SYNTHESIS OF ORGANICALLY CAPPED AND WATER SOLUBLE METAL

SULFIDE SEMICONDUCTOR NANOPARTICLES

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ABSTRACT

Well-defined faceted shaped organically and water soluble metal sulfide nanoparticles have been successfully synthesized using a hybrid solution based high temperature colloidal route in the presence of organic surfactants as both stabilizers and crystal growth modifiers. The structure and morphology of the as-prepared metal sulfide nanoparticles were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), UV-Vis and photoluminescence spectrophotometry. By varying important parameters such as the metal precursors, reaction temperature, reaction time and organic surfactants, various nanomaterials with a range of morphologies and sizes were obtained.

The morphologies of the organically soluble PbS nanoparticles was influenced by the variation in lead sources and organic surfactant. By varying the lead source HDA capped particles with morphologies ranging from close to spheres, elongated particles and perfect cubes were formed. When the capping group was changed to TOPO, predominantly rod shaped particles were obtained. The growth mechanism for the anisotropic HDA capped PbS is mostly likely due an oriented attachment mechanism. The formation of the rod shaped TOPO capped PbS is due to the impurities in TOPO. The X-ray diffraction and high resolution electron microscopy studies show that the particles are crystalline.

HDA-capped CdS nanoparticles with spherical, triangular and rod-like shape were successively synthesized. The as-prepared CdS nanoparticles have good crystallinity and a good surface chemical environment with a narrow size distribution. The experimental results show that the morphologies of CdS nanoparticles were significantly influenced by the reaction temperature and different cadmium sources. The crystallinity of the particles was determined by X-ray diffraction which shows the phase of the particles to be predominantly hexagonal. The high resolution transmission electron microscopy images also confirm the crystalline nature of the particles with distinct lattice fringes observed. The optical absorption of the as-prepared nanoparticles is obvious blue shifted in relation to the bulk band-gap of CdS which is due to the quantum-confinement effect of CdS nanoparticles.

The TEM analyses reveal interesting changes in the morphology of the ZnS nanoparticles formed from the various zinc sources. The shapes of the ZnS nanoparticles were rod-like for all the zinc sources used except for the $ZnSO_4$ in which close to spherical shape particles was obtained. The XRD patterns exhibited the cubic zinc blende structure of ZnS for the samples analysed and no other crystalline phase was detected. Optical absorption and photoluminescence spectra of the as-prepared nanoparticles were strongly blue-shifted due to quantum confinement effect

A synthetic procedure has been developed for the fabrication of highly luminescent colloidal CdS/ZnSe and CdSe/CdS core-shell nanoparticles without the purification of the core materials. The X-ray diffraction patterns confirm cubic structure for both core and core-shell semiconductor nanoparticles. The observed red shift in the absorption and photoluminescence spectra of the core-shell nanoparticles compared to the core materials is a strong indication for the formation of core-shell nanoparticles. From the PL spectra, the intensities of the emission maximum are considerably increased in the core-shell nanoparticles as compared to the core materials.

Cysteine capped metal sulfides nanoparticles were successfully synthesized by aqueous medium through a simple colloidal route. X-ray diffraction measurement confirms the structure, single cubic phase for the sample. TEM studies of cysteine capped metal sulfides nanoparticles show that particles form crystalline aggregates. From optical absorption measurements it is found that the band gaps show some dependency of the pH values used in preparing the nanoparticles.

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CERTIFICATION BY SUPERVISOR

This is to certify that this work was carried out by Mrs. A.O. Nejo in the Department of Chemistry, University of Zululand and is approved for submission in fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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DEDICATED

To my children, Oluwakayode, Oluwatomisin and Oluwatoyosi:

To my husband, who is both my leader and mentor

LIST OF PUBLICATIONS

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LIST OF ABBREVIATIONS

Å	Angstrom
a.u.	Arbitrary unit
Eg	Band gap
k	Boltzman constant
са	Calculated
CVD	Chemical vapour deposition
СВ	Conduction band
r*	Critical size
DNA	Deoxyribonucleic acid
DA	Decylamine
0-D	Zero dimensional
1-D	One dimensional
d	Diameter
DDA	Dodecylamine
DT	Dodecanethiol
	Dielectric coefficient
Е	Energy
E _{Ry}	Rydberg energy
ETA	Extremely thin absorber
e	Electron charge
eV	Electron volt
FRET	Fluorescence resonance energy transfer
	Frequency

Vo	Frequency of lattice vibration in the cluster
FWHM	Full width at half maximum
G	Free energy
G _D	Free energy barrier
	Free energy per unit area
R	Gas constant
GSH	Glutathione
HDA	Hexadecylamine
НМТА	Hexamethlenetetramine
НОМО	Highest occupied molecular orbital
HPA	Hexylphosphonic acid
HRTEM	High resolution transmission electron microscopy
h	Hole
	Pie
LED	Light-emitting diode
LUMO	Lowest unoccupied molecular orbital
m	Mass
m _e *	Electron effective mass
m _h	Hole effective mass
mRNA	Messenger ribonucleic acid
V _m	Molar volume
nm	Nanometer
S	Number of atoms surrounding the cluster
h	Plank's constant
N*	Probable number of critical sized cluster

r	Radius
N_{T}	Total of atoms in the system
OA	Oriented aggegration
OLED	Organic light-emitting diode
PL	Photoluminescence
SL	Solid-liquid interfacial energy
S	Solubility
So	Solubility of the flat surface
kT	Thermal energy
Т	Temperature
TEM	Transmission electron microscopy
ТОР	Tri-n-octylphosphine
ТОРО	Tri-n-octylphophine oxide
TOPSe	Tri-n-octylphosphine selenide
TDPA	Tetradecylphosphonic acid
UV-Vis	Ultraviolet visible
	Frequency
VB	Valence band
	Wavelength
XRD	X-ray diffraction

CHAPTER ONE

Introduction and literature review

1.0 Introduction

Nanotechnologies are the design, characterisation, production and application of structures, devices and systems by controlling shape and size at nanometre scale. It is one of the interdisciplinary technologies which promises to have implications for health, wealth and peace in future decades [1-4]. It is also regarded as the meeting ground of the engineering, biology, physics, medicine and chemistry fields [5].

Knowledge in this new field of science is growing worldwide, leading to fundamental scientific advances. This will lead to dramatic changes in the way materials, devices, and systems are understood and created. Among the expected breakthroughs are an order of magnitude increase in computer efficiency, human organ restoration using engineered tissue, designer materials created from directed assembly of atoms and molecules and the emergence of entirely new phenomena in chemistry and physics [6, 7].

Nanoparticles are particles that are composed of up to tens of thousands of atoms whose size is confined to less than 100 nm. Nanoparticles are of great scientific interest as they effectively are the bridge between bulk materials and atomic or molecular structures. These particles can be single crystallites, aggregates of crystallites, or non-crystalline, with varying morphologies. The properties of these materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. These novel properties include amongst other: nonlinear optical behaviour, enhanced optical properties, increased mechanical strength, enhanced diffusivity, high specific heat, magnetic behaviour and electric resistivity [8].

1.2 Electronic properties of nanoparticles

Semiconductor nanocrystals are a special class of materials whose crystals are composed of periodic groups of II-VI, III-V, or IV-VI materials. One of the defining features of a semiconductor is the energy gap separating the conduction and the valence energy bands. The color of light emitted by the semiconductor material is determined by the width of the gap. For a semiconductor crystal, electronic excitation consists of the loosely bound electron hole pair (Mott-Wannier exciton) usually delocalized over a length much longer than the lattice constant. For the exciton to occur, hv > energy gap [9]. Pumping energy into a semiconductor can excite an electron, e[°], into the conduction band (Figure 1.1), leaving behind a hole, h, in the normally filled valence band, and thus an electron-hole pair is created. The electron and hole each relax to the respective band edge states by non-radiative processes. During the band edge transition a photon is emitted as the excited electron spontaneously recombines with the hole. The band-edge is explained as the direct recombination of charge carriers from atomic-like orbitals. Charge carriers in bulk semiconductor recombine from deep and shallow traps giving emission at different wavelengths from the band edge [10, 11].

In the case of nanoscale semiconductor particles with smaller sizes (<10 nm), its electronic properties start to change as the diameter of the crystalline material approaches the exciton Bohr diameter. The charge carriers are confined in all three dimensions in a quantum dot and thus the exciton has zero degrees of freedom for its motion, with the result that the electron exhibits a discrete atomic like-spectrum. As a result of these geometrical constraints an electron 'feels' the particle boundaries and responds by adjusting their particle sizes. This phenomenon is known as the quantum size effect [9-11].

Nanocrystalline materials which conserve the wave function are called direct band gap materials while indirect band gap materials are those where the lowest electronic transition between valence band and conduction band is forbidden and they have very small absorption coefficients. Typically, bulk samples of CdS will absorb all electromagnetic radiation with an energy greater than the band gap (hv > 2.42 eV); irrespective of their size, once greater than 20 nm and it is classified as a direct band gap material. However, as particles become smaller, their electronic structure starts to change and eventually continuous bands break down and there are discrete bonding and antibonding orbitals in this material. The electronic properties of such small particles are more like those of the molecule than an extended solid. Figure 1.1 shows a spatial electronic state diagram showing the quantum confinement effect. As the cluster properties are intermediate between molecules and bulk semiconductors, the quantum size effect can be best explained with hybrid molecular and semiconductor nomenclature [10].

As mentioned above, in a bulk semiconductor, the electron and hole are bound together by a screened Coulomb interaction to form a so-called Mott-Wannier exciton [12]. This electronhole interaction has to be induced for a more qualitative treatment of the quantum confinement effects. By assuming the energy band to be parabolic near the band gap (i.e., the effective mass approximation), the size-dependent shift (with respect to the bulk band gap) in the exciton energy of a small cluster (cluster radius ~ exciton radius) can be derived as

$$E(R) = Eg + h^{2} {}^{2}/{2\mu R^{2}} - 1.786e^{2}/R - 0.248E^{*}_{Ry}$$
(1.1)

where *R* is cluster radius, $l/m = l/me^* + l/m_h^*$, m_e^* is the electron effective mass, m_h^* is the hole effective mass, is the dielectric constant, and E_{Ry}^* is the effective Rydberg energy,

 $e4/{}^{2}h^{2}(1/m_{e}^{*} + 1/m_{h}^{*})$. The first term in the above equation is the band gap of the bulk materials, the second represents the particle-in-a-box quantum localization energy and has a simple $1/R^{2}$ dependence, the third term the Coulomb energy with l/R dependence, and the last term is the result of the spatial correlation effect. This last size-independent term is usually small but can become significant for semiconductors with small dielectric constant. Therefore, the cluster radius can be easily determined according to the above formula based on the absorption spectra [10].

The quantum size effect can be clearly explained by a simple quantum size box model in which the electron is restricted in all three dimensions by impermeable walls. For a spherical quantum dot with radius R, this model predicts that a size independent contribution to the energy gap is simply proportional to $1/R^2$, which implies that the gap increases as the quantum dot size decreases. Moreover, quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic-like energy levels [10]. The discrete structure of energy state leads to a discrete absorption spectrum of quantum dots, which is in contrast to the absorption spectrum of a bulk semiconductor.

