied Physics, Guru Ghasidas Vishwavidyalaya, Bilaspur, India
[2]Department of Chemistry, Disha Institute of Management and Technology, Raipur, India
[3]Visiting Professor, SGGS World University, Fatehgarh Sahib-140 426, India

[a]bajpai.pk1@gmail.com (corresponding author), [b]sandhyadv614@gmail.com,
[c]arundendra@gmail.com, [d]hardevsingh.virk@gmail.com

Abstract. Chalcogenide semiconductor nanoparticles and their self-assembly structures have become the most explored group of semiconductor nanomaterials due to the interesting physics involved in quantum confinement, surface chemistry and variety of applications. In the last couple of decades, facile routes for their synthesis and strategies for controlling the size, shape and morphology have been reported. In the present review, synthesis strategies of size and shape controlled nanoparticles belonging to II-VI group of semiconductor chalcogenides are presented and each method for preparation of nanoparticles is critically analysed. Role of various factors that affect the nucleation and growth of nanoparticles is discussed at length. Nanoparticles and self-assemblies of CdSe, CdTe, HgTe and ZnSe are synthesized using new and facile single molecular precursor based noble route by our group that uses non-pyrophoric, low temperature and non-toxic chemicals, their properties and synthesis scheme are discussed as future development in this field. Some recent applications of chalcogenides QDs in the fields of solar cell, optical fibre amplifiers, biosensing and bo-imaging are discussed and reviewed.

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1. Introduction

Nanocrystalline semiconductors exhibit properties different from those of the bulk materials and have shown considerable promise in numerous applications in diverse fields including electronics and photonics [1- 4]. These nanoparticles exhibit structural, optical, luminescence and photo-conducting properties that are very different from their bulk properties [5-10]. The size dependent electronic and optical properties in semiconductor quantum dots arise from the quantum size effects and the large number of unsaturated surface atoms. These nanomaterials have been very attractive for possible applications in solar cell, photo detector, laser, high density magnetic information storage and in various devices based on semiconductor optoelectronic materials. Modifications of the physical properties of semiconductor materials depend upon the sizes, structures and morphologies of synthesized particles [11-12]. Therefore, synthesis of semiconductor nanoparticles especially with dimensions comparable to the Bohr radius (in the regime where they exhibit strong quantum confinement effect) has taken centre stage in the last couple of decades. Such particles may lead to quantum dot lasers, single electron transistors and are useful in biological applications [13-14]. Currently focus has been on harnessing these properties in the fabrication of electronic devices such as light emitting diodes (LEDs) and/or quantum dot lasers [15]. Reports have appeared on the synthesis of varieties of semiconductor nanocrystals applying different synthetic routes, including colloidal particles [16–19], nano-particles embedded in glass matrices [20] and those in zeolitic cages [21, 22]. In order to prevent agglomeration of particles, the surface atoms are passivated by long-chain organic surfactants, called capping agents such as TOPO, pyridine, alkyl amines, or thiols [8]. Another category of nanoparticles has been the core–shell structures in which a layer of a second semiconductor is deposited onto a semiconductor nano-crystallite which serves as the core of the core–shell structure [23]. Chalcogenide core-shell structures include compositions such as CdS on ZnS [24], CdSe on ZnS [25], CdSe on ZnSe [26], and HgS on ZnS [27]. Synthesis and photo-physical properties of quantum dot quantum well (QDQW) in which a three layered structure consisting of an inner core and a layer covering this core, followed by an outer shell, have also been reported [28-30].

Chalcogenide nanoparticles are widely studied due to their important applications and size dependent changes in physico-chemical and optoelectronic properties [31-33]. Metal chalcogenides have achieved significant attention in recent years and amongst them, nanoscale cadmium sulphide (CdS), cadmium selenide (CdSe), copper sulphides (Cu_xS) have been considered as very useful materials for modern industrial applications [34-35]. These nano-sized semiconductors have been synthesized by a variety of methods for tuning the properties for specific applications. Among the applications targeted include solar cells, field effect transistors, light emitting diodes, biological fluorescence labels, bio-sensors, etc. Morphology and size control of nanomaterials are key factors to improve their properties. Therefore, a variety of new fabrication routes have been investigated to control the size and shape of these QDs.

Cadmium sulphide (CdS) is an II–VI semiconductor material with a direct band gap of 2.42 eV at room temperature with many outstanding physical and chemical properties, which has promising applications in photochemical catalysis, gas sensors, detectors for laser and infrared, solar cells, nonlinear optical materials, luminescence devices and optoelectronic devices [36-39]. CdS also exhibited excellent visible light detecting properties [40]. In the last decades, many techniques have been reported on synthesis of CdS nanoparticles [41-43].

CdSe has been of interest to synthetically adjust size-dependent electronic and optical properties and also due to their potential applications including the photostable luminescent biological labels [3], solar cells [44] and light-emitting devices (LEDs) [45]. The control of these properties, when the radius of the nanoparticles becomes comparable to the bulk Exciton Bohr radius, has been of paramount interest [16]. The quantum confinement of photo-created electron-hole pair allows the tuning of optical properties of nanoparticles by controlling their size. In CdSe, the conduction or lowest unoccupied band is composed of Cd 5s orbitals, whereas, the highest occupied band is formed from Se 4p orbitals.

Copper sulfides have variable stochiometric forms, complex structures and valence states and stabilize in covellite (CuS), djurleite ($Cu_{1.95}S$), digenite (Cu_9S_5), anilite (Cu_7S_4) and chalcocite (Cu_2S), and have attracted wide attention [46-48] for a number of applications. Especially, due to the considerable narrow band gap of nanocrystalline Cu_xS (1.2-2.3eV), it has been considered as visible light active semiconductor for use in the field of pollutant treatment [49]. For example, the degradation rate of methylene blue was 82.9% when CuS microspheres were used as photocatalyst in presence of visible light [50], similarly, CuS nanotubes also showed very high catalytic activity for the oxidation and degradation of Methylene Blue with H_2O_2 [51] and reactive orange [52]. Recently, using the nanocrystalline mixed phase ($CuS-Cu_7S_4$), the degradation of Rhodamine B (Rh B) has been 99.7 % under visible light [53]. Cu_xS has been very attractive for biological application among the chalcogenide semiconductor nanomaterials. In comparison to cadmium based II-VI semiconductors, copper based nanomaterials are preferred as they contain less toxic metals [54].

Control of size, morphology and structure have been identified as critical steps in nanoparticle fabrication, as varying these parameters can lead to nanomaterials with the desired properties. Therefore, considerable efforts have been devoted to synthetic procedures and many methods have been proposed [55-60]. In the following, we present in brief various methods used for the synthesis of chalcogenide semiconductor nano-particles and summarize the basic concepts behind these methods focussing on the key parameters in each method that controls the size and shape of the nanomaterials synthesized as well as the current progress in the synthesis of CdSe, CdS and CuS nanoparticles.

2. Synthesis Routes for Chalcogenides Nanoparticles

Chalcogenides semiconductor nanoparticles have been synthesized using a number of routes. The most followed being thermal decomposition of colloidal precursors [61-67], sonochemical [68-70], single source molecular precursor route [71-80], solvothermal/ hydrothermal process [81-92], ionic liquid assisted synthesis [93], pulse plasma assisted route [94], microwave assisted route [95-96], solid state reaction [97], spray pyrolysis [98], mechano-chemical synthesis [99], synthesis from elemental powders [100, 101], self-assembled/template- assisted synthesis [102-106], γ-irradiation route [107], synthesis into micellar medium [41], etc. Uniformly dispersed and stabilized nanoparticles are successfully achieved by using capping agents and surfactants [42, 108-110]. Conjugate nanoparticles with polymers and biomolecules have been synthesized for optoelectronic and biological functionalities [10, 111-116]. Reaction conditions have been optimized in various synthesis routes by investigating the effect of process parameters such as ion source precursor's concentrations, molar ratios, reaction temperature, role of solvents and surfactants, use of co-surfactants, etc. The formation mechanism of nanoparticles has also been elucidated for several routes [117-119]. Several investigators focussed on properties relevant for specific applications such as luminescence for opto-electronics and lasers [10, 117], photo catalysts [119], bio-medical applications [40, 120]. Considering the potential applications of metal chalcogenide nanoparticles, a large number of reports have appeared related to the applications of these materials in a variety of applications including solar cells, LEDs, photocatalysis, pollutant reduction, gas sensing, etc. [3, 8, 121-137]. The materials have also been reviewed by a number of researchers.

Advances in the synthesis strategy have been to generate nanoparticles and/or nanomaterials with varying morphologies. The basic idea has been to proceed with controlled reaction to start nucleation and arrested growth so as to achieve desired size and shape [3, 8, 122-137]. However, each method has its advantages and limitations. Therefore, generation of functionalized and controlled nanoparticles and assemblies still poses a great challenge. Following sections, therefore, summarize the salient feature of each method used for the synthesis of chalcogenide semiconductor nanoparticles.

2.1. Colloidal Solution (Precipitation) Method: One common route for the synthesis of semiconductor nanoparticles is a controlled precipitation reaction giving dilute suspension of colloidal particles [30]. The basic idea of the method has been to inject slowly the solution of metal ions into the aqueous/non-aqueous solution of chalcogenide ion source precursors. The controlled size nanoparticles are produced when after nucleation step the growth is arrested by controlling the reaction equilibrium between the nanocrystals of desired chalcogenides and the solvated ions. Extensive research has been performed to identify and control the factors that affect such equilibrium. The role of solvents, molar ratio of precursor ions, reaction temperature, and concentration of precursors are found very important. In addition, to achieve monodispersed and stabilized nanoparticles, polymers, surfactants and other molecules are used as capping agents. Especially, the thiol-capped chalcogenides have been very stable. The schematic diagram for synthesizing CdTe nanoparticles using thiol-capped route is shown in Fig. 1.
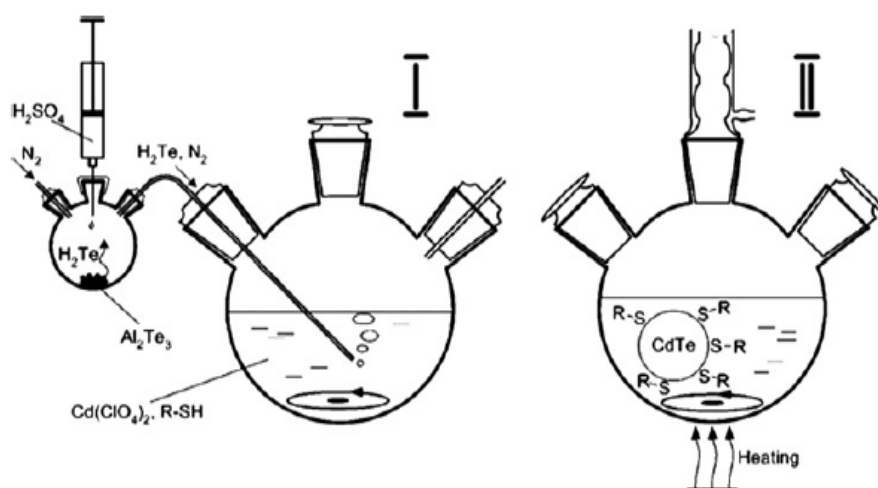

Fig. 1: Schematic presentation of the synthesis of thiol-capped CdTe QD. First stage: formation of CdTe precursors by introducing H_2Te gas. Second stage: formation and growth of CdTe nanocrystals promoted by reflux (adapted from ref. [65])

H_2S, Na_2S, thiourea and thioacetamide are normally used as the S^{2-} source [34-36, 52]. The major disadvantages of the method include: poor crystallinity of as synthesized nanoparticles, large size distribution and invariably associated surface defects [61-67].

2.2. High Temperature Injection Route: Decomposition of single molecular precursors provides convenient and effective routes for the synthesis of metal chalcogenide nanocrystals. In this method, a molecular complex consisting of both the metal and the chalcogen is thermally decomposed in a coordinating solvent. In the method reported first time for the synthesis of CdS/CdSe/CdTe nanoparticles precursor materials dispersion in an organometallic reagent tri-n-orthophosphine (TOP) is followed by the pyrolysis of organometallic reagents on injection into a coordinating solvent, tri-n-ortho phosphine oxide (TOPO) [113] at higher temperature (typically >250^{0}C) as shown in the schematic diagram below (Fig. 2):
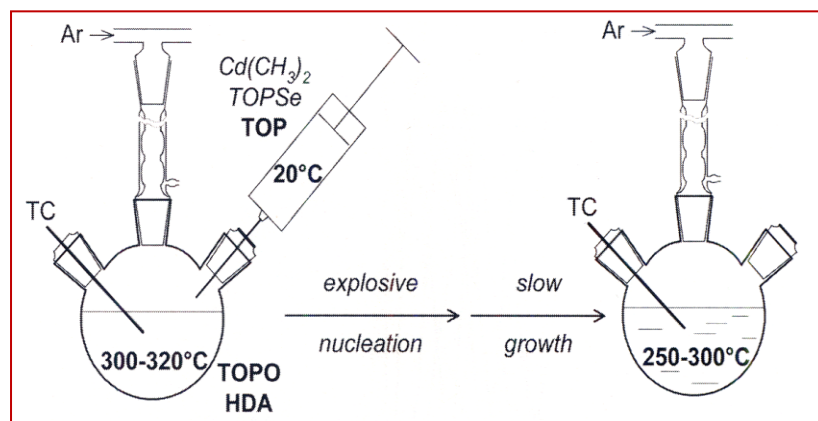
Fig. 2: Schematic representation of the hot injection technique employed in the organo-metallic synthesis of nanocrystals (adapted from reference [61]).

The decomposition of precursors initiates the formation of nanoparticles (nucleation) whereas the growth of nanoparticles is inhibited when the precursor supply is depleted. The whole process of size controlled nanoparticles synthesis occurs in terms of three steps:

(i)   initial injection of precursor
(ii)   Rapid nucleation, and
(iii)   Controlled growth of the nuclei by Ostwald ripening.

The agglomeration is arrested as TOPO passivated the resultant nanoparticles. The nanocrystallites prepared by this method have greater crystallinity than those obtained by colloidal methods [113]. The use of highly hazardous and volatile compounds such as dimethylcadmium, and noxious compounds such as H_2S has led to the development of safer and more environment friendly routes for the synthesis of semiconductor nanocrystallites. Many researchers later used simple cadmium salts [138-140] to prepare single source precursors from commercially available chemicals, viz. dithiocarbamates and selenocarbamates of divalent metals, cadmium complexes of dithiobiurea are used as single-source precursors for the deposition of high quality mono dispersed nanoparticles [75, 78]. The nano particles were also prepared by the thermolysis of the precursor in coordinating solvents like 4-ethylpyridine. However, the limitation imposed on such methods includes the use of toxic compounds such as CE_2 (E =S or Se) for the synthesis of the precursor compounds. Group 12 metal chalcogenolates [141] and cadmium thiolate and selenolate derivatives $M[E(Ox)]_2$ [E = S, Se; M = Cd; Ox = 2-(4,4- dimethyl-2-oxazolinyl)benzene] have also been reported as single source precursors, for synthesis of cadmium sulfide and selenide nanoparticles. Nearly monodisperse Cd-chalcogenide nanocrystals (CdE; E = S, Se, Te) have been synthesized by the injection of organometallic reagents such as alkylcadmium into a hot coordinating solvent in the presence of silylchalcogenides/phosphinechalcogenides [62]. Alivisatos and co-workers [3, 128] have produced Cd-chalcogenide nanocrystals by employing tri-butylphosphine at higher temperatures. CuS nanoparticles have been prepared through TOPO route using the single source precursor $[Cu(CS(NHCH_2CH_3)_2)_4Cl_4]$ dissolved in TOP and injected into TOPO solution at high temperature 200^0C whereas directly adding solid precursor to hot TOPO resulted into chalcocite (Cu_2S) phase with average particle size of 8.7 nm [142]. Peng et al. [134-136] have proposed the use of greener Cd sources such as cadmium oxide, carbonate and acetate instead of the di-methyl cadmium and shown that the size distribution of the nanocrystals is improved by the use of hexadecylamine, a long-chain phosphonic acid or a carboxylic acid. Nanocrystals of Cd, Hg, Mn, Pb, Cu, and Zn sulfides have been obtained by thermal decomposition of metal hexadecylxanthates in hexadecylamine [127]. CdSe nanocrystals have also been prepared using the phosphonium ionic liquid trihexyl (tetradecyl) phosphonium bis (2,4,4 trimethylpentylphosphinate) as a solvent and capping agent [80]. However, due to the fact that method used highly toxic and pyrophoric substances as metal sources, uses TOPO, alkyl amines as solvent which are high boiling one and needs high temperature and special inert environment makes the method very expensive and complex for scaling up.

2.3. Solvothermal/Hydrothermal Process: Solvothermal process involves the reaction between the precursors under controlled temperature and pressure and in case of aqueous solvent; the method is called hydrothermal process. Solvothermal method uses solvent well above their boiling point achieved through autogenously high pressure and at high temperature in a sealed autoclave or reactor bomb. This makes it very attractive for generating highly crystalline nanophases using inexpensive low boiling solvents. In case of hydrothermal route, use of water as a solvent limits the temperature up to super critical point. However, the innocuous nature of the solvent compensates for this limitation. During the last decade, large numbers of simple precursors (both elemental and metal salts) have been successfully used to synthesize metal chalcogenide nanoparticles through this route [138-139]. The major parameters affecting the size and morphology of as synthesized particles are: (i) nature of solvent used, (ii) temperature of the reaction, (iii) time used for solvothermal decomposition, and (iv) the type of surfactants used. Despite the fact that method has several advantages, the particle size distribution, purity of nanophase and morphology variation still remains a challenge to overcome. Nanocrystals of metal chalcogenides have been generally prepared by the reaction of metal salts with an appropriate sulfiding or seleniding agent under solvothermal or thermolysis conditions. CuS nanoparticles (11 nm) are generated using Sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$) and cupric sulphate [140], CTAB capped nanoparticles using thiourea, Cu(ac)2 and $Cu(NO_3)_2$ [143]. CuS hexagonal plates were also synthesized using CTAB, and nitric acid as assisting agent with copper chloride and sodium thiosulphate as precursor in hydrothermal process [142]. Wet chemically modified hydrothermal route using copper chloride, acetyl acetone, sodium acetate, dichloromethane, ethanol and sodium hydroxide [92]. The role of $Cu^{2+}:S_2O_3^{2-}$ mole ratio on the morphology of nanoparticles has also been studied through hydrothermal route [91]. Sodium thiosulphate penta hydrate ($Na_2S_2O_3.5H_2O$) and hydroxylamine sulphate $(NH_2OH)_2.H_2SO_4$ with cupric sulphate pentahydrate were used in hydrothermal process to produce hexagonal CuS [144]. Synthesis of capped CdSe nanoparticles (3 nm) using low boiling solvent has also been achieved by using the H_2Se produced in situ by aromatization of tetralin using Se powder [141]. CdS nanoparticles (6 nm) are also generated through solvothermal route using $Cd(NO_3)_2$, $CdSO_4$, thiourea as precursors and ethylene glycol as solvent [145]. CdSe/ZnSe and $Cu_{2-x}Se$ nanopowders are also synthesized using elemental powders as precursors in various solvents including water [146], ethylenediamine [147] and pyridine [148].

2.4. Pulse Plasma Assisted Synthesis: Electric discharges in liquid dielectrics arouse interest in the generation of nanoparticles [149-151] and it has been reported that nanoparticles can be produced by means of electric discharge in liquids. Omurzuk et al. [152] first reported the synthesis of carbon nanoparticles using pulsed plasma in liquid by the low voltage spark discharge. The pulse plasma in liquids enables the quenching from plasma state leading to the formation of nanoparticles and metastable particles. In atypical pulsed plasma in liquid process, copper electrodes are submerged in molten sulphur (120^0C) and an electric voltage of 180V, 3A at 60 Hz resulted into CuS nanoparticles of 20 nm size and nano-rod like morphology [94]. ZnMgS nanoparticles of about 10 to 50 nm are also synthesized by the pulsed plasma in liquid method [153].

2.5. Synthesis from Elemental Precursors: Copper sulfide could be synthesized directly by reacting elemental powders [154]. However, the problem has been that the direct reaction between copper and sulphur requires high temperatures and is restricted only up to the surface layer due to the formation of CuS surface over copper powder which acts as a passivating layer preventing further reaction. Several modifications were suggested to synthesize the nanoparticles directly from elemental powders [154]. These include dissolving the elemental precursors in solvent [155], increasing reaction temperature, continuous reactants milling to remove the passivating layer [156] and slow aging in inert atmosphere at low temperature providing more time for diffusion [100]. Attempts have also been made to directly synthesize CuS nanoparticles from elemental precursors in which Cu metal nanoparticles are reacted with sulphur at room temperature in chloroform. It resulted into irregular nanostructured CuS (Covellite) nanoplates [101]. The reaction takes place via breakdown of Cu nanoparticles by reactively interactive sulphur solute and via growth of the CuS nanobodies involving inter-diffusion and redox reaction of S and Cu atoms.

2.6. Ionic Liquid-assisted Synthesis: The method has been developed as a modification in soft solution route which has capability of being economical, convenient and easily scalable at industrial scale. However, the problem with the solution routes has been the poor control over size, shape and dispersion of nanoparticles and the complex formed between transition metal and chalcogenide precursor not dissociating at room temperature; the metal and chalcogenide precursors (i.e. TAA) undergo coordination reaction forming metal complex. Since the coordination ability of TAA to combine with metal ions is very strong, the complex formed is not dissociated at room temperature and often solution is heated to get the desired nanoparticles [157]. In this method, ionic liquids have been used as co-solvents in the formation of nanoparticles. It is well known that these ionic liquids possess readily modifiable and controllable physical characteristics [158] that would allow control over structural properties of nanomaterials [159]. In addition, high ionic conductivity and polarizability makes them agent for driving polar reaction for inorganic synthesis. CuS nanoparticles are synthesized using $CuCl_2$ and thioacetamide (TAA) in presence of ionic liquid 1-n-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4). This resulted into 250-300 nm nanoparticles constructed by numerous nano-flakes of 10 nm thickness [160].

2.7. Microwave Irradiation-assisted Aqueous Synthesis: In this method, microwave radiation is used to induce the chemical reaction. The high frequency electromagnetic field associated with these radiations impinges a force on the charged particles in solution, creating charge migration or molecular rotation. In polar molecules, this may create further polarization. The overall friction and collisions among molecules have been accounted in terms of thermal and non-thermal effects [161]. Submicron size materials with different morphologies were synthesized by simple aqueous route under microwave irradiation and using visible light and employing different copper and sulphur ion sources [162]. CdS nanoparticles are also generated using Cd(ac)2 and thiourea precursors in ethylene glycol solvent using microwave irradiation. CuS nanomaterials of different morphologies (tubular, spherical and leaf like) are also synthesized through microwave irradiation [95-96]. The role of precursor molar ratio has been found critical [95]. Some of the claimed advantages of this route are short reaction time, small particle size and purity of materials synthesized [163].

2.8. Sonochemical Process: The basic idea behind sonochemical method is that when ultrasonic radiation interacts with the solution, molecules start vibrating and the energy is transferred to the solution. This energy transfer assists in activating the reaction. Sonochemical route has evolved as an important method for the synthesis of nanoparticles [164]. The basic physics of ultralysis involves emulsification and surface damage (dominating at low frequencies) and cavitational heating by collapsing bubbles (in the entire frequency range) [165]. When the ultrasonic wave travels through a solution, it forms bubbles which grow and finally collapse; this process is termed as cavitation. During the bubble formation and subsequent collapsing, extreme conditions are created and the heat is transferred to the solution. This induces the chemical reaction-the sonochemistry. Several researchers have reported the synthesis of chalcogenide nanomaterials such as CdS, CdSe, CuS, Cu_2S, and CuSe [166-169] using sonochemical route. In most of the studies, ultrasonic radiation at 20 or 40 kHz is irradiated into a solution having precursors of metal and chalcogenide ions. Sonochemistry has also generated nanomaterials with specific morphologies such as nanorods, nanowires or nanotubes [170-171] by using the directed growth assisting agents. Recently, hollow spheres of CuS are reported using bubble template molecules [172]. Some of the advantages of this process include the uniform size distribution, better thermal stability and smaller particle size.

2.9. Reflux Condensation Method: Reflux condensation has been used to prepare nanomaterials with relatively high crystallinity. This has been possible as the precursors dissolved in high boiling point solvents are allowed to react at high temperature through refluxing. Reflux condensation of complex formed between copper source and thioacetamide (TAA) has been used to generate copper sulphide nanoparticles [102]. The nitrogen lone pair electrons of TAA coordinated with the vacant d-orbitals of copper ions to form complexes. Morphology of synthesized nanoparticles varies by varying the precursor's molar ratio. Different precursors for Cu^{2+} such as $CuCl_2.4H_2O$, $Cu(NO_3).3H_2O$ and S^{2-} TAA, Na_2S with varied $Cu^{2+}:S^{2-}$ molar ratio have shown to generate various morphologies. Nature of solvents (aqueous solution, ethylnediamine and ethanol) and reaction

temperature are also found to affect the shape and yield of synthesized powder [173]. There have been several problems associated with the method. These include the possible toxic nature of the solvents, process being expensive and its inability to use simple precursors.

2.10. Capping-assisted Fabrication: Capping-assisted fabrication is very promising for the development of diversified semiconducting QDs. It is well known that the final morphology of nanocrystals is largely dependant on the type of capping agent absorbed on their surfaces [174, 175].

Surfactants host assemblies play an important role in the preparation of nanoparticles especially in controlling the size, shape and morphology of generated nanoparticles as well as stabilization to particulate assemblies. These include aqueous micelle, reverse micelle, microemulsion, monolayers, Langmuir Blodgett (LB) film, vesicles, bilayer liquid membranes etc. [176]. Nanoparticles of CdS, CdSe, ZnS, PbS and CuS have been prepared using surfactant assemblies [177-178]. Cu_2S nanoparticles have been synthesized in monosize distribution using Triton X-100 water/oil microemulsion, whereas CuS nanoparticles have been obtained in aqueous phase surfactants micellar solution, sodium–bis (2-ethylhexyl) sulpho succinate (Na-AOT) [179]. Thiol capping has been the most studied one to synthesize water soluble quantum dots of CdS, CdSe and CdTe [61,180-182]; capping agents are amphiphilic molecules containing a thiol group strongly coordinated to the nanoparticles and a polar group such as -OH, -COOH, $-NH_2$ ensuring water solubility [110]. Capping of biologically active macromolecules and polymers has also been attempted extensively. A number of reports have indicated that macromolecules such as amino acids, proteins, DNA, RNA and polymers have significant role in controlling nucleation and growth of nanomaterials. Biological macromolecules conjugated nanomaterials have several advantages,viz. bioactivity, biocompatibility and biological functionality, on the nano-surfaces providing biological coupling providing extended bio-molecular attachments on nano-surfaces. This has opened up many applications such as luminescence probing drug delivery, bio-labelling, etc. Bovine Serum Albumin (BSA)-CuS conjugate and alanine – capped water soluble CuS nanoparticles are reported using copper acetate and thioacetamide in water/ methanol solvent [111]. Synthesis of hollow nano-structured materials has also been attempted as possible interconnects & functional units as well as for applications such as controlled release capsules in drugs, artificial cells, etc. Hollow copper sulphide nanoparticles assemblies are synthesized using 2-hydroxypropyl-β-cyclodextrin and glutathiones [172] as a template.

3. Progress in the Synthesis: Chalcogenide Nanoparticles
3.1. CdSe Nanoparticles: The development of a number of colloidal synthetic routes for the preparation of chalcogenide nanoparticles over the last years has yielded a remarkable degree of control over the size and shape of the nanocrystals [183]. The synthesis of CdSe nanocrystals has improved considerably over the past decade. Pyrolysis of organometallic reagents on injection into a coordinating solvent, TOPO (the TOPO method) has been most attractive. The nanocrystallites prepared by this method have greater crystallinity than those obtained by colloidal methods. Further, it permits the production of highly monodisperse nanoparticles. However, the drawbacks of the method lie in high temperatures employed and due to the use of highly toxic chemicals as the starting materials. In particular, alkyl metals such as $(CH_3)_2Cd$ and $(CH_3)_2Zn$ are pyrophoric, explosive at high temperatures and liberate highly toxic gases of metal oxide so that all the reactions involving these chemicals must be carried out with extreme precautions under an inert atmosphere. Hence, efforts have been made to modify the TOPO method with more stable and less toxic cadmium sources. A series of experiments led to the conclusion that $(CH3)_2Cd$ can be replaced by other cadmium salts, for example CdO. Cadmium salts with an anion of a weak acid, such as $Cd(Ac)_2$ and $CdCO_3$, have been very useful alternates [46-47] and were significantly better than $(CH3)_2Cd$ related ones.

The use of alternative ligands and precursors for the synthesis of CdSe nanocrystals at elevated temperatures provided a decent database to design a synthetic system that generates CdSe nanocrystals with acceptable emission properties. Among all the ligands reported, primary amines have shown the most promising results for achieving high PL efficiency for a variety of semiconductor nanocrystals. Especially the presence of stearic acid was proven to be helpful for the

formation of CdSe nanocrystals in the orange red window. In addition, cadmium stearate in amines can bear significantly high temperatures, which is required for the formation of semiconductor nanocrystals with high structural quality. The preparations of thiol-capped CdSe nanoparticles have been reported using cadmium stearate under similar solvothermal conditions. The use of stearates instead of toxic and flammable organometallic precursors has been the most important step forward in the synthesis of these nano particles [48-49].

Among the alternate methods, solvothermal decomposition has been very attractive for the production of high quality CdSe QD at a relatively lower temperature. The synthesis procedure employs low cost and less toxic materials and importantly, it avoids the use of inert atmosphere. The two-pot solvothermal approach has many advantages compared with the one-pot synthesis procedures [184]. Major synthetic routes used for the synthesis of CdSe nanoparticles along with the particle size and the capping agent used are summarized in Table 1.