1.3 Luminescence Properties

Fluorescence spectroscopy is a key tool to examine the nanoparticle's size and quality. Nanoparticles that fluoresce with a narrow line width and small Stokes shift are dominated by what is referred to as near band gap emission and characterized by a generally continuous surface with most surface atoms exhibiting the coordinated and oxidation state of their bulk counterparts. In contrast, nanoparticles that emit broadly with a larger Stokes shift are considered to exhibit deep trap emission [9]. Deep trap emission is characterized as emission from the recombination of trapped electrons and holes with broad energy distributions. For example, the sulfur deficiency in CdS is due to the $S^{2-}(V_s^+)$ defects. The V_s^+ is a deep trap and can exothermically extract an electron from the valence band and a hole is left behind by an electron, which localizes away from the V_s^+ site. It is virtually impossible for V_s^+ site to pull out another electron from the valence band. The V_s^+ vacancy sets a deep (ca 0.007 eV) trap for a photo-generated electron in the conduction band, which combines forming the V_s^+ state. The photo-generated electron is quickly trapped by the V_s^+ , forming a V_s^0 site, which could then either be quenched by some surface species or recombine with the nearest pre-existing hole [9].



Figure 1.1 The spatial electronic state diagram showing the quantum confinement effect in (a) bulk semiconductors and (b) nanoparticles [9].

The role of surface in determining the luminescence quantum yields of semiconductors is fundamental and has long been recognized and ascribed to the higher concentration of defects at the surface e.g. unsaturated bonds, ion vacancies, disorder due to adsorbed impurities, or uncommon oxidation states, which gives rise to high density mid-gap states acting as electron and hole states. The surface properties are expected to have large influence on the optical properties of the semiconductor nanocrystals because of the high surface to volume ratio. When a nanoparticle size is reduced such that the particle is essentially on the surface, the curvature of the surface is so high that virtually all the surface atoms have slightly different coordination or effective oxidation state [13-16]. The theoretical and experimental studies of very small metal chalcogenides are examples of such nanoparticle systems that are dominated by surface interactions. These small nanoparticles emit light that is characteristic of deep trap luminescence, unless they are coated with a wider band gap material which confines the carriers to the materials core.

The high emission from band edge states in semiconductor nanoparticles would be required if one wants to study their electronic structure or more practically if they are to be used as emitters in any application. The band edge emission from nanoparticles has to compete with both rediative and non-radiative decay channels, originating from surface electronic states. Surface coating of the nanoparticles with suitable organic molecules could minimize this problem [17]. The choice of passivating agent could improve the size-dependent band edge state luminescene efficiency, while promoting the solubility and the processibility of the nanoparticles. Passivation of the nanoparticles with organic molecules accomplishes this role and is widely used but can sometimes have a drawback of incomplete or irreversible passivation. This passivation can expose some of the regions of the surface to degradation effects such as

photo oxidation. In some cases, chemical degradation of the ligand molecule itself or its exchange with other ligands might lead to unstable surfaces and therefore unstable nanoparticles.

1.4 Mechanism of growth of nanocrystals

In order to achieve a high-level control over the shape of semiconductor nanocrystals prepared in a solution phase, a fundamental understanding of nucleation and growth mechanisms is a pre-requisite. In the classical models, nanocrystals have been considered to grow by atomic addition [18-20].

1.4.1 Nucleation

Nucleation is the first stage in the mechanism of growth of nanocrystals. The model for nucleation begins by determining a free energy of formation for a given cluster size. The free energy for formation is a function of temperature and cluster size and is given by equation 1.2.

$$G = 4/3 r^3 g + 4 r^2$$
(1.2)

Where r is the radius of a spherical cluster, g is the free energy difference between the solid and liquid per unit volume at atmospheric pressure and is the change in free energy per unit area at the interface. This model for free energy has been improved upon by taking into consideration other free energy terms, which better approximate the free energy required for a certain size cluster. When free energy is plotted as a function of particle size, a maximum occurs that corresponds to a critical cluster size and a free energy barrier for critical cluster formation (Figure 1.2). This critical cluster size can be determined by solving d G/dr = 0 for r* [21], which is given by equation 1.3.

$$r^* = -2 / g$$
 (1.3)

The corresponding free energy barrier for the critical cluster formation can be determined by solving equation 1 for $G(r^*)$ to obtain equation 1.4

$$G^* = 16 r^3/3 ^2$$
(1.4)

The shape of the free energy curve as a function of the particle size shows that once a particle reaches r*, growth into a larger particle becomes the favourable path to lower free energy, but if the cluster does not reach r*, the cluster will decay back into monomers and no growth will occur [21]. The number of particles that will reach the critical cluster size can be approximated by using the Boltzman factor shown in equation 1.5,

$$N^* = N_{\rm T} e^{[-G^*/kT]}$$
(1.5)

Where N^* is the probable number of critical sized clusters, N_T is the total number of atoms in the system and k is the Boltzman constant. The nucleation rate can be determined by assuming the addition of one atom will change a cluster to the critical cluster size. The frequency at which this occurs can be determined from equation 1.6,

$$\mathbf{v} = \mathbf{s}\mathbf{v}_{0}\mathbf{e}^{\left[-\begin{array}{c}G\\D\end{array}\right]} \mathbf{k}^{\left[KT\right]}$$
(1.6)

where s is the number of atoms surrounding the cluster, G_D is the free energy barrier associated with diffusion to the cluster and v_o corresponds to the frequency of lattice vibration in the cluster. The rate of formation for clusters capable of growth also known as the nucleation rate (J), is given in equation 1.7.

$$J = N_{T} sv_{o}e^{[-(G + G)/kT]}$$
(1.7)



Figure 1.2 Schematic diagram of the nucleation and growth process showing the five steps and the dependence of the Gibbs free energy (G) on the crystal size. The first step consists of the reaction of suitable monomers (step I), which results in the desirable compound. The interaction (step II) of this compound resulted in a cluster or monomer growth process. Then the cluster grows to a critical size (step III) and the process becomes irreversible. The crystal size can then be controlled with the aid of stabilizers (step IV & V) [21].

1.4.2 Growth

Once nucleation is completed and the critical cluster size is reached, particles will begin to grow from dissolved species. Continuous growth may occur by a combination of coarsening or aggregation. Growth by either of these two routes causes a decrease in surface energy, making an increase in particle size energetically favourable. Coarsening (Ostwald ripening) involves the growth of larger particles at the expense of smaller particles by way of diffusion of molecular scale species through the growth medium. The driving force of this process is the fact that the solubility of the particle (S) is related to its size [21], which can be described by the Ostwald– Freundlich equation:

$$S = So \exp \left(4 \frac{1}{SL} V_m / RTd\right)$$
(1.8)

where S_o is the solubility of the flat surface, $_{SL}$ is the solid–liquid interfacial energy, V_m is the molar volume of the solid phase, R is the gas constant, d is the particle diameter and T is the absolute temperature. In this process, the formation of tiny crystalline nuclei in a supersaturated medium occurs first and then is followed by crystal growth, in which the larger particles will grow at the cost of the small ones due to the energy difference between large particles and the smaller particles of a higher as shown in Figure 1.3. According to this mechanism, the particles tend toward an isotropic growth, generating particles with almost spherical shapes.

Penn and Banfield identified an important alternative crystal growth mechanism in nanoparticles in colloidal dispersions. They called this new mechanism "oriented attachment (OA)" or "oriented aggregation" [22-24]. This mechanism is based on the spontaneous selforganization of adjacent nanocrystals, resulting in growth by the coalescence of solid particles that share a common crystallographic orientation. Nanocrystal growth via the OA mechanism generally leads to the formation of anisotropic nanocrystals and particles of irregular shapes [22-26], as well as nanocrystals with defects. One of the characteristics of the oriented attachment mechanism not found in the Ostwald ripening mechanism is the presence of a solid-solid interface between the nanocrystals, indicating that the growth process begins only after contact is established between particles, as schematically illustrated in Figure 1.3. The number of materials obtained by the OA process is growing rapidly [25, 27-29] and has become an attractive form of processing nanomaterials with anisotropic structures. Basically, we can define two main possible ways to bring about the self-organization or mutual orientation of adjacent nanocrystals. One is the effective collision of particles with mutual orientation, while the second is coalescence induced by particle rotation (see Figure 1.3).

a) Ostwald ripening



b-1) Oriented Attachment - Collision of particles with Mutual orientation



Figure 1.3 Schematic representation of nanocrystal growth controlled by a) Ostwald ripening and b) oriented aggregation [21].

The first situation must occur in the dispersed colloidal state, in which the number of collisions among particles is high. In the second situation, particle rotation must be dominant in a weakly flocculated colloidal state in which the interaction between particles is significant, although the nanoparticles still have rotational freedom [30, 31]. The driving force for this spontaneous oriented attachment is that the elimination of the pairs of high energy surfaces will lead to a substantial reduction in the surface free energy from the thermodynamic viewpoint. Oriented attachment-like growth has been observed in the formation of CdS, ZnS and CuS nanorods [32]. Cho, *et al.* [33] have reported anisotropic PbSe nanocrystals in several shapes formed through

oriented attachment mechanism. The synthesis of SnO_2 nanowires from nanoparticles has been investigated by Lee, *et al.* [31]. Several other papers have also discussed the role of oriented attachment in the anisotropic growth of various nanocrystals [33-39].

1.5 Methods for the Preparation of Semiconductor Nanoparticles

There are two approaches to nanoparticles production that are commonly referred to as 'top-down' and 'bottom-up' methods. In top-down approach involves the creation of nanomaterials from the size reduction of bulk materials. This type of fabrication uses lithographic patterning techniques. Examples of the top-down approach include high-energy milling, mechano-chemical processing, laser ablation, inert-gas evaporation, sputtering and vapour condensation techniques. Bottom-up approaches nanomaterials are built from molecular components (atoms, molecules) which assemble themselves chemically by principles of molecular recognition. Commonly techniques used conventional salt are crystallization/precipitate methods, precursor decomposition routes. interfacial polycondensation, sol-gel methods, chemical vapour deposition (CVD), template-assisted methods, electrochemical methods and hydrothermal routes.

The control of the size, shape, and ease of manipulation of nanoparticles synthesized by chemical routes has rendered this route of synthesis the preferred method of choice in potential applications. Traditional chemical vapor deposition and molecular beam epitaxy methods have limitations as they produce particles that are attached to a substrate or embedded in a matrix, thereby limiting their potential in applications. The synthetic method employed should lead to samples of high purity, narrow size distribution and that can be surface derivatized. In this thesis the colloidal and hot injection precursor route will reviewed in detail.

1.5.1 Colloidal Routes

La Mer, et al. [18] showed that the separation of the nucleation and growth process is fundamental to the achievement of narrowly dispersed colloids. The highly monodispersed samples are obtained if nucleation and growth process are distinctly separated (fast nucleation and slow growth). In this process known as Ostwald ripening, the high surface energy of the small nanocrystals promotes their dissolution and then recrystallizes on larger and more stable nanocrystals. The average nanocrystals size increases over time with a compensating decrease in nanocrystals number. For this method to be effective, the nanoparticles must have low solubility, which can be achieved by choice of solvent, pH, and passivating agent. The colloidal growth stability of the crystals can be improved by using solvents with low dielectric constants or by using stabilizers such as styrene/maleic acid copolymer [40]. The colloidal access to nanoparticles is achieved by carrying out a precipitation reaction in a homogenous solution in the presence of stabilizers, whose role is to prevent agglomeration and further growth [9, 41-43]. One of the first attempts to produce II-VI nanoparticles by Spenhel, et al. [42, 43] was the synthesis of the colloidal suspensions where CdS was formed by the precipitation of Cd^{2+} in aqueous solution by adding H₂S. Extensive research has been done in the synthesis and characterization of colloidal II-VI semiconductor nanoparticles. In the last decade, several stabilizing agents have been reported in the literature for the synthesis of colloidal semiconductor nanoparticles, including various surfactants, organic or inorganic polymers, thiols, amines and polyphosphates [44-53]. The specific adsorption of surfactants to the individual crystallographic planes alters the relative growth rates of different facets, providing a way of controlling the nanocrystal shape. The capping agents also assist to control the photoluminescence properties of as grown nanoparticles

Recently, there have been many studies on the solution-phase preparation of semiconductor nanoparticle stabilized by various surfactants at low temperatures. Dalvand, et al. [54] have successfully synthesized CdS nanowires and nanorods with different aspect ratios by solvothermal method aided with various solvents, namely ethylenediamine, ethanolamine and triethylene tetraamine. The prefer growth orientations and the aspect ratio of CdS nanoparticles were found to depend on the nature of the solvent. CdS nanoparticles with the highest aspect ratio in the form of nanowire were obtained using ethylenediamine, whereas CdS nanorods were synthesized in the presence of ethanolamine and triethylene tetraamine solvents. More recently, a simple chemical colloidal method has been developed for the synthesis of glucose-capped CdS nanoparticle [55]. The authors proposed that the method used is eco-friendly for commercial scale production as it does not involve the use of hazardous and toxic capping agents such as thiophenol, thiourea and mercaptoaccetate [55]. Yu, et al. [56] have synthesized well-defined PbS nanocubes at room temperature by a mild solution-based simple method in the presence of sulfonated polymer which act as both stabilizer and crystal growth modifier. The method employed requires no complex procedure or high temperature and its represents a relatively green chemical alternative. Anand, et al. [56] have optimized the synthesis of ZnS nanoparticles through a simple hydrothermal route. The nanoparticles were stabilized using Hexamethylenetetramine (HMTA) as surfactant in aqueous solution. The self-assembling of the surfactant molecules in the water solution forms a unique architecture that can be adopted as the reaction template for the formation of nanomaterials.