Table 1: Particle size of CdSe nanomaterials synthesized by different routes

Synthesis route	Precursors	Solvent/ Capping agent	Particle size (nm)	Ref.
Precipitation route	Cadmium acetate, Na_2SeSO_3, sodium selenosulfate (Na_2SeSO_3), $CdCl_2$	Ammonia solution to control pH 2-mercaptoethanol	-	[185] [186]
Thermal decomposition: single source precursor	Cd-xanthates, thiocarbonates, thiophosphates	hexadecylamine HDA	5.60-3.71	[187]
High temperature injection	Selenium powder, Dimethylcadmium,	Trioctylphosphine oxide (TOPO), Triocytlphosphine TOP)	2.4-5.5	[188]
Solvothermal route	$CdCl_2$, Selenium Cadmium nitrate, Sodium Selenide Cadmium stearate	Ethylene glycol and Hydrazine hydrate, EDTA, toluene	10-15 3	[189-191]
Microwave irradiation	NaHSe, $CdCl_2.2H_2O$, selenium powder , Cadmium chloride, sodium selenite	3-Mercaptopropionic acid,Rhodamine, hydrazine, salicylaldehyde, 4-nitroaniline, aniline	5-10	[192-193]
Chemical method	selenium powder, CdCl2.2.5H2O, NaHSe	sodium borohydride, 3-MPA	7.3- 8.0	[194]
Single-source precursor	$(Li)_4[Cd_{10}Se_4(SPh)_{16}]$: SPh- phenyl thiolate, CdO, selenium powder Na_2S, Cd(NO_3)_2, Se powder, Cd(AcO)_2	Hexadecylamine, bis-(trimethylsilyl sulfide), Trioctylphosphine. Tri-n-octylphosphine oxide (TOPO), Tri-n-butylphosphine (TBP),hexadecylamine (HDA). Tri-n-octylphosphine (TOPO), sodium polyphosphate	2.0-9.0 60	[80] [195]
Modified injection route	CdO, Se powder	1-octadecene, Oleic Acid, (*O,O'*-Diethyl Se-[3,4,5-tris(octyloxy) phenyl] phosphoroselenoate), TOPO		[196]
Water-in-Oil emulsion	Ionic salts	W/O microemulsions	2-50	276
Oil-in-water emulsion	Organometallic salts	(O/W) microemulsions confined reaction media, $NaBH_4$	2-50	277

3.2. CdS Nanoparticles: Thermal decomposition has been one of the most efficient pathways for synthesizing CdS nanoparticles. In a typical thermolysis process, a cadmium thiolate powder is heated so as to nucleate CdS particles which are then grown to the desired size by controlled reaction of precursor molecules. Some of the major synthesis methods used are summarized in Table 2. A single source precursor made by reacting cadmium metal ions and a molecule containing the sulphur in a complexing solution of trioctylphosphine (TOP), trioctylphosphineoxide (TOPO), hexadecylamine (HDA), tetradecylamine (TDA) trioctylamine (TOA) or dodecylamine (DA) has been used to produce CdS nanoparticles [197-201].

CdS has both cubic (low temperature) and hexagonal (high temperature) forms, and in hydrothermal systems, a cubic to hexagonal phase transition occurs between 160^0C and 240^0C [202]; the exact temperature being a function of pressure. The transition temperature for 50 wt.% hexagonal (wurtzite–type) and cubic (sphalerite-type) nanoparticles has been reported more than 315^0C in a helium atmosphere [202]. However, the transition lies between 400^0C and 500^0C in air [203, 204]. Lowering the transition temperature is advantageous because the photocatalytic properties of the hexagonal form are better than the cubic form. Transition temperatures for such nano-materials may depend on the particle size, solvent and precursor used. The lowest temperature where such a transition occurs is in an ammonia solvent, transition temperature being $< 100^0C$.

Table 2: Particle size of CdS nanomaterials synthesized by different routes

Method	Precursor	Capping agent	Particle size (nm)	Ref.
Solid-state reaction	$CdCl_2.2.5H_2O$, $Na_2S.9H_2O$	$C_{18}H_{37}O(CH_2CH_2O)_{10}H$	5	[205]
Chemical precipitation	$CdCl_2$, Na_2S,	Volume ratio (0.6-4.0)		[206]
Single source precursor	Cadmium xanthates, ammonia		5.60-3.71	[207]
Solvothermal route	Cadmium stearate, sulfur, Tetralin	trioctylphosphineoxide		[89]
Microwave technique.	Cadmium chloride, sodium sulfide,	hydrazine, salicylaldehyde, 4-nitroaniline, aniline	3.4	[193]
Colloidal method	Cadmium Nitrate, sodium sulfide	Glucose	13	[208]
	Cadmium acetate dihydrate, thioacetamide,	oleic acid, n-hexane	2.6	[209]
Refluxing Single Precursor	Sodium hydroxide, $[(2,2'-bpy)Cd(SC\{O\}Ph)_2]$	1-Thioglycerol	370- 425	[210]
Single-source Precursor	$Cd(NH_2CSNHNHCSNH_2)Cl_2$,	TOP , TOPO	5	[78]
Single-source Precursor	*N*-methyl- and *N*-ethyl, thiourea cadmium	TOPO	8.8-10.3	[211]

3.3. Copper Sulphide Nanoparticles: Among the chalcogenide semiconductor nanoparticles, copper sulphides have been synthesized by a variety of methods as shown in Table 3. Various nanoparticles (plates, tubes, wires, spheres and other architectures) of these binary compounds have been prepared by several techniques and effect of process parameters have been extensively explored with a view to generate controlled size and shape of nanoparticles.

Table 3: Particle size of CuS nanomaterials synthesized by different routes

Method	Precursors	Size	Band gap (eV)	Ref.
Aqueous route	$CuSO_4.H_2O$, thiourea, TEA	CuS (8 nm), Cu$_2$S (10 nm) Cu$_{1.4}$S (13 nm)	1.26 2.31 1.96	[212]

	$Cu(NO_3)_2$, thioacetamide, BSA-stabilizer $CuSO_4$, Na_2S, $(NaPO_3)_n$-stabilizer	Cu_2S, CuS (10-35 nm) CuS	16.8	[111]
Single source molecular precursor (SSMP)	[bis (thiosemicarbazide) copper(II)] chloride, oleylamine ($C_{18}H_{37}N$)-solvent, Triphenylphosphine - surfactant	Cu_2S- 20-50 nm		[213]
SSMP solvothermal/ hydrothermal	$Cu(S_2CNEt_2)_2$ surfactants (PVP,CTAB, PEG, PVA) Solvents (Ethylamine, water, ethylenediamine) $[Cu(TSC)_2]Cl_2$- 150^0C ,12h Cu and S elements 60^0C	Nano flowers (2-3μm) Nano-flakes (200 nm), random morphology CuS- 30nm CuS - 2-3μm		[106] [213]
Aqueous route Microwave assisted	$Na_2S_2O_3.5H_2O$ 1:2 $Cu(CH_3COO)_2.H_2O$ Microwave (2.45 GHz) 160 W/320 watt, 15-30 minute. $Cu(ac)_2.H_2O$, H_2NCSNH_2 (1:2) (2.45 GHz, 160 W, 25 min) $CuCl_2$, $Na_2S_2O_3.5H_2O$ (2:3) (180W, 30 min)/ sunlight $CuSO_4.5H_2O$, CH_3CSNH_2 (1:3) (180W, 30 min)	CuS of varying morphology 900 nm sphere CuS (tabular) Leaf like sphere	350-1000nm	[95] [214] [96]
TOPO route	$[Cu(S_2CN Me(^nHex)_2$ in TOP 200^0C, 15 min.	Cu_2S 25 nm	3.30 eV	[215]
Aqueous route reflux condensation	$Cu(ac)_2$ .H_2O,CH_3CSNH_2 Na-AOT, CTAB, PVP $Cu(NO_3)_2$, TAA+BSA $Cu(CH_3COO)_2$, thiourea, chitosan (stabilizer), acetic acid solvent $CuCl_2$, H_2S Capping (PEG, PVP, BSA, CAS, Glutathione, cysteine) $Cu(NO_3)_2.3H_2O$, CH_3CSNH_2 (TAA), $Cu(NO_3)_2.3H_2O$, Na_2S Solvents: Water, Ethanol, ethylenediamine, Cu:S (1:2)	CuS (2-20 nm) CuS (11nm) CuS (10-35 nm) CuS (118 nm), Cu_2S (76 nm) Cu_xS (10 nm), CuS, Cu_2S (crys.), Cu_2S (amorp.,10 nm) CuS balls (7.5), randam, nano flakes, disperse particles (5-7 nm)		[88] [111] [216] [217] [8]
Aqueous route Co-precipitation	$Cu(ac)_2.H_2O$ $Na_2S_2O_3.5H_2O$ in (1:1) by filtrate $Cu(CH_3COO)_2.H_2O$, CH_3CSNH_2 (water+ methanol) alanine ($70^0C/100^0C$) $Cu(ac).H_2O$, NH_2CSNH_2 + NaOH (15 wt%) $CuSO_4$, $Na_2S_2O_3.5H_2O$ (2:1) Cu_2S nanoparticles, Na_2S $Cu(ac)_2.H_2O$,TAA (1:1) ($Cu(ac)_2.H_2O$, TAA, Na-AOT) $Cu(ac)_2.2H_2O$, $Na_2S_2O_3.5H_2O$ (	C_7S_4 (80-110 nm) CuS (250-50 nm) CuS 21-34 nm $Cu_{2-x} S$ $Cu_{1.8} S$ CuS nano boxes CuS (20-60 nm)		[218] [110] [219] [214] [220] [221]

	1:6) pH - 5.5 pH-11.5	$CuS, Cu_9S_5, CuS_2,$ $Cu_3(SO_4)(OH)_4$- (70-150 nm) CuS>500nm		[179]
Injection reaction	Ammonium di-ethyl di-thiocarbonate, copper (II) acetyl acetonate (dodieanethiol, oleic acid)	Dispersed nanoparticles 3-5 nm		[222]
Solvothermal/ hydrothermal	$Cu(ac)_2.2H_2O, CS_2$, toluene, hexadecylamine $CuCl_2.H_2O$ $Na_2S_2O_3.5H_2O$ (CTAB+HNO$_3$) $Cu(NO_3)$ and $Na_2S_2O_3.5H_2O$ in 1:2 at 155^{0}C $Na_2S_2O_3.5H_2O, CuSO_4.5H_2O$ (200^{0}C , 90 min) $CuCO_3$ +HCl, H$_2$S gas $CuCl_2.2H_2O$ [water+ ethanol] $Na_2S.9H_2O$ (Cu:S 1:1 to 1:5 140^{0}C, 12 h $Cu(ac)_2.H_2O$ + citric acid, thiourea anhydrous ethanol 160^{0}C, 8h Cu:S molar ratio 0.5, 1, 2, 3, 3.2, 4 $CuCl_2.2H_2O, Na_2S.9H_2O$ CTAB (180^{0}C, 24 h)	CuS plates CuS plates CuS CuS (7nm) 1:1 CuS 1:2 CuS, Cu$_7$S$_4$ 1:3 CuS, C$_9$S$_5$ 1:4 C$_9$S$_5$ 1:5 C$_9$S$_5$,Cu$_{1.93}$S CuS flower shape (3-6 nm) CuS nanoplates (15 nm x 60nm)		[143] [142] [92] [140] [49] [223] [91]
Microwave- assisted	$Cu(ac)_2.H_2O/Cu(NO_3)_2.3H_2O$, thiourea CTAB as surfactant $Cu(ac)_2.2H_2O, H_2NCSNH_2BIN$ 1:3, Ethylene glycol (800 W, 20 min) microwave assisted	CuS nanorode (30-70 nm) CuS (16 nm)		[224] [225]
Sonochemical route	$Cu(ac)_2.H_2O$, Sulphur, NaOH(1:4:6)ethylene glycol (sonication at 35 KHz, 5h) $Cu(ac)_2.H_2O+Na_2S.9H_2O)$ 1:1 ethylene glycol $Cu(ac)_2.H_2O, CH_3CHNH_2(TAA)$ (20 KHz, 60W/cm2) $[Cu(en)_2]SO_4$ + propylene glycol + HCl+ thiosemicarbazide (100^{0}C, 75 watt, 15-60 min) Sulfur powder, $Cu(ac)_2. H_2O$ ethylenediamine-solvent, PVA	CuS nanoplates (100 nm,20 nm) (10-30 nm) particles CuS 13nm CuS Cu$_2$S CuS (250 nm)	 2.08 eV	[173] [169] [168] [57]
W/O Micro- emulsion	$Cu(ac)_2.H_2O$, thiourea, Triton X-100 in cyclohexane 2- methyl propanol-co surfactant Aqueous- SDBS anionic surfactant micellar – cationic CTAB solution – non ionic NP-30	 Cu$_2$S CuS		 [176] [140]
Template- assisted synthesis route	$Cu(ac)_2$, Thiourea 2-hydroxypropyl-β-cyclodextrin (Template)	CuS hollow sphere (10 nm)		[104]
Mechano-chemical	Copper acetate, sodium sulfide	CuS (10µm)	-	[99]

Spray pyrolysis	$CuCl_2$, thiourea, Solvents (water :Alcohol) (Water:ethanol:glycerine)			[98]
Solid- state reaction	Cu (II) montmorillonite, Na_2S	Intercalated CuS (2-9 nm)		[97]
Indirect synthesis	CdS nanoparticles, $Cd(CH_3COO)_2$, Na_2S, $(NaPO_3)_n$	CuS- 4.5 nm		[225]

In hydrothermal reaction, CuS nanoplates are synthesized using $CuCl_2.2H_2O$ and Na_2S in presence of CTAB. The optimized reaction conditions (180^0C, 20 h) were identified. CTAB, as a capping agent, adsorbed selectively on different planes of CuS seed, lowers the surface tension and stabilize the plate [91]. Tri-n-octylphosphine oxide (TOPO) capped Cu_2S nanoparticles were also reported using single source precursor $[Cu(S_2CNMeHex)_2]$ dissolved in tri-n-octylphosphine (TOP) and injected into hot TOPO at 200^0C [215]. The nano phase shows large blue shift in band gap in comparison to bulk and a broad PL band with a maximum at 477 nm. Hexagonal CuS nanoparticles with uniform spherical shape and 15 nm size were achieved using microwave irradiation in aqueous route using $Cu(ac)_2.H_2O$ and $Na_2S_2O_3.5H_2O$ [95]. Bovine serum Albumin (BSA) capped CuS nano composites with a size distribution from 10 to 35 nm in diameter using copper nitrate and thioacetamide have been reported; size of the nanocomposite depends on the BSA concentration [111]. Copper sulphides preparation has been achieved even with elemental precursors, i.e. copper and sulphur. This reaction does not proceed below 150^0C and occurs only at the surface of the copper particles [100] as the CuS layer formed acts as passivating layer and prevents the further reaction. Thus, synthesis of CuS using solid state elemental powders have been processed by using solvent [154], condition ball milling [155], or slow aging in an inert atmosphere at low temperature [156].

A large number of reports have probed the role of various factors in the synthesis of CuS nanoparticles using different routes [see Table 3 and references there in]. The nature of sulphur source has also been probed. H_2S has been the most direct ore. However, many alternate sulphur sources have been tried that decompose to H_2S, elemental sulphur or S^{2-} ions. Therefore, reactions conditions were optimized using microwave irradiation, sonicator, hydrothermal, solvothermal (pressure & temperature), γ irradiation, etc. using a number of Cu^{2+} and S^{2-} sources.

The factors controlling the morphologies of grown nano-particles have also been probed. Crystalline morphology is governed by both nucleation and growth steps. CuS (covellite phase), unit cell is not CuS as the empirical formula suggests rather, $(Cu)_3(S)(S_2)$; it has been argued that the key reaction should consist of a series of redox reactions which build up the core crystal unit of Cu^+, S^- and $(S_2)^{2-}$ [46]. Therefore, the crystallographic phase of the nuclei during nucleation process and its surface selective crystallization in the growth process should control the morphology of the product; the control of morphology also depends upon surface energy and is considered as Ostwald ripening process. In addition, choice of reactants (mild reactants) such as copper (II) nitrate and sodium thiosulphate or (all highly reactive) hydrogen sulphide [92] also play an important role. Ammonium sulphide and sodium sulphide could create different morphologies and stable phases. Further, most of the approaches do not yield to functionalize and monodispersed nanoparticles. Therefore, solvent based alternative routes have been attempted to generate CuS nanoparticles. In these solvent based chemical approaches, the precursors of Cu^{2+} and S^{2-} are dissolved in appropriate solvents to reduce the reaction temperature. Complexing agents are used to arrest the growth and to control the reaction in order to get desired size and shape of nano-material. The decomposition is carried out by a varieties of methods including temperature, solvothermal/hydrothermal, γ-irradiation, microwave assisted synthesis, and sonochemical. The critical parameters have been identified for reactions induced through various means. These are: (i) solvent used, (ii) concentration of precursors, (iii) reaction temperature, (iv) complexing agent, (v) power and time of irradiation, (vi) pH of the solution, etc. For example, in solvothermal process, different morphologies are stabilized based upon reaction solvent and temperature; by simply adjusting the

molar ratio of copper (II) chloride and sodium sulfide in solvothermal process, different phases of copper sulphides were reported with different morphologies (CuS, Cu_7S_4-CuS; Cu_9S_5; dispersed particles, hexagonal plates, octahedron) and their morphologies were also found to be Cu^{2+}/S^{2-} ratio dependent [49, 173, 223]. Similarly, in hydrothermal process [Cu(TSC)$_2$]Cl$_2$ as a precursor at 150^0C for 12 h yielded CuS nanoparticles, whereas, the thermal decomposition at 210^0C of the same precursor generated Cu_2S; by changing the ratio of Cu^{2+} and S^{2-} ions in the reaction mixture, various phases of nano Cu_xS are reported [213]. The selection of solvent proved important in deciding the morphology of CuS nano-products. In ethylene glycol, flower like shapes are generated, whereas in aqueous solvent, the tube like particles are produced [223, 225]. The role of temperature has been investigated; by increasing the temperature, hydrothermal process yielded hollow CuS spheres [104]. Complexing agent and surfactants were also found to influence the size and morphology of the Cu_xS nanomaterials. A large number of surfactant including CTAB, TEA, EDTA have been attempted to this effect [57, 91]. The role of reducing agent and the concentration of precursor material have been highlighted in simple aqueous route synthesis of CuS using copper acetate and thiourea in presence of sodium hydroxide. The particle size decreases with increasing the reaction time and agglomeration could be removed by decreasing the precursor concentration [218, 219].

Using mild reactants, Cu(ac)$_2$H$_2$O and Na$_2$S$_2$O$_3$.5H$_2$O, as the source of Cu^{2+} and $S_2O_3^{2-}$ ions, it is observed that nanocrystalline phases were of smaller dimensions in alkaline medium than those synthesized in acidic medium. However, the spherical or discoidal particles were bonded as bigger aggregates [179]. Cu_2S nano crystals with an average size of 5.4 - 0.4nm were produced using copper (II) acetyl acetonate and ammonium diethyl dithiocarbonate in a mixed solvent of dedecanethiol and oleic acid [222].

The understanding of the assembly of nano-scale building blocks into nano and micro-structures with differing morphology has been followed through oriented-attachment mechanism. Self assembly nano-flakes have generated flower like microspheres in solvothermal synthesis of CuS using single source precursor Cu(S$_2$CNEt$_2$)$_2$. The role of surfactants such as polyvinylpyrrolidone (PVP), Cetyltrimethylammonium bromide (CTAB), poly ethylene glycol (PEG) and polyvinyl alcohol (PVA) has been probed. Similarly, the role of reaction media using ethylamine, water, ethylenediamine has also been probed; selection of solvents with suitable coordinating abilities and molecular structure is found crucial in controlling morphology [105]. Cu_2S nanoplatelets and Cu_2S nanowires were prepared by solventless thermolysis of the copper thioplates precursors. Cu_2S has been synthesized by thermal decomposition of precursor [bis-(thiosemicarbazide)copper(II)]chloride ([Cu(TSC)$_2$Cl$_2$]), in presence of oleylamione (C$_{18}$H$_{37}$N) and triphenylphosphine (C$_{18}$H$_{15}$P) as surfactants, whereas CuS particles were synthesized by hydrothermal decomposition without surfactants (20-50nm) [213]. Controlled morphology hexagonal plates could be synthesized by controlling the (Cu^{2+}: S$_2$O$_3^{2-}$) mole ratio 1:2 and the reaction temperature at 155^0C for 12 hrs in hydrothermal process using Cu(NO$_3$)$_2$ and sodium thiosulphate as precursors [92]. Similar CuS plate like structure were synthesized using solvothermal and hydrothermal processes with different precursor, copper acetate and carbon disulphite with toluene and hexadecylamine as assisting agent [143] and CuCl$_2$ and sodium thiosulphate with CTAB and nitric acid as arresting agent. A number of morphologies such as rod like [213] needle like [224], wire like [214], tube like and sphere like [104] are reported. Solvothermal (with aqueous solvent) processes have been identified as the most preferred ones for controlling the morphologies as the reaction parameters such as copper:sulphur ion ratio and reaction temperature and time are the ones that control the size and morphology of final nano products synthesized at the same time provides conditions for impurity free products. By simply adjusting the molar ratio of copper (II) chloride and sodium sulphide in solvothermal process, different phases of copper sulphides (CuS, Cu_7S_4-CuS, Cu_9S_5) with varying morphologies (dispersed particles, hexagonal plates, and octahedron) have been synthesized; the morphology depends on Cu^{2+}/S^{2-} molar ratio.

Even though a large number of reports are available on the role of reaction parameters using solvothermal/hydrothermal routes on the morphology and crystal structure, a systematic study identifying the role of various parameters, viz. source species used and their concentration /molar ratio, reaction temperature, reaction time, the role of assisting agents, etc. still needs to be explored, especially, the formation mechanism of Cu_xS_y type final product could not be predicted beforehand, thus designing the experiments still being trial and error based.

4. Applications of Chalcogenide Nanoparticles

Chalcogenide nanoparticles or quantum dots have been generated over the past two decades due to their potential application from materials science to medical technology. These particles bear tunable quantum efficiency, long term photo stability, narrow emission, and continuous absorption spectra, invaluable for different photovoltaic, biomedical and other applications as reviewed recently [226]. Recent examples of their applications include solar cells (both QD sensitized and organic-inorganic hybrid), photoctalysis, photochemical applications, photo reduction of pigments and dyes, degradation of pollutants, and photo catalyst, opto-electric materials for LEDs, etc.

Among the biomedical applications, the observation of diagnosis, DNA labeling, drug delivery and cancer therapy have attracted recent attention. The new generations of QDs have far reaching potential for the study of intracellular processes at the single-molecule level, high-resolution cellular imaging, and long-term in-vivo observation of cell trafficking, tumour targeting, diagnostics and drug delivery. The potential biomedical applications are bio-sensing and bio-imaging as classified below (Fig. 3).
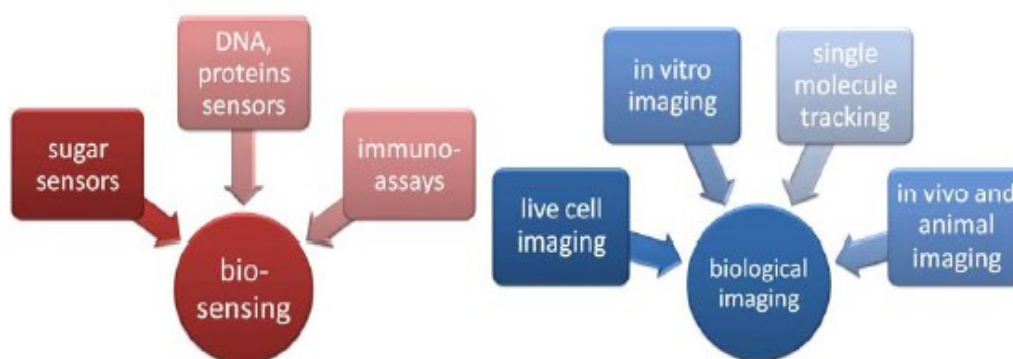

Fig. 3: Common bio-medical applications of QDs (adapted from reference [227])

Recently, the possibility of employing semiconductor nanoparticles as fluorescence labelling reagents for biological imaging experiments has been demonstrated by the attachment of CdSe/CdS [228] and CdSe/ZnS [229] core-shell nanocrystals to DNA molecules [228, 229] and proteins. Due to their unique luminescent properties, many-color probes can be simultaneously excited by a single narrow-band excitation source and distinguished in a single exposure. This makes semiconductor nanocrystals (QDs) superior to commonly used organic chromophores. QDs have been considered as the best tools for intracellular studies such as visualizing the cellular structure, studying the dynamic cellular processes, and tracking single molecules in the cell [230, 231]. However, chalcogenide bare QDs have hydrophobic surface and possess toxicity, therefore, cannot be applied in vivo without modifying their surface. By appropriate surface modification, it has been possible to increase hydrophilicity and reduce toxicity. Xie et al. [232] used bovine serum albumin (BSA) modified CdSe/ZnS QDs and demonstrated the application of chalcogenide QDs to FISH detection of the clinically relevant HER-2 locus in breast cancer cells (Fig. 4).
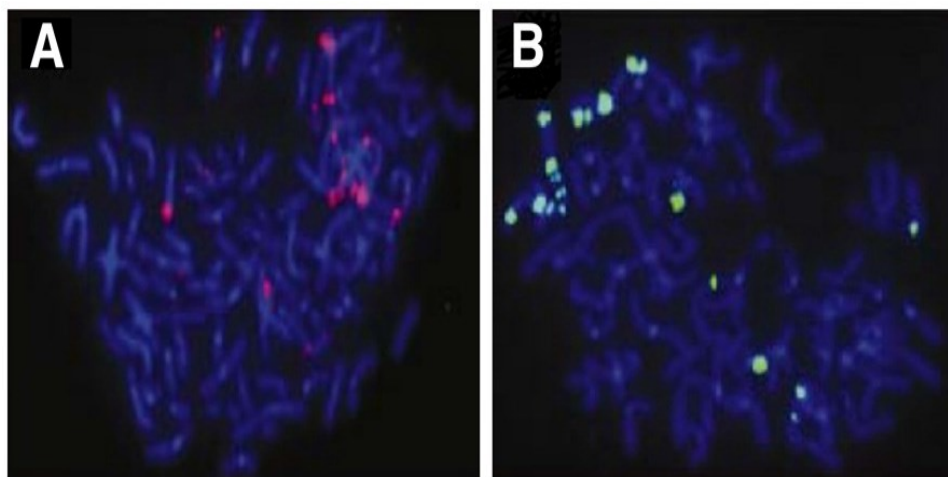
Fig. 4: Qualitative FISH detection of HER-2 gene-amplified SKBR-3 breast cancer cells: (A) streptavidin-conjugated Qdot605, and (B) FITC, respectively (after Xao and Barker [233].

However, cytotoxicity still remains the serious problem. Chen et al. [234] have studied the cytotoxicity of CdTe/CdS (core-shell) as well as CdTe/CdS/ZnS (core-shell-shell) structured aqueous synthesized QDs, and their results suggest that the cytotoxicity of CdTe QDs not only comes from the release of Cd^{2+} ions but also intracellular distribution of QDs in cells and the associated nanoscale effects [235]. Recently, clinical applications of QDs have been reviewed [233]. The application areas include: (1) biomarker detection in various cancers, (2) imaging and sensing of infectious diseases, and (3) other clinical therapeutic applications. QDs with intense and stable fluorescent properties could enable the detection of tens to hundreds of cancer biomarkers in blood assays, on cancer tissue biopsies, or as contrast agents for medical imaging.

IR-emitting nanocrystals (HgTe, lnAs/CdSe) have potential for use as optical amplifier media fibre optics in the transmission optical window 1.30 and 1.55 micron regions of the IR spectrum. One of the major limitations to the implementation of future high-capacity, ultra-broadband optical networks is the expansion of the fiber bandwidth beyond that available from the current state-of the-art signal amplification devices, particularly erbium-doped fiber amplifiers. Erbium atoms can amplify light only corresponding to the transition energies between the fixed energy levels which do not cover the whole of the 1.30 or 1.55 micron windows. The quantum confinement effect in colloidal semiconductor nanocrystals gives rise to size-dependent optical properties. Thus, for a given material, the spectral width, position, and profile of the luminescence band can be tailored to requirements by controlling the size and the size distribution of nanocrystals. The challenge is to have available IR emitting nanoparticles with high emission quantum yields. Additionally, these should be highly processable and compatible with the existing integrated optics technologies [236, 237].

Semiconductor nanoparticles having size below the Bohr Exciton size for the materials (QDs) have been viewed as the potential materials for solar cells both hybrid and sensitized one in which these are used as light harvesting molecules and/or sensitizers. Quantum dot (QD)-sensitized solar cells (QDSCs) have shown promising developments for the next generation of solar cells [238-243] as an alternate of dye sensitized solar cells (DSCs) [244].

Narrow-band-gap semiconductor QDs, such as CdS, CdSe, PbS, etc. have been used as the photosensitizer instead of organic dyes due to their versatile optical and electrical properties [245, 246]. The important being tunable band gap depending on the QD size, larger extinction coefficient, higher stability toward water and oxygen, and multiple exciton generation (MEG) with single-photon absorption [247-249]. The basic cell structure of a QDSC consists of a wide-band-gap mesoporous oxide film (TiO2 or ZnO), QDs (the sensitizer), an electrolyte, and a counter electrode. The basic operation and factors affecting the performance of QDSCs are reviewed by Tian and Gao

[250]. Accordingly, the illuminated photons are captured by QDs, yielding electron-hole pairs that are rapidly separated into electrons and holes at the interface between the nanocrystalline oxide and QDs. The electrons jump into the oxide film, and the holes are released by redox couples in the electrolyte (Fig. 5).
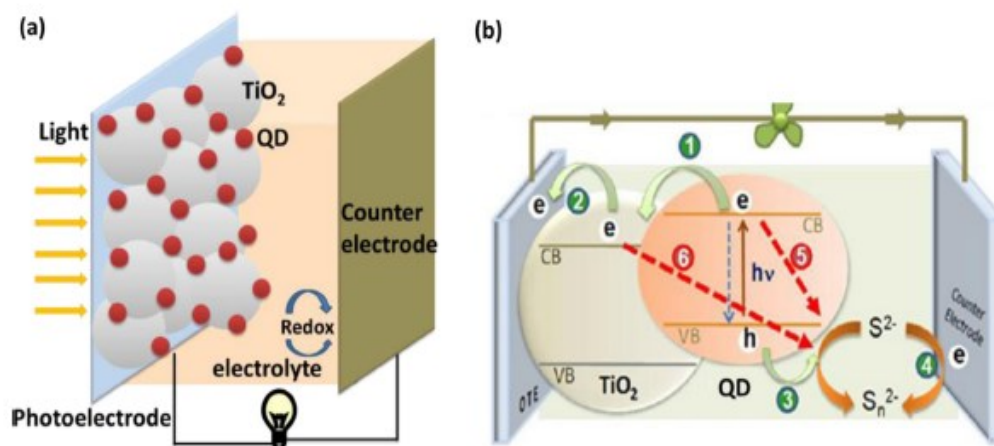

Fig. 5: (a) Schematic illustration of the structure of a quantum dot sensitized solar cell (QDSC), and **(b)** schematic illustration of photo induced charge transfer processes following a laser pulse excitation (after Kamat, ref. [243]).