In recent years, thiol-containing molecules such as L-cysteine, glutathione, 2mercaptoethanol and thioglycolic acid have been used as capping agents for the direct synthesis of semiconductor nanoparticles in aqueous solution at lower reaction temperature (80–100 °C) [58-61]. The resulting nanoparticles are water soluble and have excellent biocompatibility for use in biological imaging. In addition to synthetic thiol-containing molecules, naturally occurring cysteine-rich peptides, which are employed as chelating agents to remove a variety of heavy metals, have also been employed for synthesis of water soluble semiconductor nanoparticles. The use of the tripeptide glutathione (GSH) as the capping agent for the synthesis of CdS, PbS, ZnS, ZnSe, CdSe, and CdTe nanocrystals have been reported. [62-68].

1.5.2 Hot injection routes

In the so called 'hot injection' route metal precursors and chalcogenide sources are injected into high boiling point solvents. Murray, et al. [69] pioneered this route when they injected a volatile metal alkyl (dimethylcadmium) and a chalcogen source TOPSe (tri-noctylphosphine selenide mixed in tri-n-octylphosphine (TOP) into hot TOPO (tri-noctylphosphine oxide), a polar co-ordinating Lewis base solvent. During this preparation method, nucleation is arrested by the sudden decrease in temperature following the injection. The large supersaturation left after injection leads to a uniform growth of all nuclei at very similar rates, thus decreasing the size dispersion. This is then followed by the addition of the solvent to a cooled solution, thereby increasing the barriers to flocculation. The solid nanoparticles were then separated from decomposition by-products in the centrifuge, and then the solids were dissolved in a solvent (e.g toluene) followed by centrifugation to dispose the by-products resulting in an optically clear solution of TOPO-capped nanoparticles. The coordinating solvent plays a major role in stabilizing the nanocrystalline colloidal dispersions and passivating the semiconductor surface. The hot injection method has enabled the creation various types monodisperse and high quality nanocrystals such as CdSe, CdTe, CdS, PbSe, and ZnSe [70-73].

Further development of the hot injection synthetic routes to well dispersed nanocrystals was explored by Peng, et al. [74-77] who proposed to use more environmentally benign cadmium precursors such as cadmium oxide, cadmium carbonate and cadmium acetate instead of highly toxic, expensive, and pyrophoric Cd(CH₃)₂. Peng and Peng described the formation of highquality CdSe nanocrystals using CdO as a precursor together with hexylphosphonic acid (HPA) or tetradecylphosphonic acid, which led to the intermediate formation of a cadmium HPA/TDPA complex. The injection of selenium dissolved in tributylphosphine yields nearly monodisperse rods and dots nanocrystals [75]. Potential interest in these new cadmium precursors is caused by green chemical principles and is motivated by the development of environmentally benign chemical methodologies and materials. Revaprasadu and co-workers have also developed a hybrid solution based high temperature route for the synthesis of metal chalcogenides [78-80]. The method involved the reduction of the elemental chalcogenide powder with sodium borohydride in water to produce the chalcogenide ions, which act as the source of the chalcogenide, followed by the addition of the metal salts (chlorides, nitrates, sulphates, carbonate and acetate). The resultant metal chalcogenide is dispersed in tri-n-octylphosphine (TOP) and the metal chalcogenide-TOP mixture is then thermolyzed in mild organic surfactant to passivate the surface of the nanoparticles. This method allows for shape control of the nanoparticles by varying the reaction parameters. The technique is environmentally benign, inexpensive, involving the use of relatively non-toxic reagents and has a short reaction time.

1.5.3 Single-molecule precursors

The problems associated with the use of toxic and volatile compounds such as metal alkyls at elevated temperatures led to the development of alternative chemical routes to nanoparticles. One of the approaches for overcoming this problem is the use of single molecular
precusors, i.e. a single compound containing all elements required within the nanocrystallite, such as alkyldiseleno- or alkyldithiocarbamato complexes. The O'Brien's group has explored the decomposition of various single molecular precursors [81-87] and the effect of different organic ligands such as TOPO, octylamine [87] and haxadecylamine [88] in the synthesis of CdS, CdSe, PbS. PbSe, CuS, InS, InSe, CdP, ZnO, InAs, GaAs, ZnSe nanoparticles [88-93]. The use of heterocyclic dithiocarbamate cadmium and lead complexes for CdS and PbS nanoparticles was investigated by Revaprasadu and co-workers.

Recently, Nyamen, *et al.* [95] reported using a single source precursor method to synthesize hexadecylamine capped CdS nanoparticles. Heterocyclic cadmium dithiocarbamate were used as the precursors. Combinations of shapes (spherical, rods, bipods and tripods) were obtained by varying the reaction parameters such as precursor concentration and temperature. Nyamen, *et al.* [96] also reported the synthesis of lead piperidine and lead tetrahydroquinoline dithiocarbamate (DTC) complexes and their use as single source precursors for the preparation of anisotropic PbS nanoparticles. The complexes were thermolysed in different coordinating solvents such hexadecylamime (HDA), tri-n-octylphosphine oxide (TOPO), oleylamine (OA) and decylamine (DA) at various reaction temperatures. HDA-capped PbS gave particles with shapes ranging from close to spheres, cubes and rods. TOPO-capped PbS particles appeared spherical and agglomerated. The OA-capped PbS were regular cubic shaped at lower temperatures but changed to rods at higher (270 °C) temperatures. The DA-capped particles were very crystalline, forming perfect cubes and rectangular shaped particles at 230 °C. The X-ray diffraction and Fast Fourier Transform studies confirm the cubic rock salt phase of PbS.

There have been many other types of precursors all having the metal sulfur bond that have been used for the synthesis of CdS nanoparticles. The closeness in structure of xanthates in relation to dithiocarbamates makes them ideal precursors for CdS nanoparticles. Cadmium ethylxanthate was thermolyzed in TOPO at 160 °C to give monodispersed, spherical TOPOcapped CdS nanoparticles with an average particle size of 4.2 nm [97]. The thermolysis of the identical xanthate precursor in hexadecylamine (HDA) at various temperatures gives rod-shaped CdS nanoparticles [98]. Spherical and nonspherical MS particles (M = Cd, Zn, Pb, Hg, Ni, Cu, Mn) have also been synthesized using metal alkylxanthates in HDA [98]. The authors described the use of reaction time, temperature, and/or concentration to achieve size and spectroscopic tunability of the particles. A cadmium(II) complex of dithiobiurea, Cd(SCNHNH₂)₂Cl₂ has also been used to synthesize CdS nanoparticles with a narrow size distribution [99]. Metal complexes of alkylthioureas have also proven to be very good precursors for nanoparticle synthesis. There has been extensive work reported by Revaprasadu and O'Brien on ZnS [100], ZnSe [92], CuSe [101], InSe [93], InS [93], GaS [102], and PdS [103] nanoparticles synthesized in various coordinating solvents using the respective metal dithio- and diselenocarbamates.

Cheon and co-workers have synthesized faceted shaped PbS nanoparticles by thermal decomposition of a single source precursor, $Pb(S_2CNEt_2)_2$, which was injected into a hot phenyl ether solvent at 230 °C containing dodecanethiol (DT) as capping agent. The shapes of PbS nanoparticles studied evolve from metastable one-dimensional (1-D) rod-based structures through star-shaped structures as a transient species to stable truncated octahedron and cubes. The use of dodecylamine (DDA) as capping agent instead of DT resulted in exclusive formation of the cube-shaped nanoparticles [104]. The group have also reported the synthesis of anisotropic CdS nanoparticles using thermal decomposition of an air-stable single-source molecular precursor, $Cd(S_2CNEt_2)_2$, in hot hexadecylamine. The shape of the synthesized CdS

nanoparticles varied between the monorod, bipod, tripod, and tetrapod as well as pencil-type rod by simply changing either the growth temperature or the precursor concentration [105].

Sun, *et al.* [106] reported the synthesis of hexagonal phase ZnS nanoparticles by microwave thermolysis of a single-source molecular precursor of zinc diethyldithiocarbamate $(Zn(DDTC)_2)$ in ethylene glycol at 110 °C for 5 min. A new nonhydrolytic single-precursor approach on the synthesis of CdS nanoparticles has been reported [107]. Cadmium 2-mercaptobenzothiazole complex Cd(C₆H₄NS)₂ was used as a single-source precursor. The size of the synthesized CdS nanocrystals could easily be controlled by adjusting the ratio of OA/C₆H₄NS)₂. CdS nanorods were also reported by Cai, *et al.* [108] by thermolysing a single source precursor (Me₄N)₄[S₄Cd₁₀(SPh)₁₆] in a single surfactant system.

1.5.4 Parameters that influence shape control of nanocrystals

The major critical factor responsible for the shape determination of the nanocrystals is the crystallographic phase of the initial seed (nuclei) formed during nucleation processes. The seed formed may have variety of different crystallographic phases, but the stable phase is highly dependent on the temperature of its environment. After the determination of a preferred crystallographic phase during the initial nucleation stage, the subsequent growth stage and the final shape of the nanocrystals are determined through a delicate balance between the kinetic growth and thermodynamic growth regimes. Isotropic growth of nanocrystals is preferred under the thermodynamic growth regime that is characterized by a sufficient supply of thermal energy (kT) and a low flux of monomers. In contrast, anisotropic growth along a specific direction is facilitated under a kinetic growth regime that is promoted by a high flux of monomers.

A suitable system for examining the different growth regime effects is the shape evolution of PbS nanocrystals with a symmetric rock salt structure [104]. Rapid injection of a PbS molecular precursor [Pb(S₂CNEt₂)₂] into a hot phenyl ether solvent at 230 °C containing dodecanethiol as surfactant induces the formation of tetrahedral seeds that are terminated by {100} and {111} faces. Subsequent competitive growth between these two different crystalline faces determines the final shape. The surface energy of the crystallographic face of the seed is also an important factor, since the kinetic energy barrier (G) is inversely proportional to the surface energy. These surface properties could also be tailored by the types and the amount of the absorbing organic surfactant molecules present. In the presence of dodecanethiol surfactants, the $\{100\}$ surface has a higher surface energy than the $\{111\}$ surface. When excess thermal energy (i.e. high temperature) is supplied, the formation of thermodynamically stable 0D truncated-cube-shaped PbS nanocrystals was formed (Figure 1.4). However, under lower temperature conditions (120 °C), the growth process shifts into the kinetic regime which results in 1D rods and multipod structures. At intermediate temperature (e.g. 180 °C), star-shaped PbS nanocrystals possessing both the characteristics of 0D and 1D was formed (Figure 1.4).



Figure 1.4 The Schematic energy diagram of PbS nanoparticles, their growth and the TEM images of resulting shapes of the nanoparticle depending on the growth mode [109]

1.6 Applications of nanotechnology

The benefits derived from nanotechnology depend on the fact that it is possible to tailor the essential structures of materials at the nanoscale to achieve specific properties. Nanotechnology is already in use in many computing, communications, and other electronics applications to provide faster, smaller, and more portable systems that can manage and store larger amounts of information. Some of the nanoparticles synthesized in this present study may found applications in light-emitting devices, solar cells and biological uses.

1.6.1 Light-emitting devices

Light-emitting devices (LEDs) can be made more efficient by using nanostructured materials that optimise the emission spectrum of LEDs. Luminescent semiconductor nanocrystals were successfully integrated into the thin film polymer-based LEDs as emitting materials [110-119]. Advantages of using polymer-nanocrystal composites are the processing of both polymer and nanocrystals from solution and the superior luminescent properties of the nanocrystals. Another strategy for the fabrication of LEDs is based on the use of aqueous thiol-capped CdTe integrated into a polyaniline or polypyrrole semiconducting matrix [119, 120]. A device emitting in the near-IR spectral region with an external efficiency of ~0.5% based on InAs/ZnSe core-shell nanocrystals has been reported (Figure 1.5) [121].



Figure 1.5 Infrared light-emitting diode

Displays for many new laptop computers, digital cameras, cell phones, televisions and other devices incorporate nanostructured polymer films known as organic light-emitting diodes, or OLEDs. OLED screens offer brighter images in a flat format, as well as wider viewing angles, lighter weight, better picture density, lower power consumption, and longer lifetimes.

1.6.2 Solar cells

The increasing demand for sustainable energy is the biggest challenge that the world is facing today. Renewable energy is increasingly viewed as critically important globally. The energy from the sun seems to be the most probable solution as the energy obtained is renewable and pollution free unlike fossil fuels. Solar cells or photovoltaics, convert the energy of the sun into electricity and has become the focus of research interest regarding the utilization of solar energy. There are three basic types of solar cell namely monocrystalline, polycrystalline and amorphous or thin-film. Monocrystalline cells are made from larger crystal of silicon and they are the most efficient and most expensive panels currently available. Polycrystalline cells are using multiple silicon crystals. They are less efficient and less expensive than monocrystalline panels. Amorphous cell are made by depositing a thin film of silicon onto a sheet of another material such as steel. They are cheaper but less efficient (Figure 1.6). The single crystal silicon based photovoltaic devices that are commercially available can achieve up to 26.5% efficiencies for commercial products [122]. However, such single crystalline solar cells are relatively expensive with the silicon itself making up 20-40% of the final cost [122]. These first generation devices suffer from high cost of manufacturing and installation.



Figure 1.6 Types of solar cells (a) monocrystalline (b) polycrystalline and (c) amorphous

The second generation devices consisting of polycrystalline semiconductor thin films can be produced at lower temperatures and deposited on low-cost flexible substrates such as plastics or metal foils, but their efficiency needs to be enhanced for making them practically viable [122]. Now the focus is on the third generation devices that can deliver high efficiency devices at economically viable cost.

The solar energy being radiated towards the earth has not been optimally converted into electricity. The fundamental path way for enhancing the conversion efficiency can be accessed through photovoltaic cells composed of nanocrystal arrays, through the dispersion of nanoparticles in organic semiconductor polymer matrices.

Hybrid solar cells consist of a mixture of nanostructures of both organic and inorganic materials. They combine the unique properties of inorganic semiconductor nanoparticles with properties of organic/polymeric materials [123]. Inorganic semiconductor nanoparticles have high absorption coefficients and particle size may induce tunability of the optical band-gap. Hybrid solar cells are produced using different concepts such as solid state dye-sensitized solar cells [124-126] and hybrid solar cells using the bulk heterojunction concept with different nanoparticles such as TiO_x [127], ZnO [128], CdS [129], PbS [130], CdSe [131, 132] and CuInS₂ [133].

Dye-sensitized solar cell of Grätzel-type is a third generation solar cell which comprises of several different materials such as nanoporous TiO₂ electrodes, organic or inorganic dyes, inorganic salts and metallic catalysts [134-137]. After absorption of a photon, the excited electron within the sensitizer molecule is transferred to the conduction band of TiO₂, and diffuses through the porous TiO_x network to the contact the sensitizer is regenerated by donation of electrons from the electrolyte [137, 138]. This photovoltaic conversion system is based on light harvesting by a molecular absorber attached to a wide band-gap semiconductor surface [136]. Semiconductor nanoparticles have a number of potential advantages as light-absorbing materials in Grätzel-type cells. The photo- and thermo-stability of the nanocrystals are superior to those of organic dyes. The optical absorption and band edge positions of the nanoparticles can be easily designed both by their elemental composition and by the nanocrystal size via the quantum confinement effect. Efficient charge transfer from the nanocrystals to the conduction band of wide-band gap semiconductors (TiO₂, ZnO, Ta₂O₅) in combination with high extinction coefficients in the visible spectral range makes them attractive for applications in Grätzel-type cells [139-141].

Solid state dye-sensitized solar cell is similar to the Grätzel-type cells in the which the electrolyte is replaced with a p-type semiconductor or organic hole conductor materials [142-144] avoiding problems such as leakage of liquid electrolytes [145]. The excitation of the dye via photon absorption leads to the injection of an electron into the conduction band of the semiconductor oxide electrode. The sensitizer dye is regenerated by the electron donation from the hole conductor [146]. In this solid state cell, the charge transport is electronic whereas in the case of liquid or polymer electrolyte, ionic transportation takes place [135]. CuI, CuBr and CuSCN have been successful used to replace the liquid electrolyte [143, 147-149]. The energy conversion efficiency of the fully solid state solar cell of nanoporous n-TiO₂/cyanidin/p-CuI has been reported to be up 1% [147]. The efficiency of this device was further improved by Tennakone, *et al.* [142] employing CuI as hole transporter and ruthenium bipyridyl dye complex as a sensitizer instead of cyanidin. A maximum power conversion efficiency of 6% corresponding was achieved which correspond to a fill factor of about 45%.

Another type of solar cell which is conceptually close to the solid state dye-sensitized solar cells is the extremely thin absorber (ETA) solar cells [150]. In the ETA solar cells, an extremely thin layer of a semiconductor such as CuInS₂ or CdTe or CuSCN replaces the dye in TiO₂ based solar cells [151]. It has the advantage of enhanced light harvesting due to the surface enlargement and multiple scattering. The operation of the ETA solar cell is also based on a heterojunction with an extremely large interface [152]. Nanu et al. [152] fabricated TiO₂/CuInS₂

ETA solar cell using atomic layer chemical vapour deposition technique. A 2 nm Al_2O_3 tunnel barrier and a 10 nm thick In_2S_3 buffer layer were inserted between TiO_2 and $CuInS_2$ to overcome the interfacial recombination problem and the cell gave an energy conversion efficiency of about 4%.

Another good strategy for hybrid solar cells is to use blends of inorganic nanocrystals with conducting polymers as a photovoltaic layer. The basis of this is the bulk heterojunction concept [129, 133, 153]. Bulk heterojunction concept in inorganic/organic hybrid solar cells is similar to that used in organic/organic solar cells. Bulk heterojunction hybrid solar cells have been demonstrated in various semiconducting polymer blends containing CdSe [132, 153, 154], CuInS₂ [133], CdS [129] or PbS [155] nanocrystals. The combination of electron-conducting nanocrystals and hole-conducting polymers in a single composite provides effective charge separation and transport. Hybrid solar cells based on nanoparticles of CuInS₂ in organic matrices have been reported by Arici et al. [123, 133]. The authors used nanocrystalline CuInS₂ with fullerene derivatives to form interpenetrating interface donor-acceptor acceptor heterojunction solar cells. Also bulk heterojunctions blending of CuInS₂ and a p-type polymer; poly(3,4ethylenedioxythiophene):poly(styrene sulfonic acid) in the same cell configuration showed better photovoltaic response with external quantum efficiencies up to 20% [133]. In another study, Zhang, et al. [156] demonstrated hybrid solar cells from blends of MEH-PPV and PbS nanocrystals. They investigated the effect of different surfactants on the photovoltaic performance of the hybrid devices using PbS nanoparticles exhibiting 250 nA short-circuit current and an open circuit voltage of 0.47 V.

1.6.3 Biological and medical applications

The biological and medical research communities have exploited the unique properties of nanomaterials for various applications. Semiconductor nanoparticles have been reported to have a wide array of potential biomedical applications, especially when combined with antigenspecific coatings or functional groups on their surfaces [157]. The therapeutic and diagnostic usefulness of inorganic nanoparticles depend on their size and physical properties in addition to their chemical composition. They must be small enough to circulate through the bloodstream and tissues without becoming lodged in capillaries or other microanatomies (Figure 1.7) [158]. Semiconductor nanoparticles have also been used in DNA or mRNA tracking. Several groups made studies on quantum dot, which are covered by a surfactant that includes carboxylic groups, conjugated oligonucleotide sequences that binded to DNA or mRNA [159, 160]. When semiconductor nanoparticles compared with organic fluorophores, nanoparticles have great advantages over organic fluorophores in terms of optical properties, such as brighter light, greater photostability, etc. Semiconductor nanoparticles can serve as detectors for pathogens and toxins [161, 162]. These nanocrystals can be used for defining pathogens and toxins properties, including virulence. Magnetic nanoparticles, bound to a suitable antibody, are used to label specific molecules, structures or microorganisms. Gold nanoparticles tagged with short segments of DNA can be used for detection of genetic sequence in a sample [163].

Nanotechnology could be used in medical field for delivering of drugs to specific cells using nanoparticles. The overall drug consumption and side-effects can be lowered significantly by depositing the active agent in the morbid region only and in no higher dose than needed. This highly selective approach reduces costs and human suffering. Some potentially important applications include cancer treatment with iron nanoparticles or gold shells [164, 165].



Figure 1.7 Phase contrast micrographs (left column) and corresponding fluorescence images (right column) of hepatocyte colonies cultured with CdSe QDs on day 1 (a and b) and after 7 days (c and d) [158].

A targeted or personalized medicine reduces the drug consumption and treatment expenses resulting in an overall societal benefit by reducing the costs to the public health system. Tissue engineering makes use of artificially stimulated cell proliferation by using suitable nanomaterial-based scaffolds and growth factors. For example, bones can be regrown on carbon nanotube scaffolds. Tissue engineering might replace today's conventional treatments like organ transplants or artificial implants. Advanced forms of tissue engineering may lead to life extension.

1.7 Aims and Objectives

The aim of this research work will be directed toward the synthesis and physical characterization of semiconductor metal sulfide nanoparticles of cadmium, lead and zinc. In this work, we focus on the application of green-chemistry principles to the synthesis of the metal sulfide nanoparticles. The first part of this work will focus on the synthesis and physical characterization of organically capped semiconductor metal sulphide nanoparticles of cadmium, lead and zinc while the second part will focus on water soluble semiconductor metal sulfide nanoparticles of the above-mentioned metals.