The photo induced charge transfer processes have been identified employing S^{2-}/S_n^{2-} as the redox couple and are:
- Charge injection from an excited QD into TiO2,
- Transport of electrons to the collecting electrode surface,
- Hole transfer to the redox couple,
- Regeneration of the redox couple,
- Recombination of electrons from the QD and the oxidized form of the redox couple, and
- Interfacial recombination of electrons from TiO_2 and the oxidized form of the redox couple.

Therefore, the focus has to be in developing QDs with high absorption coefficient, lower threshold, high MEG effect and tunable band gap so as to approach larger wave length range for QDSCs solar cell applications.

Copper sulphides on account of their variable stoichiometric forms, complex structure and valence states such as covellite (CuS), djurleite ($Cu_{1.95}S$), digenite (Cu_9S_5), anilite (Cu_7S_4) and chalcocite (Cu_2S), have attracted wide attention. Further, due to the considerable narrow band gap of Cu_xS in nanocrystalline form (1.2-2.0 eV), these nanomateriales have been considered as visible light active semiconductors for use in the field of pollutant treatment [49]. Many examples include, the degradation rate of methylene blue was 82.9% by using CuS microspheres under the visible light for 20 minutes; CuS nanotubes showed very high catalytic activity for the oxidation and decomposition of the methylene blue with H_2O_2. They also exhibit high photocatalytic activity for reactive orange. The degradation of Rhodamine B (Rh B) using the nanocrystalline mixed product ($CuS-Cu_7S_4$) was recently reported as 99.7% under visible light illumination. Cu_xS_y has far more biological applications compared to cadmium based II-IV semiconductors as they contain a less toxic metal [49]. Capping has been used extensively to prepare stabilized mono-dispersed nanoparticles [111]. In the thiol-capped nanoparticles, capping molecules are amphiphile molecules containing a thiol group strongly coordinated to the QDs surface and a polar (-OH,-COOH, -NH2). Alanine – capped water soluble CuS nanoparticles arereported using copper acetate and thioacetamide in water/methanol solvent [110]. Cu_xS has been very attractive for biological application among the chalcogenides semiconductor nanomaterials. In comparison to cadmium based II-VI semiconductors, copper based nanomaterials are preferred as they contain less toxic metals [110].

5. Recent advances in Chalcogenide Synthesis: New Single Source Molecular Precursors

As discussed above, a variety of fabrication routes have been investigated to control the size and shape of CdS and CdSe, CuS quantum dots. The synthesis of CdS/CdSe quantum dots has been standardized, and focus is now on synthesis routes that use low temperatures, better yield, and non-toxic precursors and gives better control to size and shape so as to tune the size-dependent electronic and optical properties. The use of single source precursors for the synthesis of metal chalcogenide nanoparticles has proven to be efficient route for the synthesis of high quality nanocrystals, also avoiding the need for volatile, sometimes toxic or pyrophoric precursors. Further, ligand properties of the metal complexes used as precursor in single source molecular precursor route could be used in the modification of the size and shape of the nanoparticles [15-17].

In the following sectionof the review, we summarize our recent efforts in and present facile synthetic routes for the production of CdSe, CdTe and ZnSe QDs at a relatively lower temperature through solvothermal decomposition using new single source molecular precursors. The synthesis procedure employs low cost and non-toxic materials and avoids the use of inert atmosphere. Recently, we reported the preparation of CdSe, CdTe and HgTe using the novel single source molecular precursor Cd(ii) complex of bis-(aminoethyl) selenide. Quinoline is used as a co-coordinating solvent; this single source molecular precursor based solvothermal approach employed has many advantages compared with the already reported similar approaches using toxic precursors or strict control of inert environment. The use of quinoline as a solvent has however not resulted into capping which need to be tackled using other solvents.

5.1. CdTe Synthesis: Among the II-VI semiconducting nanomaterials, CdS and CdSe are widely synthesized, because of their high crystallites' size dependent features of photoluminescence and absorption [5] and great deal of work has been done to characterize CdS and CdSe nanocrystals. Reports on CdTe nanomaterials are very few. This is because tellurium anions susceptibility to aerial oxidation, and that it also requires higher temperature for the reduction of elemental tellurium during the synthesis of organotelluride ligands [251, 252]. Nanostructures such as nanorods and nanowires are reported to have better materials properties for solar cell applications in comparison to classical semiconductors [253]; nanoparticles network charge can be transferred through the optimal arrangement of nanorods or nanowires without losses because of recombination at the nanoparticle boundaries in contrast to bulk semiconductor. Further, the energy band gaps of nanostructured materials are sensitive to their size of nanoparticles; hence, nanorods with varying diameter are more useful for solar cell application than nanoparticles and fixed diameter nanorods [254]. CdTe nanorods are a better alternative for CdS because of smaller band gap (Eg ≈ 1.45 eV) which it is easily adjusted to the solar spectrum [137].

In contrast to versatile method of synthesis of CdTe quantum dots [122, 137, 255-259], growth of one dimensional nanorods and nanowires is discussed rather limited in literature. Peng et al. [6] have reported the synthesis of CdSe nanorods [260] and branched nanorods [122, 137] using binary mixture of the surfactant hexylphosphonic acid and trioctylphosphonic oxide. Many reports present data in which the lengths of CdSe nanorods are controlled [137, 128, 261-263]. Guo et al. [264] prepared array of CdTe nanowires by dc electrochemical deposition using porous aluminium oxide as a template. Growth of CdTe nanorods has also been demonstrated using catalytic driven pulsed laser deposition (PLD) technique, in which selective area epitaxy on sapphire substrate and a catalytically driven vapor liquid solid growth have been found critical for the growth of 1D nanomaterials [265]. Li et al. [266] reported water soluble CdTe nanorods prepared with the assistance of mixed ligand system of cysteine and thioglycolic acid; the aspect ratio and photoluminescence controlled by the refluxing time. Multi armed CdTe nanorods were prepared by Nie et al. [267] using myristic acid as complexing agent. Wang et al. [268] prepared CdTe nanorods with diameter of 150 nm and 1 μm length using thermal chemistry method. An attractive route for the preparation of nanostructures has been the decomposition of single source of molecular precursor, using non-aqueous high boiling co-coordinating solvent such as trioctylphosphine and its oxides [269, 270]. The use of single source molecular precursor (SSMP) having metal chalcogen bond is very efficient route for generation of metal chalcogenide nanomaterials.

Recently, our group has reported the synthesis of CdTe nanorods using solvothermal route from two different single source molecular precursors and their subsequent characterization by XRD and SEM [271]. Initially, the single source molecular precursor Cadmium complex of bis-(aminopropyl) telluride has been prepared as per the scheme shown below (Fig. 6):
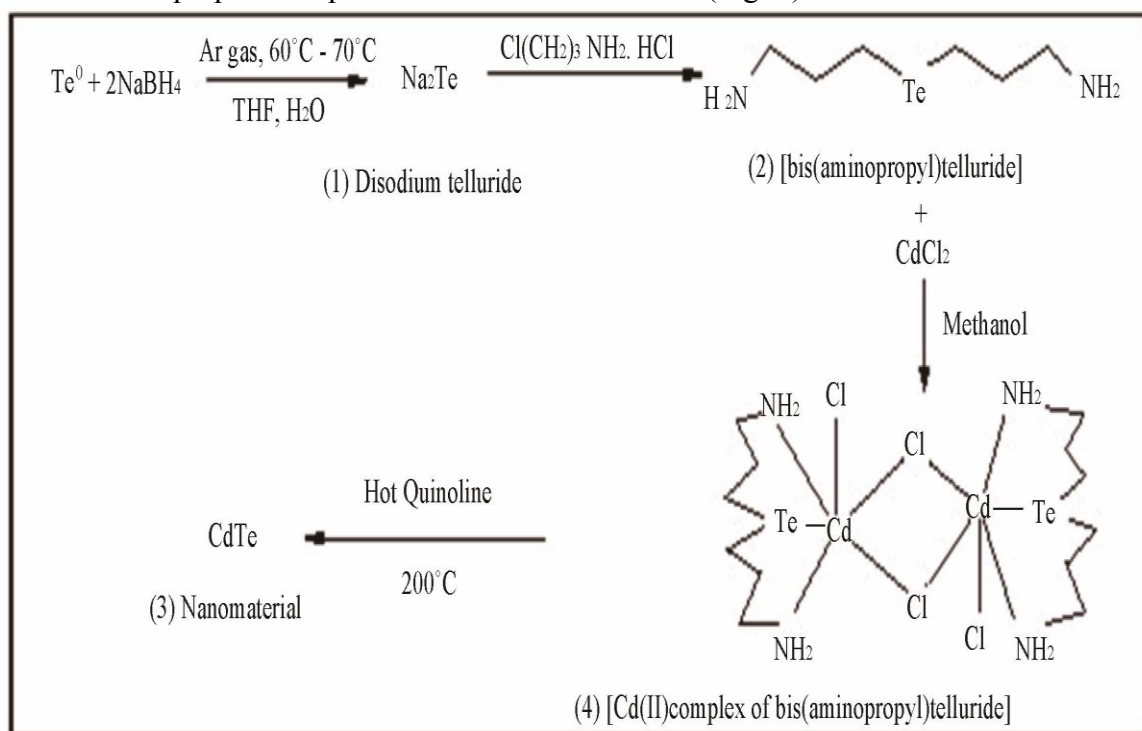

Fig. 6: Scheme for the synthesis of Cd(II)bis-(aminopropyl) telluride (Tiwari et al. ref. [271]).

Cd (II) complex of bis-(isopropyl telluro) propane is prepared and decomposed to obtain CdTe nanoparticles. Briefly, bis-(isopropyl)di-telluride is first synthesized by the reduction of tellurium powder, synthesis of SSMP pale yellow Cd (II) complex of bis-(isopropyltelluro)propaneis followed by reacting the compound with cadmium chloride in acetonitrile; finally pyrolysis of precursor molecule in hot quinoline at 205°C generated grey colored CdTe nanoparticles (Fig. 7).
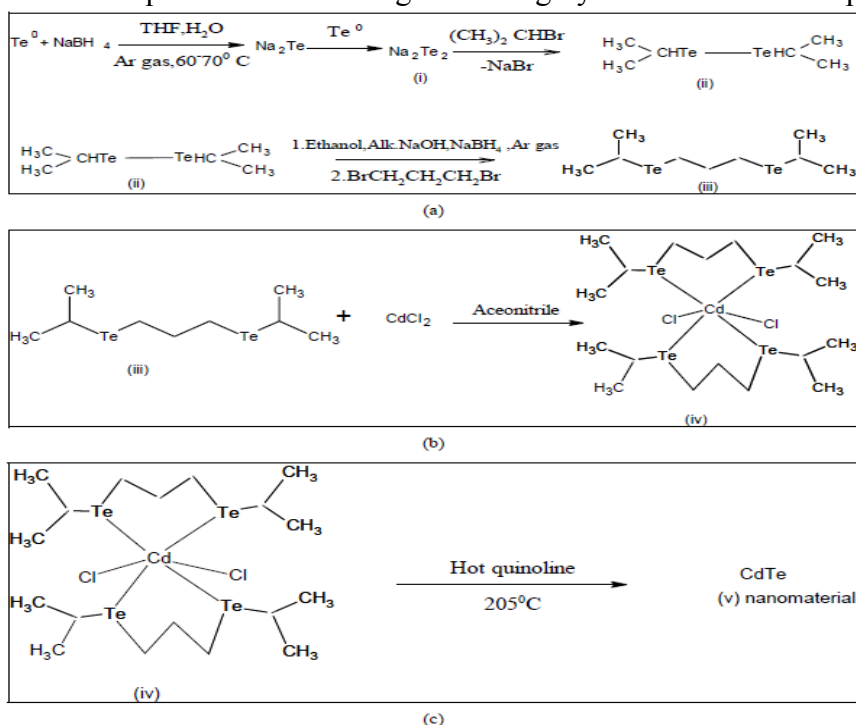
Fig. 7: Scheme for (a) Synthesis of bis-(isopropyl)di-telluride, (b) synthesis of SSMP Cd (II) complex of bis-(isopropyltelluro)propane, and (c) Synthesis of CdTe (Tiwari et al., ref. [271]).

X-ray diffraction revealed face centred cubic nanocrystalline phase of CdTe (Fig. 8). Debye Scherer equation is used to estimate the average particle size; nanoparticles of average size of 29 nm are obtained from both SSMPs.
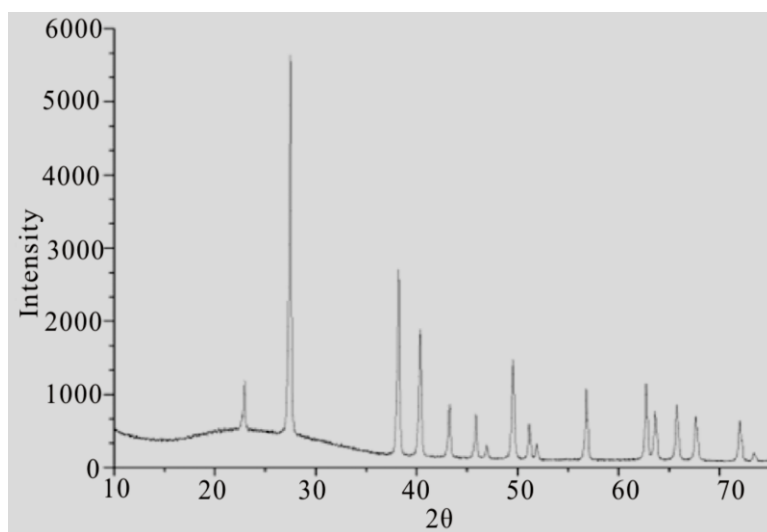
(a)
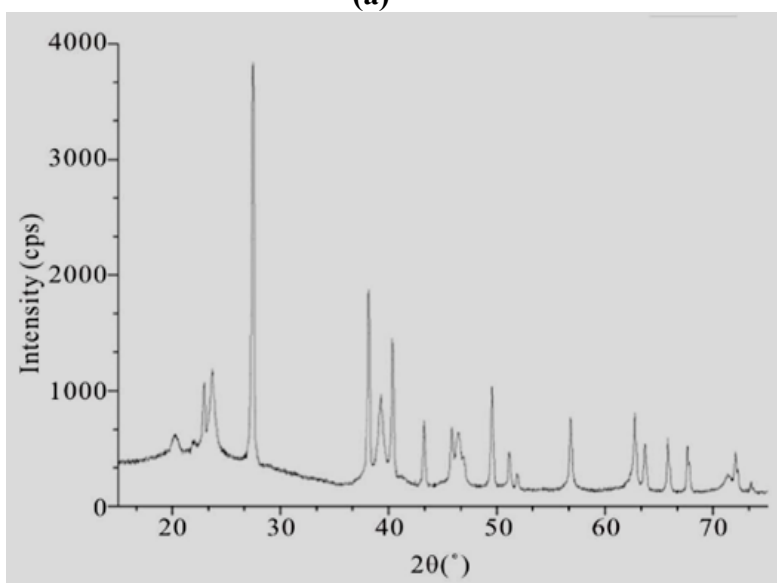
(b)

Fig. 8: X-ray diffraction pattern of CdTe nanoparticles synthesized from SSMP: **(a)** Cadmium (II) complex of bis-(aminopropyl)telluride, and **(b)** Cd (II) complex of bis-isopropyltelluro propane (Tiwari et al., ref. [271]).