The research goals are:

- (1) To synthesize HDA and TOPO capped CdS, PbS and ZnS nanoparticles via a chemical reduction route.
- (2) To synthesize water soluble L-cysteine capped CdS, PbS and ZnS nanoparticles.
- (3) To study the influence of the precursors source, concentration, reaction temperature and capping agents on the morphology of the as-synthesized nanoparticles.
- (4) To study the particle growth and size distribution.

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CHAPTER TWO

Synthesis of organically capped metal sulfide nanoparticles

2.1 Lead sulfide (PbS)

2.1.1 Background

Amongst nanocrystalline semiconductors, metal sulfides are significant due to their optical, electronic and magnetic properties. Metal sulfide nanoparticles such as CdS, ZnS and PbS have found applications in fluorescent biological labelling [1, 2], in optoelectronics such as nonlinear optics, flat panel displays, light emitting diodes, transistor components [3-6], photocatalysts [7], sensors [13], photoelectric and thermoelectric materials [9], photoimaging and photodetection [10, 11] etc. The interesting properties of semiconductor nanoparticles are due to electronic quantum confinement and the large number of exposed atoms on the surface [12].

In recent years, colloidal chemistry methods have resulted in unprecedented control of the sizes and shapes of semiconductor nanostructures,[13-15] which translates to control of a wide range of electrical, electronic, and optical properties. Nanoparticles grown in solution are usually prepared in the presence of surfactants which are continuously adsorbed and desorbed from the surface allowing the nanoparticles to grow in a controlled manner. While the growth of a nanoparticles is governed by factors related to both thermodynamics (e.g., surface energies) and kinetics (e.g., activation energies for adsorption/desorption), the equilibrium shape of the crystal under a given set of processing conditions is largely determined by the thermodynamics.

As an important branch of semiconductor nanoparticles, near-infrared nanoparticles are currently receiving widespread attention due to their strong effect of quantum confinement and broad luminescence emission. PbS is a direct band gap IV–VI semiconductor with a band gap of 0.41 eV and an exciton Bohr radius of 18 nm at room temperature [16, 17]. It has been widely used in many fields such as Pb^{2+} ion-selective sensors, photography, IR detectors and solar absorbers [18-21]. One-dimensional PbS nanoparticles have been applied in electroluminescent devices such as light emitting diodes and optical devices such as optical switches due to the high third order non-linear optical properties [22-26].

Monodisperse PbS nanoparticles were first synthesized in poly(vinyl alcohol) (PVA) by Nenadovic, et al. in 1990 [27]. The synthesis of colloid PbS nanoparticles utilizing an organometallic approach was first reported by Scholes, et al. [33]. They synthesized PbS nanoparticles with a broad absorption band from 800 to 2000 nm using lead oleate and bis (trimethylsilyl) sulphide (TMS) stabilized by oleic acid. With oleic acid as surfactant, Warner, et al. [29] succeeded in synthesizing very small PbS nanoparticles by using H₂S as a sulphur source. The reason for using high-reactive TMS and H₂S is that sulfur and lead carboxylate in the presence of oleic acid can react readily into bulk-like particles. Hyeon, et al. [30] have reported the synthesis of PbS nanoparticles capped by oleylamine of sizes from 6 to 13 nm with lead chloride and sulfur. A similar solventless approach to synthesize PbS nanoparticles stabilized with oleylamine was developed by the Ozin group [31] with a narrow full width at half-maximum (FWHM) of the photoluminescence peak and a quantum yield (QY) of 40%. Qian, et al. [32] have reported a one-step route to crystalline PbS by a solvothermal reaction between lead oxalates and elemental sulfur in organic solvents such as ethylenediamine and pyridine. Cheon, et al. [33] have synthesized PbS nanoparticles with various rod-based structures including highly faceted star shapes, truncated octahedrons and cubes from the thermal decomposition of a molecular precursor, Pb(S₂CNEt₂)₂. Zou, et al. [34] have also synthesized PbS microcrystals including dendrites, flowers, multipods and cubes from the reaction of dissoluble lead salt (lead nitrate or lead acetate) and thiourea through a simple hydrothermal process. Li, *et al.* [35] have reported a surfactant-assisted homogenous hydrolysis reaction route for preparing PbS nanorods in the presence of sodium dodecyl sulphate (SDS) as surfactant. The third nonlinear optical properties of PbS nanorods were investigated by the Z-scan technique with 8 ns pulses at 532 nm. O'Brien and co-workers have also used a series of symmetrical and unsymmetrical *N*, *N*–dialkyldithiocarbamatolead(II) complexes as single source precursors to grow PbS nanoparticles by thermolysis in oleylamine at temperature as low as 60 °C [36, 37]. Recently, our group has reported the use of heterocyclic dithiocarbamate complexes as precursors for metal sulfide nanoparticles. Nyamen, *et al.* [38] have successfully synthesis anisotropic PbS nanoparticles using lead piperidine and lead tetrahydroquinoline dithiocarbamate (DTC) complexes as single source precursors. The results show that the variation of the reaction conditions and precursors produced PbS particles with shapes ranging from spheres to cubes and rods.

In this current work, highly faceted PbS nanoparticles in the form of spheres, rods and cubes using a hybrid solution based high temperature route have been successfully synthesized. The effects of temperature, surfactants and lead sources on the morphologies of the final PbS nanoparticles were investigated.

2.1.2 Experimental

2.1.2.1 Chemicals

All reagents and solvents were analytical grade and used without further purification. Hexadecylamine (HDA), tri-n-octylphosphine oxide (TOPO), and tri-*n*-octylphosphine (TOP)

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were purchased from Sigma-Aldrich. Methanol, lead nitrate, lead carbonate, lead sulphate, lead acetate, lead chloride and acetone were purchased from Saarchem, UnivAR, Merck chemicals.

2.1.2.2 Synthesis of PbS nanoparticles

In a typical procedure, 0.64 mmol of sulfur powder was mixed with 20 mL deionised water in a three necked flask. 1.58 mmol of NaBH₄ dissolved in 20 mL deionised water was added to this mixture and was left to stir for 12 h under nitrogen atmosphere at room temperature. 0.64 mmol of lead salt (PbCl₂, Pb(CH₃COO)₂,PbSO₄, Pb(NO₃)₂ and PbCO₃) dissolved in 20 mL deionised water was added to the sulfide ion solution to give a brownish-black solution. The solution was stirred for 30 minutes followed by the addition of excess methanol. The resultant solution was then centrifuged and decanted to isolate the solid products which were dispersed into 6 mL TOP and injected into hot HDA or TOPO at 190 °C (230 °C or 270 °C) for 2 h. The reaction was quenched by adding excess methanol to the solution. The flocculate was separated from the supernatant by centrifugation. The resultant particles were dissolved in toluene for characterization.

2.1.2.3 X-Ray diffraction analysis

The crystalline phase was identified by powder X-ray diffraction (XRD), employing a scanning rate of 0.05° min⁻¹in a 2 range from 20 to 80° , using a Bruker AXS D8 diffractometer equipped with nickel filtered Co K radiation (= 1.5418 Å) at 40 kV, 40 mA and at room temperature.

2.1.2.4 Electron microscopy

The morphology and particle sizes of the samples were characterized by a JEOL 1010 TEM with an accelerating voltage of 100kV, Megaview III camera, and Soft Imaging Systems iTEM software. The detail morphological and structural features were investigated using HRTEM images with a JEOL 2010 transmission electron microscope operated at an accelerating voltage of 200 kV.

2.1.2.5 Optical characterization

A Varian, Cary 50 Conc UV-Visible spectrophotometer was used to carry out the optical measurements and the samples were placed in silica cuvettes (1cm path length), using toluene as reference solvent. A Perkin Elmer, LS 55 Luminescence spectrometer was used to measure the photoluminescence of the particles. The samples were placed in a quartz cuvette (1cm path length).

2.1.3 Results and Discussion

2.1.3.1 Structural characterization

Colloidal semiconductor CdSe nanoparticles represent a particularly well understood system. The physical and chemical properties have been thoroughly studied along with the synthetic methods [39-42]. Extensive studies also have been carried out on PbSe nanoparticles in the past two decades [43-45]. Traditional methods of obtaining these selenides often require relatively high temperatures, as well as dangerous and often costly reagents. PbS nanoparticles have attracted considerable attention because of its interesting properties similar to those of CdSe and PbSe nanoparticles. Various shapes of PbS nanoparticles have been successfully synthesized in this work without any post-preparative size fractionation. The method used is a hybrid solution based high temperature route which is simple, reproducible and inexpensive.

PbS bulk was synthesized by the reduction of sulfur powder in water followed by addition of different lead salts (chloride, acetate, nitrate, carbonate or sulphate) which acts as the lead precursor. The PbS nanoparticles were grown by thermolysis in hot HDA or TOPO which act as the solvent and surface passivating agent. The choice of the temperature range used in this work was based on previous work done on PbTe and CdTe nanoparticles [46, 47]. Size and shape evolutions of PbS nanoparticles were simply achieved by changing the lead precursor sources, reaction temperatures and organic surfactants. The reaction scheme is shown below:

$$4NaBH_4 + 2S + 7H_2O = 2NaHS + Na_2B_4O_7 + 14H_2$$
(2.1)

$$NaHS + PbX$$
 $PbS + NaX + HX$ (2.2)

$$PbS + HDA/TOPO HDA/TOPO-PbS$$
(2.3)

where X = Cl, NO₃, CO₃, SO₄ and CH₃COO

Scheme 1. The reaction scheme for the preparation PbS nanoparticles.

The PbS nanoparticles produced when the thermolysis was carried out in HDA were found to be well dispersed. The Transmission Electron Microscopy (TEM) images of the PbS nanoparticles prepared from PbCO₃ source at different temperatures (190 °C, 230 °C and 270 °C) are shown in Figure 2.1. The TEM images show how significantly the reaction temperature affects the growth and shape of the nanocrystals. At 190 °C, the PbS nanoparticles were spherical in shape with average diameter of 9.95 \pm 2.17 nm as shown in Figure 2.1(a). At 230 °C, the PbS particles appear as unaggregated, monodispersed rods with an average width of 9 \pm 2 nm and average length of 17.04 \pm 5.11 nm as shown in Figure 2.1(b). This result is consistent with previous work from our group on PbTe whereby nanorods of PbTe were obtained when PbCO₃ was used as lead source [46]. At 270 °C, nanorods were also obtained with average width of 12.09 \pm 3.12 nm and average length of 25.41 \pm 7.08 nm (Figure 2.1(c)). The TEM



Figure 2.1. (a-c) TEM images of HDA capped PbS from PbCO₃ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped PbS from PbCO₃ at 230 °C

image shows how the primary particles (nuclei) are combining together to form the nanorods. The HRTEM image of the PbS nanoparticles from the PbCO₃ source at 230 °C are shown in Figure 2.1d. The HRTEM image shows that the nanoparticles formed are crystalline in nature. The HRTEM also shows distinct lattice fringes with the lattice d-spacing of 0.30 nm, indexed to the (200) plane of cubic PbS. In this reaction series the temperature determines whether the reaction would either undergo a kinetic or a thermodynamic growth regime. At 190 °C, the thermodynamic growth regime favoured the formation of spherical particles while at higher degree of temperatures the reactions were kinetically driven to form anisotropic shape in form of nanorods.