SEM micrographs exhibited micro size rods homogeneously distributed with diameters ranging from 1.125-1.350 mm and average length more than 5 mm (Fig. 9). This is due to self- assembly of nanoparticles due to agglomeration.
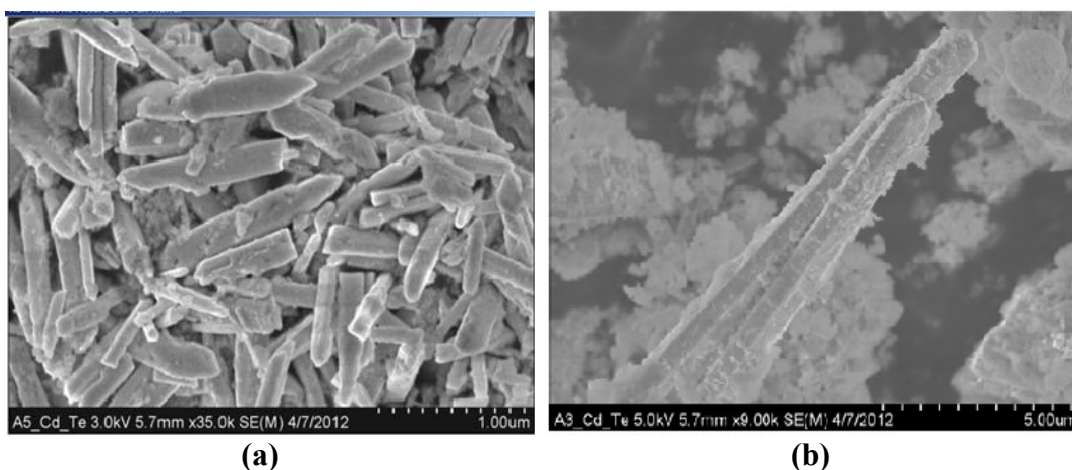
Fig. 9: SEM micrographs of CdTe nanorods from: **(a)** Cadmium (II) complex of bis-(isopropyltelluro) propane, and **(b)** Cadmium (II) complex of bis-(isopropyl)telluride (Tiwari et al., ref. [271]).

5.2. Synthesis of HgTe Tubes: Synthesis of HgTe nanorods has been successfully carried out using solvothermal decomposition of single source molecular precursor [272]. Essentially, mercury telluride nano material was prepared by solvothermolysis of known single source molecular precursor, which was prepared by slight modification of reported method [25], quinoline was used as a capping agent. Bis-(isopropyltelluro) propane was prepared, with the reaction of bis-(isopropyl)di-telluride and 1,3 di-bromopropane in ethanol solvent. It was generated by reduction of elemental tellurium with alk.NaBH$_4$ under argon atmosphere followed by formation of di-sodium di-telluride and in situ addition of isopropyl bromide. The nanoparticles are finally generated as per the scheme shown below (Fig.10):
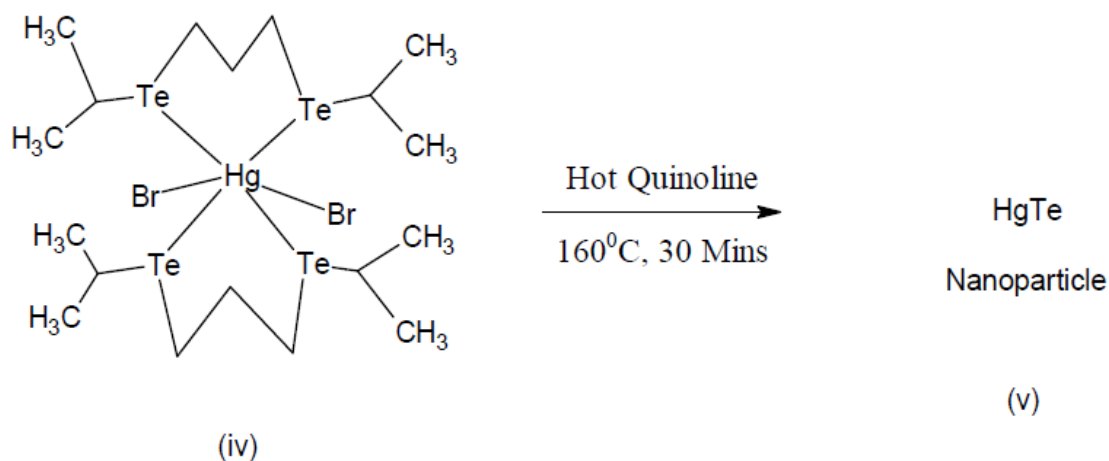
Fig. 10: Scheme for the synthesis of HgTe nanorods from SSMP

Hexagonal primitive structured HgTe nanoparticles are confirmed by XRD (Fig.11 (b)). SEM micrographs revealed rod shaped nanoparticles composed of nano-crystallites stacking along the rod growth direction. This was further confirmed by TEM micrographs as shown in Fig. 11(a). For TEM studies the sample powder was suspended in methanol using ultrasonification and small drop of it was put on the porous copper grid and allowed to dry. Average diameter of rod shaped nanoparticles was found 179 nm [272].
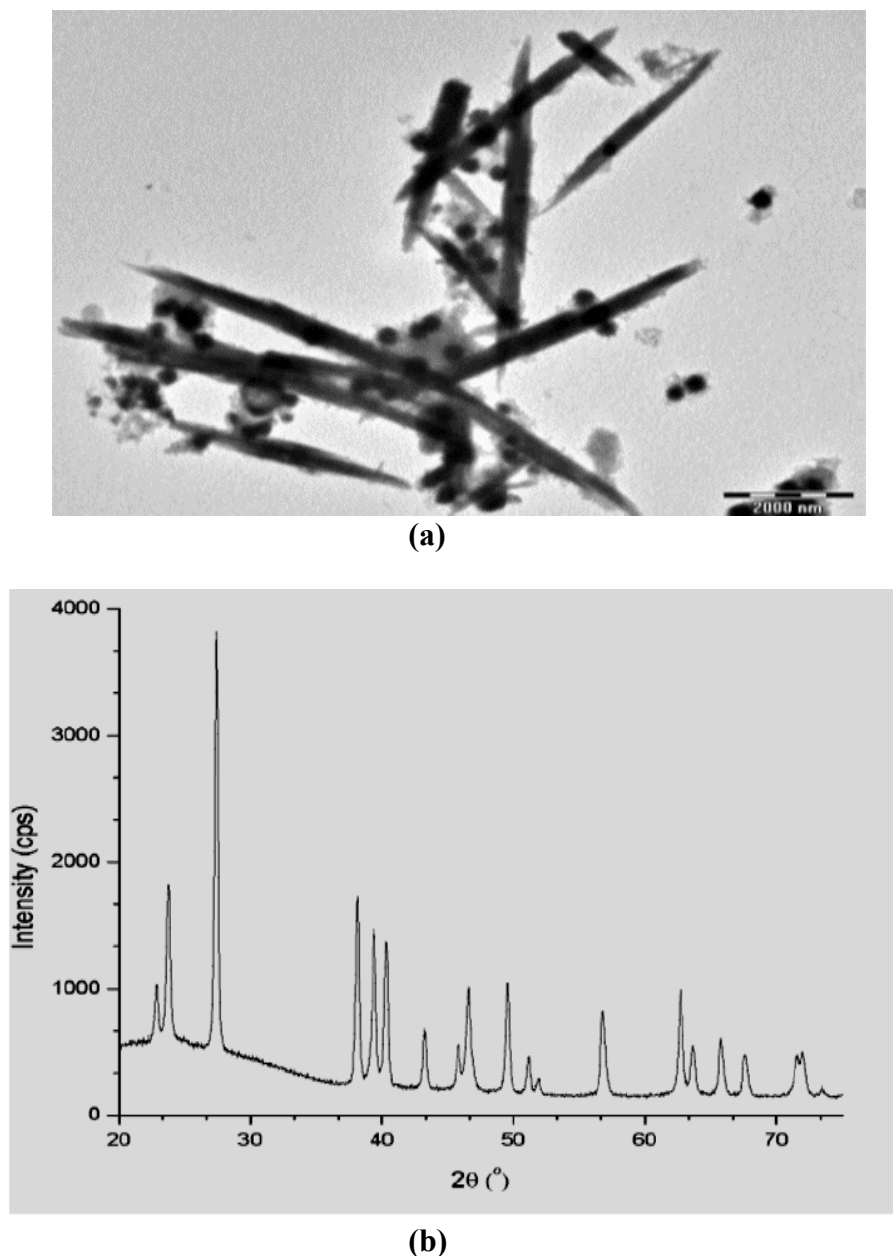
(a)

(b)

Fig. 11: (a) Transmission Electron Micrograph, and **(b)** XRD pattern of of self assembled HgTe nanorods (179 nm) (Tiwari et al., ref. [272]).

5.3. Synthesis of CdSe Nanoparticles: Almost spherical semiconducting CdSe nanoparticle were conveniently synthesized by solvothermal decomposition of novel single source molecular precursor Cd (II) complex of bis(aminoethyl)selenide in quinoline at 200^0C. The process is low cost and uses non-toxic materials and avoids the use of inert atmosphere. Quinoline is used as a co-coordinating solvent. Solvothermal approach employed in this work has many advantages compared with the already reported similar approaches using toxic precursors or strict control of inert environment.

The scheme for the synthesis of CdSe quantum dots incorporates $CdCl_2$ in a coordinate mixture consisting of single source molecular precursor bis-(aminoethane)selenide. Quinoline was used as the capping agent as well as the solvent system for the growth of CdSe nanocrystals, which also facilitates the focusing of the particle size, resulting in a much smaller size distribution. These, in combination with fine control of the stoichiometry among reactants, led us to successfully prepare CdSe quantum dots of size $\approx$7nm [273]. The synthesis scheme is as described below in Fig. 12.
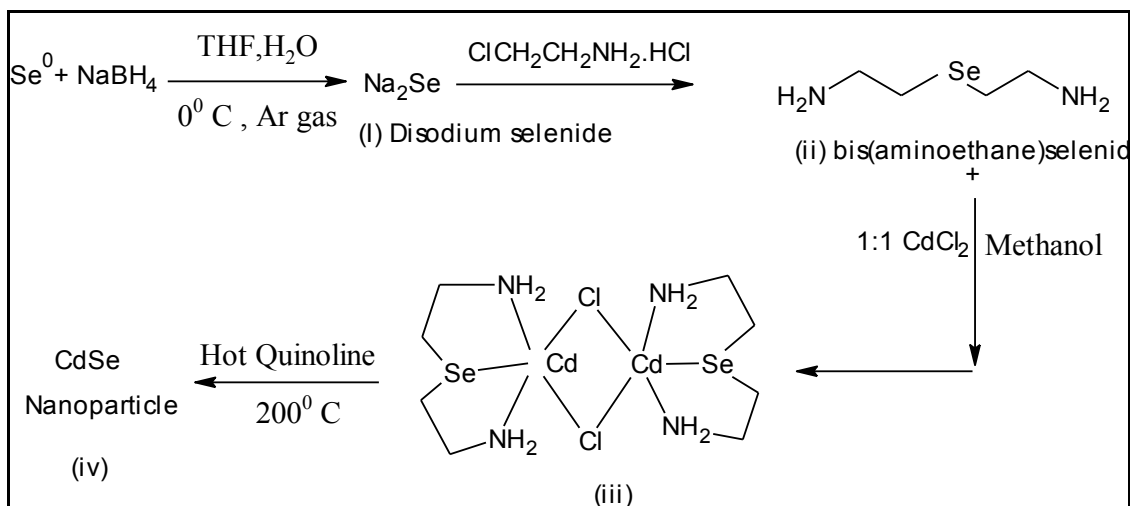
Fig. 12: Scheme for synthesis of CdSe nanoparticles synthesized by solvothermal decomposition of SSMP: Cd(II) bis-(aminoethane)selenide (Tiwari et al., ref. [273])

XRD confirms the nearly phase pure powder with hexagonal crystalline structure as shown in Fig. 13(a), EDAX analysis shows nearly stoichiometric composition and TEM micrograph shows somewhat agglomerated nanoparticles with spherical shapes (Fig. 13(b)). The inexpensive, non-toxic and relatively low temperature route may be an attractive way to synthesize metal chalcogenides [273].
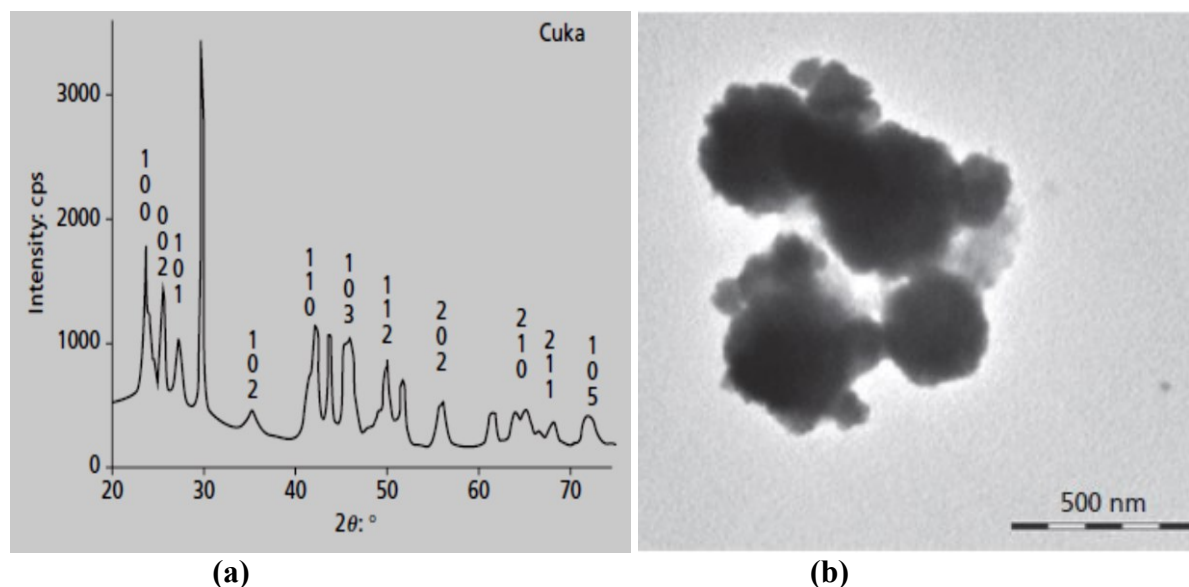
Fig. 13: (a) XRD pattern of 7 nm CdSe nanoparticles, and **(b)** TEM micrograph of agglomerated CdSe nanospheres (Tiwari et al., ref. [273])

Optical absorption spectra is used to calculate the energy band gap (Fig. 14) and the Urbach energy for the as synthesized nanopowders, resulting in $E_g = 3.94$ eV; Urbach energy = 1.33 eV.
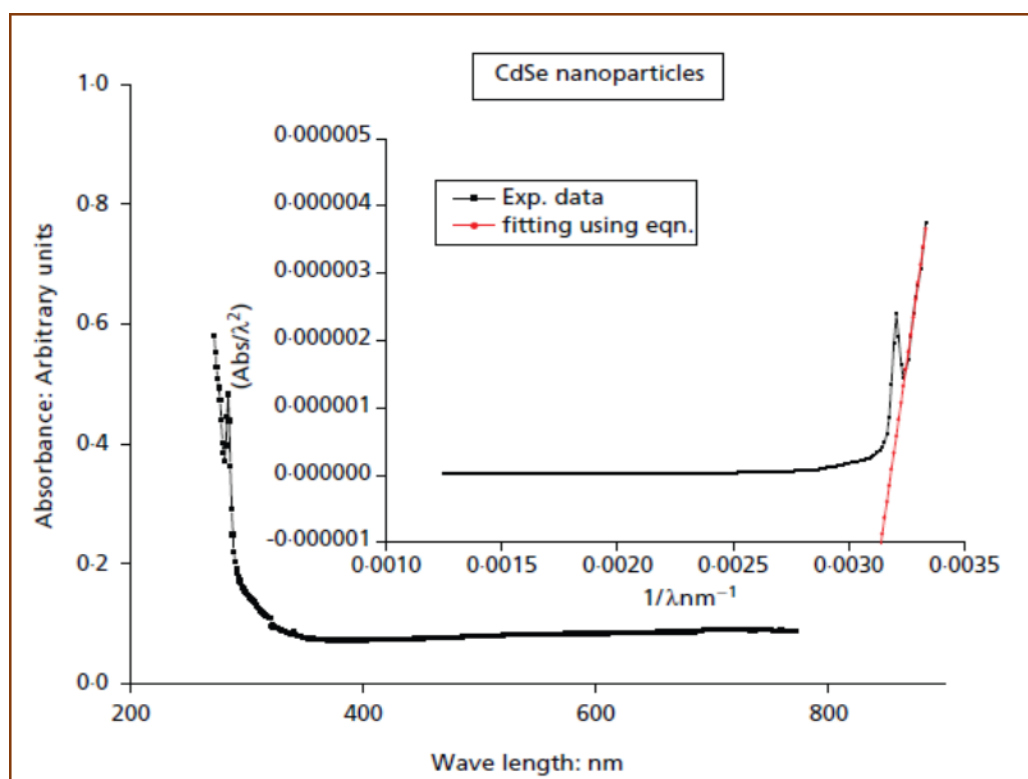
Fig. 14: Optical absorption spectrum of CdSe nanoparticles; inset shows the Tauc plot for calculating energy band gap (Tiwari et al., ref. [273]).

In order to understand the role of single source molecular precursors (SSMPs) on the properties of prepared nanoparticles, we synthesized CdTe, CdSe and ZnSe nanoparticles using new SSMPs.

6. Preparation of CdSe, CdTe and ZnSe: New SSMPs

Recently, we have further explored new single source molecular precursor (SSMP) for the preparation of chalcogenides nanoparticles. CdSe nanoparticles are successfully prepared by solvent less pyrolytic route using Cd(II) complex of Bis(aminopropyl) selenide, CdTe nanoparticles were synthesized using Cd(II) complex of Bis(aminoethyl) telluride and ZnSe by Zn(II) complex of Bis(aminoethyl) selenide. Basic features of synthesis and some characterization of synthesized nanoparticles are presented here. The details will be presented elsewhere [274].

6.1. Synthesis of CdSe Nanoparticles: In the synthesis scheme, we changed the carbon chain length in the precursor and used aminopropyl derivatives instead of ethyl derivative used earlier. In first part of synthesis, Bis(aminopropyl)selenide is obtained as per the scheme given below (Fig. 15(a)):


(a)
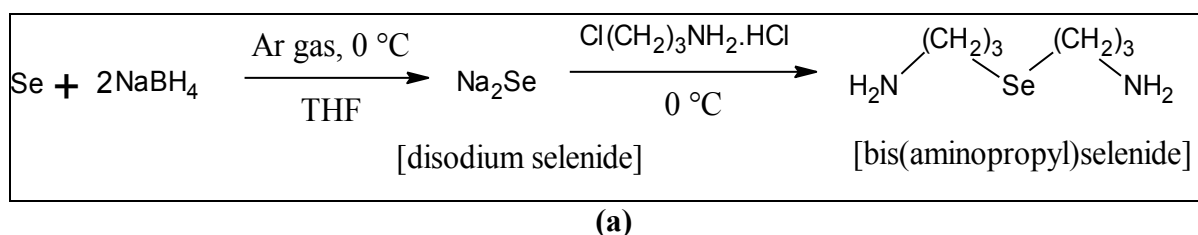
Synthesis of single source molecular precursor - [Cd (II) bis-(aminopropyl)selenide] is achieved by reacting cadmium chloride with bis-(aminopropyl) selenide in presence of methanol as shown below (Fig. 15(b)):
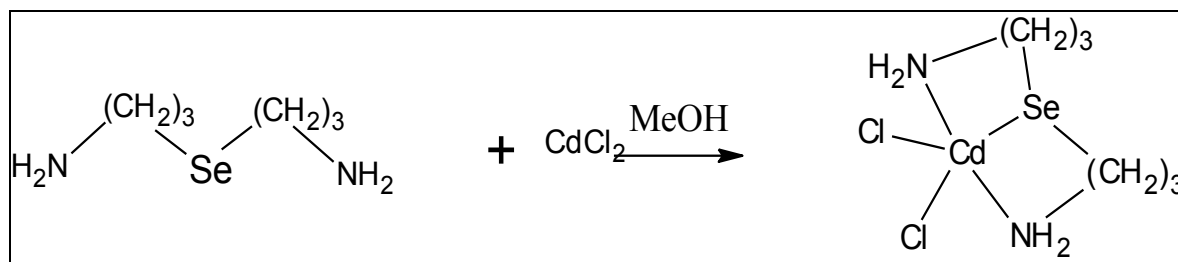
(b)

The vacuum dried powder of the SSMP precursor is injected into hot quinoline to achieve CdSe nanopowders via solvothermal decomposition as shown below (Fig. 15(c)):
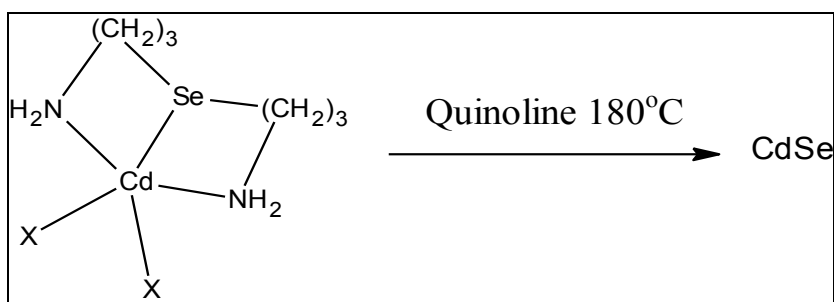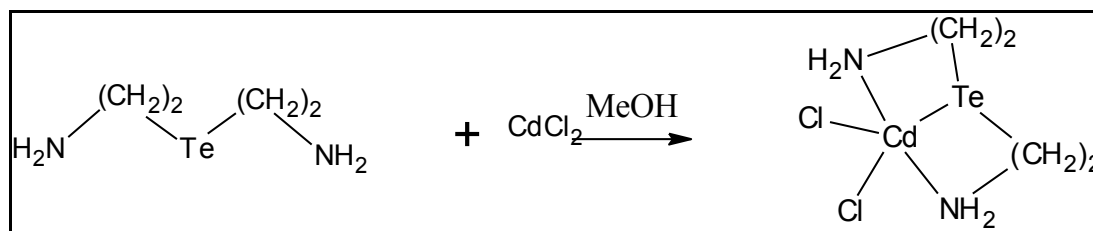

(c)

Fig. 15: Scheme for synthesis of CdSe nanoparticles using SSMP: **(a)** synthesis of bis-(aminopropyl)selenide, **(b)** SSMP Cd(II) bis-(aminopropyl)selenide, and **(c)** CdSe (Tiwari et al., ref. [274]).

6.2. Synthesis of CdTe Nanoparticles: CdTe nanoparticles are synthesized by first synthesizing bis-(aminoethyl)telluride by reducing the Tellurium powder using sodium borohydrates in presence of THF under the contuous flow of Ar gas at $60\text{-}70^0$C. Disodium telluride is then converted into bis(aminoethyl)telluride as shown in the scheme below in Fig. 16(a):
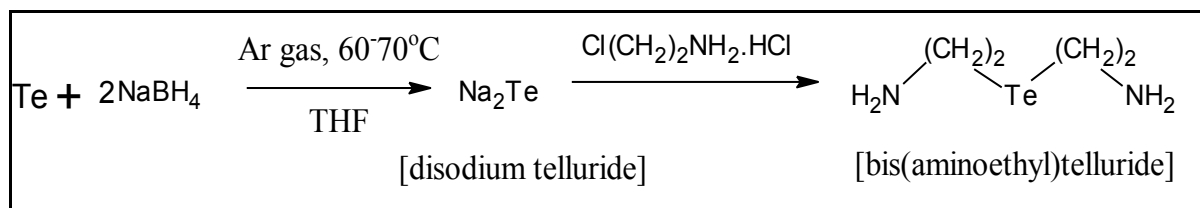
(a)

The compound is then reacted with cadmium chloride in methanol resulting into SSMP [Cd(II) complex of Bis(aminoethyl)telluride)] as shown below in Fig. 16 (b).

(b)

The SSMP is then injected into hot quinoline solution under the constant flow of Ar gas, the solvothermal decomposition of SSMP resulted into greyish powder of CdTe nanoparticles.
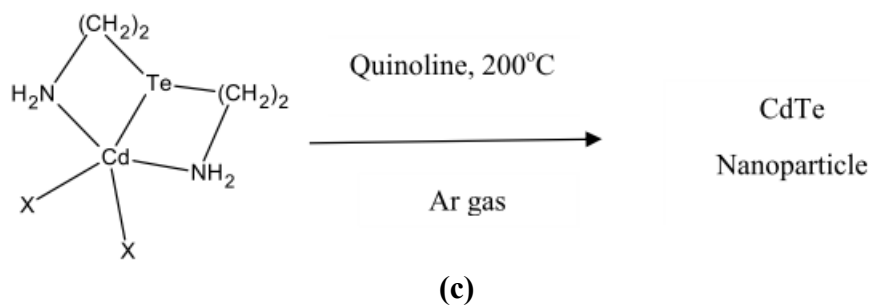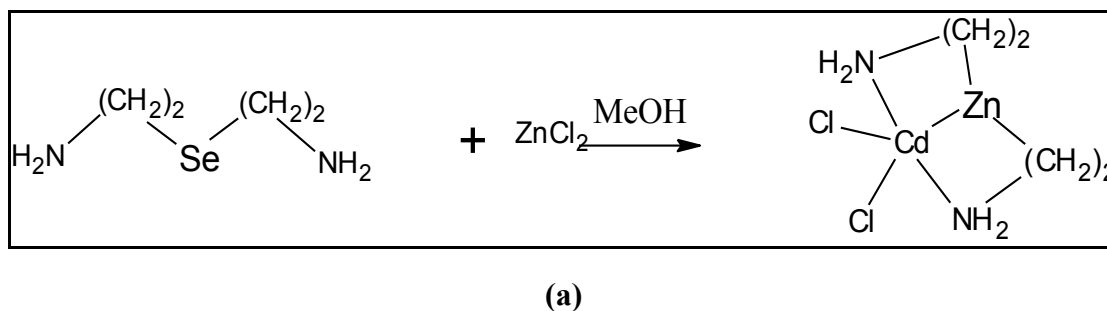
(c)

Fig. 16: Scheme for synthesis of CdTe nanoparticles using SSMP: **(a)** synthesis of bis-(aminoethyl)telluride, **(b)** SSMP Cd(II) bis-(aminoethyl)telluride, and **(c)** CdTe (Tiwari et al., ref. [274]).

6.3. Synthesis of ZnSe: To synthesize ZnSe nanoparticles, bis-(aminoethyl) selenide is prepared as described earlier. The compound is then reacted with zinc chloride in methanol resulting into single source molecular precursor [Zn(II) complex of Bis(aminoethyl)selenide as shown below in the scheme (Fig. 17(a)):

(a)

The SSMP is then injected into hot quinoline solution (180^0C) under the constant flow of Argon gas, the solvothermal decomposition of SSMP resulted into greyish powder of ZnSe nanoparticles as shown below in Fig. 17(b).
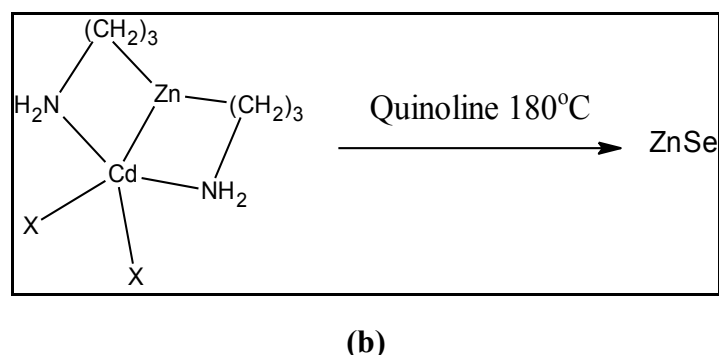

(b)

Fig. 17: Scheme for synthesis of ZnSe nanoparticles using SSMP: **(a)** SSMP Cd(II) bis-(aminoethyl)telluride, and **(b)** ZnSe (Tiwari et al., ref. [274]).