When Pb(NO₃)₂was used as the lead source and all other conditions kept constant, both spherical and nanorods shaped particles were formed. Figure 2.2(a) shows irregular shaped rods and dots were formed at reaction temperature of 190 °C. At 230 °C, there was a progression of shape from sphere to nanorods as shown in Figure 2.2(b). These nanorods have an average width of 22.17 \pm 8.04 nm and average length of 8.33 \pm 2.06 nm which longer in relative to the rods obtained from PbCO₃ source. There was some degree of aggregation or attachment of particles observed in the TEM image (Figure 2.2(b)). The HRTEM image (Figure 2.2(d)) confirms the attachment of particles. There is a crystallographic alignment of two particles leading to the formation of an elongated particle. At 270 °C, the growth regime became thermodynamic driven to form to spherically shaped nanoparticles as shown in Figure 2.2(c). The diameter of the spheres was estimated from the TEM image to be 5.51 ± 1.23 nm. The final morphologies of the PbS nanoparticles formed from the Pb(NO₃)₂source at the three different reaction temperatures were driven by both thermodynamic and kinetic growth regimes.



Figure 2.2. (a-c) TEM images of HDA capped PbS from $Pb(NO_3)_2$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped PbS from $Pb(NO_3)_2$ at 230 °C

The effect of the PbSO₄ source on the morphology of the PbS nanoparticles was also observed. At 190 °C and 230 °C, spherical shaped nanoparticles were obtained as shown in Figure 2.3 (a & b). The average diameters of these spheres were 3.24 ± 0.72 nm and 3.13 ± 0.70 nm respectively. At 270 °C, the PbSO₄ source gave very uniform, monodispersed, self-assembled cubic shaped particles with an average size of 7.09 ± 1.12 nm (Figure 2.3(c)).



Figure 2.3. (a-c) TEM images of HDA capped PbS from $PbSO_4$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped PbS from $PbSO_4$ at 270 °C

The HRTEM image (Figure 2.3(d)) confirms the regular cube shape. The self-assembled PbS nanocubes had an average side-to-side of double-particle distance of about 1.80 nm as shown in Figure 2.3(d).

Figure 2.4 shows the TEM images of the PbS nanoparticles formed when $PbCl_2$ was used as the lead source. At 190 °C, monodispersed nanodots were obtained and the size as estimated from the TEM image was 3.92 ± 0.83 nm (Figure 2.4(a)).



Figure 2.4. (a-c) TEM images of HDA capped PbS from PbCl₂ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped PbS from PbCl₂ at 230 °C

It is apparent from the TEM image in Figure 2.4(b) that the PbS nanocrystals formed at 230 °C consist of rod-like nanoparticles with very few spherical nanoparticles in the domain. The primary nanoparticles formed during nucleation might have been spherical particles which coalescence during growth process to formthe nanorods. The average length and width of the nanorod estimated from the TEM image are 13.05 ± 3.21 nm and 3.07 ± 0.84 nm respectively. The crystallinity of the PbS nanorods is confirmed with distinct lattice fringes observed in the

HRTEM image as shown Figure 2.4(d). The lattice d-spacing of 0.299 nm observed corresponds to (200) of a cubic PbS crystal. At 270 °C, dot particles with average diameter of 4.04 ± 1.19 nm were formed as shown in Figure 2.4(c). It seems that thermodynamic growth regime takes over the kinetic growth due to the coexistence of the two regimes leading to the formation of nanodots.

Spherical shaped PbS nanoparticles were formed when Pb(CH₃COO)₂ was used as the lead source at reaction temperatures of 190 °C and 230 °C as shown in Figure 2.5 (a & b). The average sizes of the particles were estimated from the TEM images as 8.07 ± 2.16 and 14.03 ± 4.14 nm respectively. The nanoparticles formed at 230 °C are larger in size and aggregated when compared to the particles formed at 190 °C. At 270 °C, a mixture of rod-like and spherical shaped nanoparticles were formed in the domain as shown in Figure 2.5(c). The average diameter of the sphere as estimated from the TEM image was 4.02 ± 2.18 nm while the average width and length of the rod was 4.47 ± 1.06 and 15.12 ± 2.04 nm respectively. The corresponding HRTEM image in Figure 2.5(d) shows that the particles consist of single crystal. The image reveals the sharp lattice fringe, which further support single-crystalline nature of the PbS nanoparticles. The displayed interplanar spacing is estimated to be about 0.294 nm, corresponding to the (200) lattice plane of the face-centered cubic phase of PbS.



Figure 2.5. (a-c) TEM images of HDA capped PbS from $Pb(CH_3COO)_2$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped PbS from $Pb(CH_3COO)_2$ at 270 °C

The use of five lead sources to produce particles with varying shapes can be explained by the probable different growth mechanisms. The PbS nanorods and nanocubes morphologies could be attributed to the HDA surfactant which provides a template for assembling the lead sulfide structures and making the crystals grow preferentially in a specific direction. The growth rates on the different facets in the system are dominated by the surface energy. For halite type crystals the $\{111\}$ face with high surface energy grows faster than the lower-surface-energy $\{100\}$ face which favours $\{100\}$ facets leading to either nanocubes or nanorods. In the case of the PbCO₃ source, the insoluble nature of the carbonate results in a suspension of the undissolved cadmium carbonate which selectively adheres to the surface of the PbS nanoparticles thereby accentuating the difference in the growth rate between the crystallographic phases. This results in kinetically induced anisotropic growth. These results are similar to those of CdTe nanoparticles synthesized under the same reaction conditions [47].

When the lead source is Pb(NO₃)₂, there is evidence of growth by an oriented attachment process. Oriented aggregation (OA) is a special case in which the secondary particles are new single crystals composed of oriented primary particles [48, 49]. This mechanism is based on the spontaneous self-organization of adjacent nanocrystals, resulting in growth by the coalescence of primary particles that share a common crystallographic orientation. Nanoparticles growth via the oriented attachment mechanism generally leads to the formation of anisotropic nanoparticles and particles of irregular shapes, as well as nanoparticles with defects. The HRTEM image (Figure 2.2(d)) shows two particles attached to each other. The TEM image also shows the fusion of particles resulting in elongated particles. The PbSO₄ source gave perfect cube shaped particles which is the most thermodynamically stable morphology of PbS.

Recent studies have shown that selective anisotropic growth between different crystallographic surfaces can be adjusted by the use of appropriate absorbing organic surfactants [50]. It is well known that, the presence of the surfactant could kinetically control the relative growth rates of different crystal planes by allowing the growth along one facet to proceed while inhibiting the growth along another facet [33]. To explore the influence of the organic surfactant on the morphologies of PbS nanoparticles under otherwise similar reaction conditions, TOPO
another organic capping agent was used in the place of HDA. TOPO is expected to exhibit different interaction with certain PbS crystal facets due to its phosphine functional group. The same lead sources were used and thermolysis temperatures of 190 °C, 230 °C and 270 °C were also used for the TOPO capped PbS nanoparticles.

Figure 2.6(a-c) shows the TEM images of TOPO-capped PbS nanoparticles prepared from PbCO₃ source. The images revealed that rod-like shaped PbS nanoparticles were formed at the three different reaction temperatures observed.



Figure 2.6. (a-c) TEM images of TOPO capped PbS from PbCO₃ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of TOPO capped PbS from PbCO₃ at 230 °C

The average width obtained from measurement of the PbS nanoparticles for 190 °C, 230 °C and 270 °C growth temperatures were 14.16 ± 4.05 nm, 12.01 ± 2.31 nm and 8.06 ± 3.13 nm, respectively. With increase in reaction temperature from 190 °C to 230 °C, the length of the nanorods becomes longer. The average length of PbS nanorods were 72.33 ± 37.09 nm, 90.14 ± 24.12 nm and 20.32 ± 5.07 nm for 190 °C, 230 °C and 270 °C reaction temperature respectively. It is obvious from the above measurements that the largest variation in the size of the PbS nanorods is due to the length variations. This may be due to the fact that the PbS nanorods grow along their length axis and that the different growth rate of the length within the ensemble resulted in slightly different lengths of the nanorods. The HRTEM image of the PbS nanoparticles prepared at 230 °C is shown in Figure 2.6(d). The lattice fringes visible in the HRTEM image are indicative of high crystallinity of the nanoparticles. The displayed interplanar spacing is estimated to be about 0.295 nm, corresponding to the (200) lattice plane of cubic phase of PbS.

Similarly, rod-like morphology were also observed in PbS nanoparticles prepared using $Pb(NO_3)_2$ source. Nanoparticles aggregates are clearly visible in the TEM image (Figure 2.7(a)) prepared at reaction temperature of 190 °C. The average length and width of the particles estimated from the TEM image are 61.14 + 18.42 nm and 5.01 + 1.20 nm respectively. The obtained PbS nanoparticles at 230 °C and 270 °C are monodispersed rod-like shape with average diameters of 7.37 ± 2.35 nm and 10.11 ± 2.08 nm and average lengths of 65.23 ± 22.09 nm and 111.16 ± 34.27 nm respectively as shown in Figures 2.7(b & c). Figure 2.7(d) show the HRTEM image of the PbS nanorods formed at 230 °C. The lattice spacing was found to be about 0.289 nm. This d-spacing was indexed as (200) plane of cubic PbS.



Figure 2.7. (a-c) TEM images of TOPO capped PbS from Pb(NO₃)₂ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of TOPO capped PbS from Pb(NO₃)₂ at 230 °C

Figure 2.8 shows the TEM images of monodispersed nanorods particles with average length of about 58.03 ± 10.22 nm (Figure 2.8(a)), 62.04 ± 11.39 nm (Figure 2.8(b)) and 77.31 ± 17.14 nm (Figure 2.8(c)) prepared from PbSO₄ source at 190 °C, 230 °C and 270 °C, respectively. The average widths of the nanorods were estimated to be in the range of 11-8 nm. The morphologies of the particles formed in HDA-capped nanoparticles from PbSO₄ are completely different from those formed in TOPO-capped nanoparticles. From the above results,



Figure 2.8. (a-c) TEM images of TOPO capped PbS from $PbSO_4$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of TOPO capped PbS from $PbSO_4$ at 190 °C

it seems that the capping groups are responsible for the morphologies of the particles obtained at the end of the reaction. Figure 2.8(d) show the HRTEM image of PbS nanoparticles prepared at 190 °C. The HRTEM image of the particles show lattice fringes with d-spacing of 0.301 nm matching the spacing between the (200) plane of cubic PbS.

The TEM images (Figure 2.9(a-c)) show the sizes and morphologies of the assynthesized PbS nanoparticles from $PbCl_2$ source.



Figure 2.9. (a-c) TEM images of TOPO capped PbS from $PbCl_2$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of TOPO capped PbS from $PbCl_2$ at 230 °C

The products obtained are mainly fine nanorods with width in the range of 6–8 nm and lengths of 48–90 nm. The average length obtained from measurement of the PbS nanoparticles at 190 °C, 230 °C and 270 °C are 62.15 ± 22.16 nm, 48.04 ± 6.27 nm, and 90.18 ± 17.40 nm, respectively. The average length of the nanorods formed at the highest reaction temperature (270 °C) was the largest. Temperature is a known factor that influences the growth and size of particles.



Figure 2.10. (a-c) TEM images of TOPO capped PbS from $Pb(CH_3COO)_2$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of TOPO capped PbS from $Pb(CH_3COO)_2$ at 230 °C

Higher temperature favour larger particle sizes. From the view of kinetics of crystal growth, when the surface of PbS nanocrystallites is partially capped by TOPO, their growth rate in some certain direction will be confined, which will finally lead into anisotropic growth towards one-dimensional direction. From the HRTEM image (Figure 2.9(d)) of the PbS nanoparticles grown at 230 °C appears to be no discontinuities in the lattice fringes indicating a perfect crystal. The

lattice spacing was estimated to be about 0.291 nm. This d-spacing was indexed as (200) plane of cubic PbS.