7. Characterization of Nanoparticles

7.1. Structural characterization: The as-prepared and vacuum-dried powders of CdSe, CdTe and ZnSe, synthesized by the solvothermal decomposition of single-source molecular precursors, injected in quinoline as a coordinating solvent as described above, have been subjected to structural characterization. Room temperature XRD patterns of these nanopowders are shown in Fig. 18. The observed pattern of CdSe nanoparticles matches closely with that reported in JCPDS file No.08-0459, whereas that of CdTe matches closely with JCPDS File No.39 -8053 and of ZnSe with File No. 37-1463.
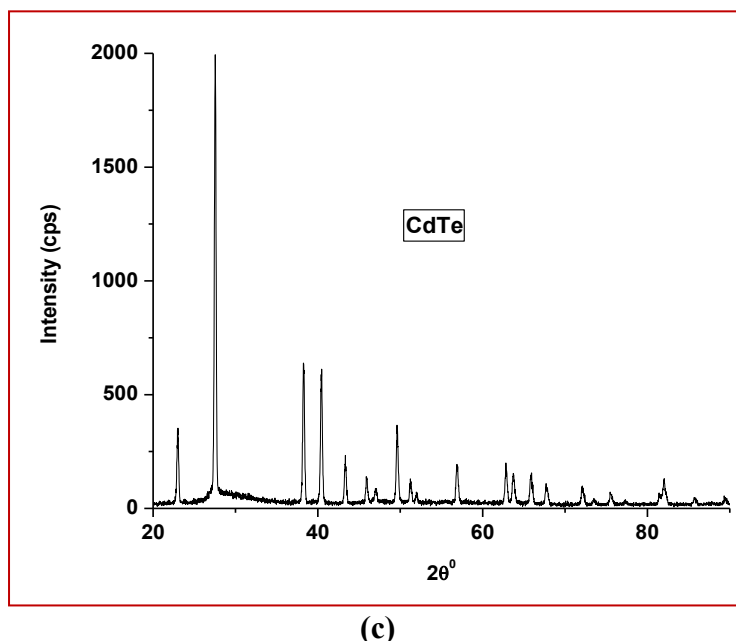
(a)

(b)

(c)
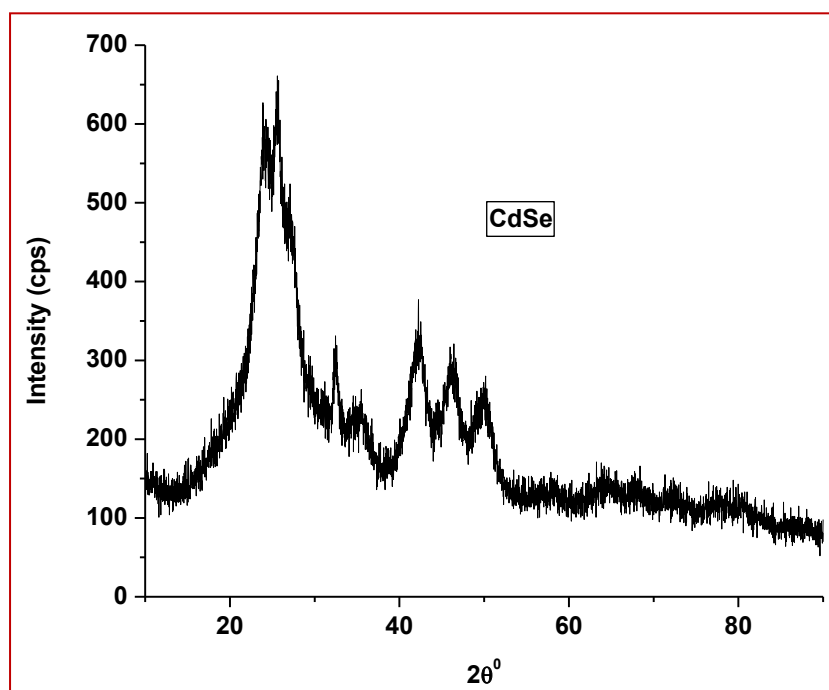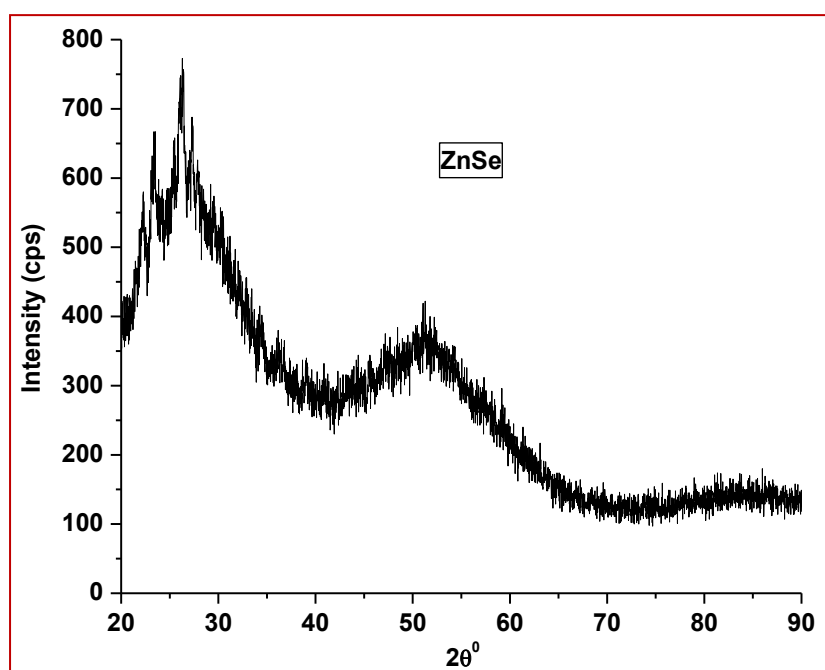
Fig. 18: X-ray diffraction pattern of **(a)** CdSe, **(b)** ZnSe, and **(c)** CdTe nanoparticles synthesized by solvothermal decomposition of single source molecular precursors.

The average size of the crystallite is calculated from line width data of the XRD peaks using Debye Scherer equation. The average sizes of crystallites using the FWHM of observed major peaks were estimated for CdSe ≈2 nm, CdTe ≈27nm, and ZnSe ≈ 5nm, respectively.

7.2. Optical Characterization: UV–Vis absorption spectra were obtained with a Shimadzu Asia Pacific Ltd. (Singapore) UV-1800 spectrophotometer. UV–Vis absorption spectra of CdSe, CdTe and ZnSe nanoparticles are shown in Fig. 19. The absorption spectra of the CdSe nanoparticles were considered without taking into account the reflection losses. The Tauc equation relates the absorption coefficient $\alpha(v)$ due to inter-band transitions near the band edge to the incident photon energy by

$$\alpha(v)hv = B (hv - E_g)^n \tag{1}$$

Where $\alpha(v)$ is the absorption coefficient, B is constant and hv is incident photon energy; n is the index that takes different values for different types of semiconductors and $n = 2$ for direct-bandgap semiconductors.
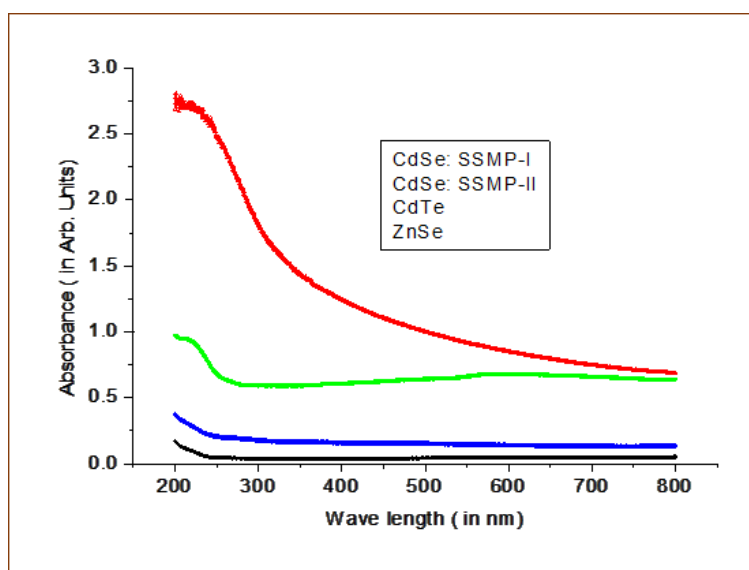

Fig. 19: Electronic absorption spectra of chalcogenide nanoparticles synthesized from SSMPs. CdSe(red) from SSMP-I: Cd(II) bis(aminoethyl)selenide; CdSe(green) from SSMP-II: Cd(II) bis(aminopropyl)selenide; CdTe(blue) from Cd(II) bis(aminoethyl)telluride; and ZnSe(black) from Zn(II) bis(aminoethyl)selenide.

Plotting $[\alpha(\nu)/\lambda]^2$ vs. $1/\lambda$, we obtained the value of λ_g; band gap energy values are calculated as $E_g=1239.83/\lambda_g$, as shown in a typical plot for CdTe nanoparticles giving energy band gap of 3.78 eV (Fig. 20). Similar plots give energy band gap for CdSe from SSMP-I = 4.0 eV, from SSMP-II = 4.05 eV; and for ZnSe = 3.95 eV, respectively. The bulk values for chalcogenides are shown in table 4 along with the values obtained for various chalcogenide nanoparticles prepared by our group. The large blue shift clearly indicates the quantum confinement effect and ultra small nanoparticles generated.
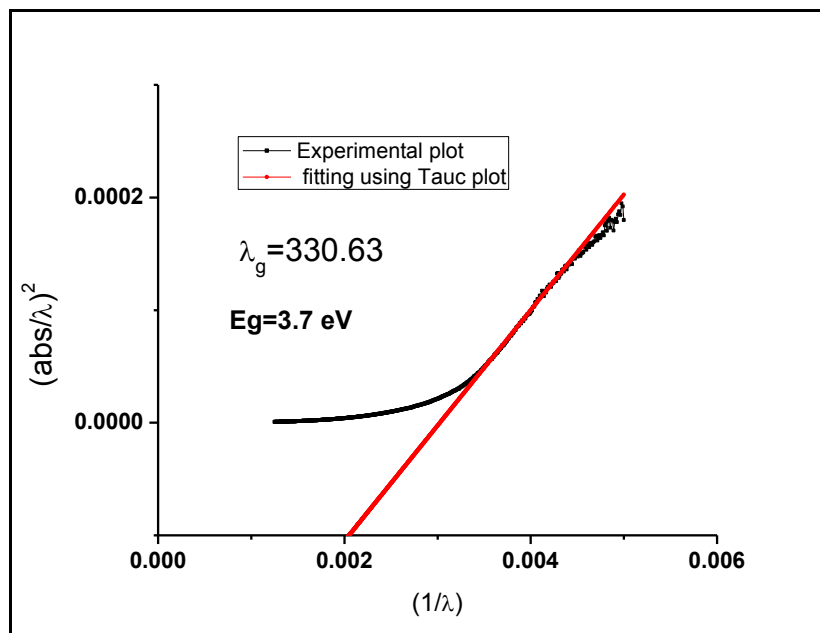
Fig. 20: (Absorbance/λ)^2 vs. $1/\lambda$ plot for CdTe nanoparticles with estimated band gap energy using Tauc equation [274].

Table. 4: Optical characteristics of some chalcogenide based semiconductor materials in bulk and nanoform at room temperature.

Semiconductor	Optical band-gap energy, eV (Bulk)	Approximate threshold wavelength, nm	Optical band-gap Energy, eV (Nanoparticles)
ZnS	3.2	388	3.50 [234]
ZnSe	2.58	481	3.95 [274]
CdS	2.42	512	-
CdSe	1.70	729	3.95[273] 4.00[274] 4.05 [274]
CdTe	1.50	827	3.78 [274]
PbS	0.50	2480	-
HgS	0.50	2480	-
HgTe	0.14	8857	

7.3. Raman Spectral Characterization: Room temperature micro Raman spectra of synthesized nanopowders were scanned using micro Raman (STR-500 Micro-Raman Spectrometer) set up at room temperature using laser 532nm (50mW) diode laser. The spectral resolution was 1 cm^{-1}. The typical Raman spectrum of CdSe nanoparticles is shown in Fig. 21.

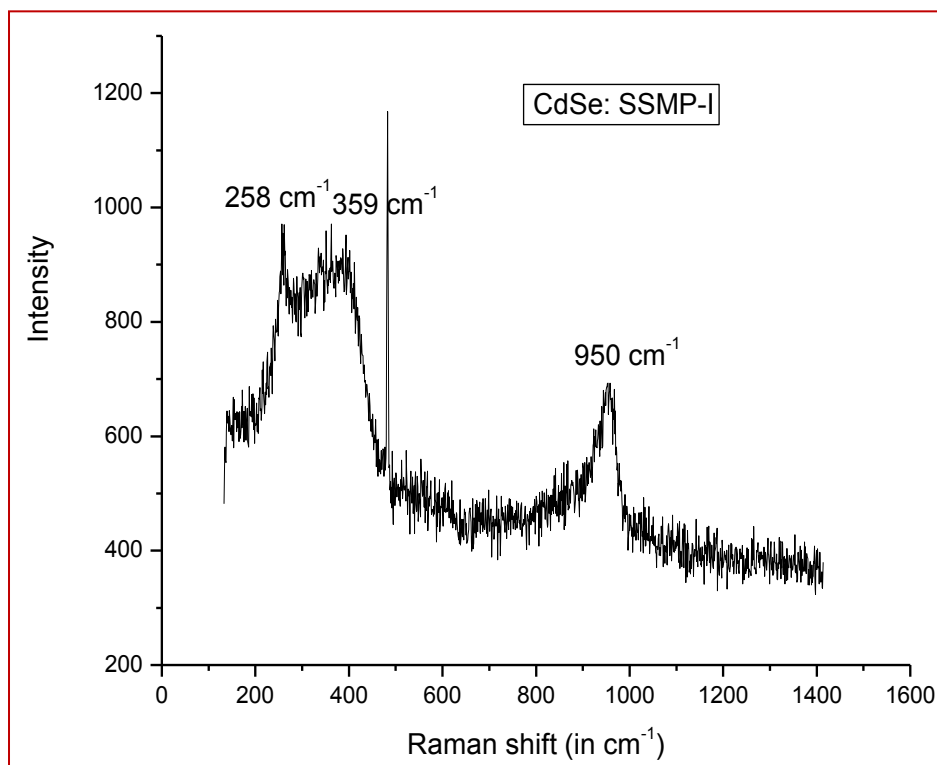**Fig. 21:** Room temperature Raman spectra of CdSe nanoparticles

Other nanoparticles show similar spectra. The bands observed in different nanoparticles are summarized in Table 5 along with tentative assignments of modes.

Table. 5: Observed Raman modes and their assignments in chalcogenide nanoparticles synthesized from SSMPs.

S.No./Raman modes → ↓	CdSe In cm^{-1}	ZnSe In cm^{-1}	CdTe In cm^{-1}	Assignments
01	258	143	206	LO
02	359	240	411	2LO
03	950	457	476	LO+TO

In the spectra of CdSe, three modes at 258, 359 and 950 cm^{-1} are clearly observed. In general, the LO and TO phonons are observed along with the surface modes in polar nanocrystals in resonance Raman spectra and/or surface enhanced Raman spectra [275]. However, LO and TO modes are observed simultaneously only in randomly oriented nanoparticles. Resonance Raman Spectra (RRS) of CdTe nanoparticles give band due to Longitudinal optical (LO) phonons at 170 cm^{-1} (LO), 340 cm^{-1} (2LO) and 510 cm^{-1}(3LO); mode frequency is found to shift due to quantum confinement effect and confined phonons are observed using surface enhanced Raman spectroscopy [275]. Transverse optic (TO) phonon is reported at 145 cm^{-1} and its position is invariant with decreasing particle size as the dispersion curve for TO phonon branch is almost flat [275]. In CdSe nanoparticles, LO phonons are reported in the range 180- 200 cm^{-1}, wheras in ZnSe at 140 cm^{-1} [Ref. 275 and references therein]. Thus, the Raman spectra observed in the present work well identifies the phonons in these nanoparticles.

8. Conclusions

Chalcogenide nanoparticles both dispersed in water and functionalized through various biologically significant molecules still remain the focus of research for their wide spread applications. Various synthetic approaches used for the generation of these technologically significant nanomaterials are

reviewed with a view to get present status of controlling their sizes and shapes. Further, considering the environmental concerns, new single molecular precursors developed for the preparation of chalcogenide nanoparticles are presented and their important properties are critically presented.

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