The synthesis of PbS nanoparticles using Pb(CH₃COO)₂ source also gave rod-like shaped particles at the different growth temperatures as shown in Figure 2.10 (a-c). The nanorods formed were well dispersed. The average width of the nanorods are 3.15 ± 0.92 nm (190 °C), 4.19 ± 1.26 nm (230 °C) and 4.05 ± 1.45 nm (270 °C) while the average length are 13.17 ± 3.36 nm (190 °C), 17.14 ± 4.02 nm (230 °C) and 20.03 ± 7.11 nm (270 °C). The crystallinity of the PbS nanoparticles is confirmed by HRTEM image (Figure 2.10(d)) in which the lattice fringes are easily observedThe formation of these anisotropic PbS nanoparticles suggest that the nucleation and growth of PbS nanoparticles are well controlled by the nature of surfactant (TOPO). The anisotropic nature of the TOPO capped PbS nanoparticles could be due to the impurities present in the technical grade TOPO. It is well known that impurities such as hexylphosphonic acid (HPA) facilitate the growth of anisotropic CdSe nanoparticles [51]. The HPA binds selectively to a specific axis thereby inhibiting growth along other facets favouring rod-like single crystal growth, with preferred growth along the length axis.

The crystallinity of the as-prepared PbS nanoparticles were investigated by X-ray diffraction (XRD), as shown in Figure 2.11 (a & b). The results of the XRD patterns of the HDA and TOPO capped PbS nanoparticles prepared from $Pb(NO_3)_2$ indicates that these two samples crystallized well and the patterns are in good agreement with the bulk PbS crystal. The five major peaks can be indexed as 111, 200, 220, 311, and 222, respectively. No diffraction peaks arising from any impurities can be detected. All XRD patterns show obvious size-broading effects, indicating the finite size of these nanoparticles, which were similar to those, reported in the literature [25, 52].



Figure 2.11. XRD patterns of the PbS nanoparticles from $Pb(NO_3)_2 230$ °C: (a) HDA capped PbS nanoparticles (b) TOPO capped PbS nanoparticles





Figure 2.12. XRD patterns of the HDA capped PbS nanoparticles from: (a) $PbCl_2$ and (b) $PbCO_3$ sources at 190 °C



Figure 2.13. XRD patterns of the HDA capped PbS nanoparticles from: (a) $PbSO_4$ and (b) $Pb(CH_3COO)_2$ sources at 270 °C

The XRD patterns of HDA capped PbS nanoparticles for other lead sources are shown in Figure 2.12 and Figure 2.13. The XRD patterns were similar for all the other lead sources regardless of the different lead sources and the temperature of reaction.

2.1.3.2 Optical characterization

Figure 2.14 shows the UV–Vis absorption spectra of the PbS nanocrystals dispersed in toluene. A representative spectra of PbS nanocrystals prepared when $Pb(NO_3)_2$ is used as lead source at the three different thermolysis temperatures (190 °C, 230 °C and 270 °C). It can be seen that absorption spectra feature no obvious excitonic peak in the near UV and visible region (300 – 800 nm). Recently, an excitonic peak at around 1300 nm and a corresponding fluorescence peak at around 1350 nm have been observed for PbS nanocrystals with the diameter of 6.5 nm [28].



Figure 2.14 UV-Visible spectra of PbS nanocrystals synthesized from $Cd(NO_3)_2$ (i) 270 °C (ii) 190 °C (iii) 230 °C

It is therefore possible that the first direct band gap excitonic peak occurs at a redder wavelength beyond our detection range. No fluorescence has been detected at room temperature for PbS nanocrystals studied in the detection range from 300 to 1000 nm. However, near-infrared (IR) fluorescence can still exist in the range from 1000 to 2000 nm if there is a first excitonic peak above 1000 nm [28, 53].

2.1.3.3 Conclusion

HDA and TOPO capped PbS nanoparticles have been synthesized via a simple hybrid solution based thermolysis route. By varying the lead source HDA capped particles with morphologies ranging from close to spheres, elongated particles and perfect cubes were formed. When the capping group was changed to TOPO, predominantly rod shaped particles were obtained. The growth mechanism for the anisotropic HDA capped PbS is mostly likely due an oriented attachment mechanism. The formation of the rod shaped TOPO capped PbS is due to the impurities in TOPO. The X-ray diffraction and high resolution electron microscopy studies show that the particles are crystalline.

2.2 Cadmium sulfide (CdS)

2.2.1 Background

Control over the dimensions and shape of nanomaterials represents one of the main challenges in modern materials science. The anisotropic growth of nanomaterials has led to the development of complex and diverse nanostructures such as rods [54, 55], tetrapods [56], prisms [57], cubes [58], and other non-spherical morphologies [59, 60]. As one of the most important group II-VI semiconductors, CdS with a direct bandgap of 2.4 eV at room temperature, which has attractive photonic properties, has been extensively investigated during the past decades. The so called 'hot-injection' route involving the thermolysis of dual or single source precursors in high boiling point coordinating solvents has proved to be an efficient route to achieve the shape control of nanoparticles. In the case of CdS nanoparticles, CdCl₂ [61, 62], Cd-oleate [63] or CdO [64, 65] have been used as cadmium precursors and dodecanthiol [63] or a solution of elemental sulfur in oleylamine [62] or in octadecene [65] were identified as sulfur precursors. The related single-molecular precursor route has also been very successful in producing CdS nanoparticles with varying morphologies. Dithiocarbamate complexes of cadmium have been extensively used as precursors for CdS nanoparticles [38, 66-69]. Mthethwa, et al. and Nyamen, et al. [38, 70] have both reported the use of heterocyclic dithiocarbamates complexes as single source precursors for the synthesis of organically-capped CdS nanoparticles. Nyamen, et al. [38] results showed that nanoparticles in the form of rods, bipods and tripods were obtained for the HDAcapped CdS whereas spherical nanoparticles were obtained when TOPO was used as the capping agent. Nair, et al. [71] prepared monodispersed TOPO-capped CdS nanoparticles using cadmium ethylxanthate as single source precursor through thermolysis in hot TOPO at 160 °C. The thermolysis of the identical xanthate precursor in hexadecylamine (HDA) at various temperatures gives rod-shaped CdS nanoparticles [72].

CdS particles in the form of one dimensional (1D) nanowires (NWs) have recently attracted considerable attention due to their unique band and/or ballistic charge transport capabilities [73], dielectric contrast effects [74] and intrinsic polarization sensitivities [75]. Routkevitch, *et al.* [76] have fabricated CdS nanowire arrays by electrochemical deposition into porous anodic aluminium oxide (AAO) template (a hard template). Li, *et al.* [77] have reported the synthesized of CdS nanowires in hexagonal liquid crystals formed by surfactant $C_{16-18}EO7$ (a soft template). Qian and coworkers [78] have investigated the effect of cadmium salt on the shape of prepared CdS nanoparticles with solvothermal method. Warner and Tilley [79] have synthesized triangular and hexagonal CdS nanocrystalsusing simple colloidal techniques.

In the present work, a similar route as described for PbS has been used to prepare CdS nanoparticles with varying morphologies. Sulfur is reduced by sodium borohydride in solution to produce sulfide ions, followed by the reaction with a cadmium salt to give CdS which is then dispersed in tri-*n*-octylphosphine (TOP) followed by thermolysis in HDA or TOPO.

2.2.2 Experimental

2.2.2.1 Chemicals

Cadmium chloride, cadmium acetate, cadmium carbonate, cadmium sulphate, cadmium nitrate, sodium borohydride, methanol, toluene, acetone and sulphur were purchased from Saarchem, UnivAR, Merck chemicals. Hexadecylamine, tri-n-octylphosphine oxide and tri-n-octylphosphine were purchased from Sigma-Aldrich. All the chemicals were used as purchased.

2.2.2.2 Synthesis of CdS nanocrystals

The procedure employed for preparing CdS nanoparticles is as follows. In a typical reaction, sulphur powder (0.64 mmol) was mixed with deionised water (20 mL) in a three neck flask. A solution of NaBH₄ (1.58 mmol) was carefully added to this reaction mixture and the flask was immediately purged with nitrogen to facilitate an inert atmosphere. After 12 h, cadmium salt (0.64 mmol) was added to the reaction mixture. The suspension was stirred for 30 min followed by the addition of excess methanol. The resultant suspension was then centrifuged. The precipitate was dispersed in tri-n-octylphosphine (6.0 mL) and injected into hot HDA or TOPO (6.0 g) at 190 °C, and the reaction was allowed to continue for 2 h. After heating excess anhydrous methanol was added to the solution resulting in HDA or TOPO capped CdS nanocrystals. Several experiments were repeated with the above reaction procedure. The injection temperature was changed to 230 °C and 270 °C.

2.2.3 Results and Discussion

2.2.3.1 Structural characterization

High quality CdS nanoparticles were synthesized by the thermolysis of pre-formed CdS in HDA at 190 °C, 230 °C and 270°C. The initially formed CdS was synthesized by reacting cadmium salts with reduced sulphur in water. Figure 2.15 (a-c) shows the TEM images of the well-defined HDA capped CdS nanoparticles. The TEM images showed that faceted CdS nanoparticles in the shape of triangles and sphere were formed when CdCl₂ was used as the cadmium source at growth temperatures of 190 °C, 230 °C and 270°C.



Figure 2.15. (a-c) TEM images of HDA capped CdS from CdCl₂ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped CdS from CdCl₂ at 230 °C

The average particle sizes of the spherically shaped nanoparticles are estimated to be 6.13 ± 0.62 nm, 7.74 ± 0.80 nm and 6.33 ± 0.71 nm in diameter for the reaction temperatures of 190 °C, 230 °C and 270°C respectively. The formation of the triangular shaped CdS nanoparticles are limited in number when compared to the number of the spherical nanoparticles formed in the ensemble as shown in Figure 2.15 (a, b & c). The formation of triangular shaped CdS nanoparticles has been previously reported [80, 81]. Pinna et al. reported the formation of flat triangular CdS nanoparticles with a wurtzite crystal structure in (ethyl-2-hexyl)sulfosuccinate (AOT) reverse

micelles while Warner et al. reported on the formation of triangular shaped CdS with sizes up to 50 nm grown at 240 °C by injecting a solution of sulphur dissolved oleylamine into a hot solution of $CdCl_2$ in oleylamine. The corresponding HRTEM image shows that the CdS nanocrystals were highly crystalline, which was confirmed by the clearly observable lattice fringes as shown in Figure 2.15(d). All the triangular and spherical nanoparticles observed were single crystals with no discontinuities in their lattices.



Figure 2.16. (a-c) TEM images of HDA capped CdS from $Cd(CH_3COO)_2$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped CdS from $Cd(CH_3COO)_2$ at 230 °C

The effect of the cadmium acetate on the size and morphology of CdS nanoparticles was also observed. The TEM images show that the CdS nanocrystallites are approximately spherical and are close to monodisperse (Figure 2.16(a-c)). The mean particle diameter of the CdS nanocrystals prepared at 190 °C, 230 °C and 270 °C as estimated from the TEM images are 2.63 ± 0.95 nm, 4.42 ± 1.03 nm and 7.62 ± 2.09 nm, respectively. The increase in particle size with the growth temperature indicated that Ostwald ripening appeared to determine the final size of CdS nanocrystallites in the present preparation procedure. The crystallinity of CdS nanoparticles is confirmed by HRTEM. The HRTEM image shows an oblate particle with distinct lattice showing no discontinuities or stacking faults (Figure 2.16(d)).

Further investigation on the effect of the cadmium sources on the growth morphology of the nanoparticles was carried out using cadmium nitrate source. TEM images of the CdS nanocrystals formed when cadmium nitrate was used as cadmium source are shown in Figure 2.17. The images reveal that the particles are exclusively made of nanorods/nanowires with uniform width and length. The nanowires obtained at 190 °C were found to be 107.31 \pm 72.05 nm in length and 6.22 \pm 1.14 nm in width (Figure 2.17(a)). When reaction temperature was increase to 230 °C, shorter nanorods were obtained (Figure 2.17(b)). The average length and width of these rods/wires as estimated from the TEM image are 91.07 \pm 35.16 and 5.05 \pm 1.38 nm, respectively. There was an obvious increase in the length and width of the nanowires obtained when the growth reaction temperature was carried out at 270 °C as shown in Figure 2.17(c). The average sizes are 142.19 \pm 72.04 and 8.36 \pm 2.11 nm for the length and width respectively. Further evidence for the single crystalline nature of the nanowires could be obtained from the HRTEM image (Figure 2.17(d)) in the lattice fringes are visible.



Figure 2.17. (a-c) TEM images of HDA capped CdS from $Cd(NO_3)_2$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped CdS from $Cd(NO_3)_2$ at 270 °C

Figure 2.18(a) shows TEM of CdS nanorods grown at 190 °C from CdCO₃ source. It can be seen that particles are irregular nanorods with different length and interwoven at tail end of their lengths. The average length and width of the nanorods estimated from the TEM image are 153.01 ± 27.04 nm and 16.27 ± 3.16 nm respectively.



Figure 2.18. (a-c) TEM images of HDA capped CdS from CdCO₃ source at 190 $^{\circ}$ C, 230 $^{\circ}$ C & 270 $^{\circ}$ C respectively and (d) HRTEM image of HDA capped CdS from CdCO₃ at 270 $^{\circ}$ C

At 230 °C and 270 °C, the particles formed consist mainly of nanorods with very few spherical shaped nanoparticles as shown in Figure 2.18(b and c). The TEM images reveal that the rod-shaped crystals are preferentially grown along the length axis and some of the nanorods are agglomerates. As shown in Figure 2.18(b & c), the average length of the CdS nanorods changes from 40.31 ± 16.05 nm to 50.42 ± 22.37 nm when the reaction temperature was changed from

230 °C to 270 °C and a slight increase was observed in the diameter of the rods (5.60 \pm 2.10 nm to 5.92 \pm 2.14 nm). The HRTEM image (Figure 2.18(d)) shows the crystallinity of particles confirmed by the lattice planes observed on the images.

When cadmium sulphate was used as cadmium source, the CdS nanoparticles formed consist of a mixture of rod-like and spherical nanoparticles for the different reaction temperatures. The rod-like shaped nanoparticles formed at 190 °C has an average length of 12.18 \pm 2.01 nm and width of 2.45 \pm 0.54 nm as shown in Figure 2.19(a). The average diameter of the spherical particles is estimated to be about 3.34 \pm 1.09 nm. At 230, majority of the particles are rod-like in shaped with very few spherical nanoparticles in the domain (Figure 2.19(b)). The average length and width of the nanorods are 13.13 \pm 5.25 and 3.28 \pm 0.44 respectively. Similar morphology was obtained at reaction temperature of 270 °C (Figure 2.19(c)). The average width of rods is 2.14 \pm 0.30 nm, and the length is 23.08 \pm 3 nm. The HRTEM image of individual nanorods reveals regularly spaced lattice fringes. Thus, the nanorods are indeed single-crystalline.

It seems from the above observations, that the majority of the nanoparticles formed have rod structure at the end of the reaction and a small part remained with spherical structure. This indicates that the initial seeds formed were spheres which are changed into particles with rod-like structure as the reaction progresses. A good explanation for the above observation is that the reaction falls under mixed control by kinetics and thermodynamics. Thus spherical nanoparticles and short nanorods coexist under this condition.



Figure 2.19. (a-c) TEM images of HDA capped CdS from $CdSO_4$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped CdS from $CdSO_4$ at 230 °C

The elongated growth of the CdS nanoparticles when cadmium nitrate is used can be explained when considering the growth mechanism of particles. Anisotropic shape control is mainly through the preferential growth of a particular crystallographic surface of nanoparticles during a kinetically controlled growth process [51, 69, 82]. After the formation of a preferred crystalline phase seed, the surface energy of the crystallographic faces has a dominant effect on the anisotropic growth pattern. The HDA seems to increase the growth rate in the (001) directionThe elongated growth of the CdS nanoparticles when cadmium nitrate is used can be explained when considering the growth mechanism of particles. Anisotropic shape control is mainly through the preferential growth of a particular crystallographic surface of nanoparticles during a kinetically controlled growth process [51, 69, 82]. After the formation of a preferred crystalline phase seed, the surface energy of the crystallographic faces has a dominant effect on the anisotropic growth pattern. The HDA seems to increase the growth rate in the (001) directionunder high temperature conditions [69]. It is also possible that undissolved cadmium nitrate also adsorbs onto the crystalline faces thereby accentuating the difference in surface energy and modulating growth along the (001) plane. This explains the presence of wire-like structures at the growth temperature of 270 °C.

The morphology for most of the TOPO capped CdS nanoparticles formed from the various cadmium sources were closer to spherical, a result consistent with a preferential mode of arrangement of the CdS particles when they settle on the carbon coated copper grid. It was difficult to determine the shape of some of particle from the TEM images, as the particles tend to agglomerate rapidly. In some cases, the particles failed to assemble on the carbon coated copper grid. A possible explanation might be that the nanoparticles formed are poorly capped by the surfactant (TOPO).

The crystallinity of the as-prepared CdS nanoparticles from CdCl₂ source at the different reaction temperatures were investigated by powder X-ray diffraction (XRD), as shown in Figure 2.20. CdS nanoparticles have been reported to exist in either the cubic or hexagonal phase. The X-ray powder diffractions of the CdS nanoparticles obtained in this work have patterns consistent with the hexagonal phase.











Figure 2.21. XRD patterns of the HDA capped CdS nanoparticles from Cd(NO₃)₂ at (a) 190 °C and (b) 270 °C

The major diffraction peaks could be indexed as (100), (002), (101), (102), (110), (103) and (112) of hexagonal CdS structure. Compared with the standard diffraction pattern, no peaks of impurities were detected, indicating the high purity of the products [65]. Although the different reaction temperatures used influence the growth of the particles but there were no visible changes in the phase of XRD patterns obtained in this work. It is clear from Figure 2.20 that the

CdS nanoparticles produce at the different reaction temperatures have the same hexagonal crystal structure. A possible explaination for this trend may be due to the long duration of heating (2 h), where the nanparticles obtained might have attained a single phase. These same trends were observed for the other cadmium sources used in this work. Figure 2.21 show the XRD patterns for CdS nanoparticles from the Cd(NO₃)₂ at 190 °C and 270 °C reaction temperatures. The X-ray diffraction patterns showed peaks corresponding to the hexagonal phase.

2.2.4 Optical properties

A fundamental property of semiconductors is the band gap; the energy separation between the filled valence band and the empty conduction band. The size/shape-dependent optical properties of semiconductor nanoparticles can be used as convenient probes to study the growth and shape evolution of nanoparticles. It has been established that temperature is a major factor which influence the particles size and growth rate of nanoparticles. The effect of temperature on the CdS nanoparticles synthesized from the different cadmium sources was studied. Figure 2.22 shows absorption spectra of the CdS nanoparticles synthesized from $CdCl_2$ source at the growth temperatures of 190 °C, 230 °C and 270 °C for reaction time of 2 h. The absorption band edges estimated from the spectra are 3.07 eV (404 nm), 3.03 eV (409 nm) and 2.82 eV (439 nm) respectively for 190 °C, 230 °C and 270 °C reaction temperatures. It was observed that a systematic shift in the absorption edge occurs, as the growth temperature is increased. The absorption edge shifts towards the longer wavelength. This is due to the quantum confinement effect, where more discrete energy states are formed, resulting in change of the band gap of the nanoparticles [67]. A similar effect was observed in the CdS nanoparticles synthesized from $Cd(CH_3COO)_2$ source as shown in Figure 2.23.



Figure 2.22. UV-Vis spectra of CdS nanoparticles synthesized from $CdCl_2$ at (i) 190 °C, (ii) 230 °C and (iii) 270 °C for 2 h



Figure 2.23. UV-Vis spectra of CdS nanoparticles synthesized from $Cd(CH_3COO)_2$ at (i) 190 °C, (ii) 230 °C and (iii) 270 °C for 2 h

The absorption band edges estimated from the spectra are 3.11 eV (398 nm), 3.0 eV (413 nm) and 2.83 eV (438 nm) respectively for 190 °C, 230 °C and 270 °C reaction temperatures. Other cadmium sources used in this study followed the same trend as observed for the CdCl₂ and Cd(CH₃COO)₂.

The growth of the CdS nanoparticles was also monitored as a function of time by recording the optical absorption spectrum of aliquots taken after 15 min, 30 min, 1 h and 2 h of reaction time. Figure 2.24 shows the evolution of absorption spectrum over time for the rod-like shaped CdS nanoparticles synthesized at a growth temperature of 270 $^{\circ}$ C when Cd(NO₃)₂ was used as cadmium source.



Figure 2.24. UV-Visible spectra of CdS nanoparticles synthesized from $Cd(NO_3)_2$ at 270 °C (i) 15 min (ii) 30 min (iii) 1 h and (iv) 2 h.

A distinct excitonic shoulder is observed in all spectra. The absorption band edges as estimated using the direct band gap method are 2.73 eV (454 nm, t = 15 min), 2.82 eV (440 nm, t = 30 min), 2.68 eV (464 nm, t = 1 h) and 2.62 eV (473 nm, t = 2 h). The absorption edges for all samples are blue-shifted from that of CdS bulk crystal (2.41 eV, 515 nm) [67] a clear indication of quantum size effects. These results are in agreement with the value of the reported literatures [38, 67-68, 83].

CdS nanoparticles frequently display excellent photoluminescence generally in the visible region of the electromagnetic spectrum depending on the size of CdS nanoparticles.



Figure 2.25. Photoluminescence spectra of as-prepared CdS nanocrystals from $Cd(NO_3)_2$ source at 270 °C dispersed in toluene (i) 15 min (ii) 30 min (iii) 1 h and (iv) 2 h reaction time.

Figure 2.25 shows typical room temperature luminescence spectra of CdS nanoparticles prepared from $Cd(NO_3)_2$ at 270 °C. The as-prepared CdS nanoparticles only show a band edge emission and the emission maximum appear at about 436 nm for reactions time of 15 min, 30 min, 1 h and 2 h as shown in Figure 2.25. The emission peaks of samples are identical because the fluorescence involves the same initial and final state despite differences in the reaction time. This also implies that there is only one emitting species in the samples. For all emission spectra, the peak height varies in magnitude and all the spectra have same general features.



Figure 2.26. Photoluminescence spectra of as-prepared CdS nanocrystals from CdCl₂ source dispersed in toluene at (i) 190 $^{\circ}$ C (ii) 230 $^{\circ}$ C (iii) 270 $^{\circ}$ C for 2 h reaction time.

The emission peaks of the samples have identical narrow shape, which is an indication of monodispersed particles that are well passivated. The presence of smooth single peaks is also

indicative of the existence of predominantly simple morphology. Figure 2.26 shows the room temperature photoluminescence spectra of the CdS nanoparticles from $CdCl_2$ source at the different reaction temperatures. The emission maximum for all the samples at the different reaction temperatures centre at about 436 nm as estimated from the luminescence spectra. This is also an indication that the emitting species from the nanoparticles prepared at the different reaction temperatures are the same.

2.2.5 Conclusions

HDA capped CdS nanoparticles with spherical, triangular and rod-like shape have been successively synthesized. The as-prepared CdS nanoparticles have good crystallinity and a good surface chemical environment with a narrow size distribution. The experimental results show that the morphologies of CdS nanoparticles were significantly influenced by the reaction temperature and different cadmium sources. The crystallinity of the particles was determined by X-ray diffraction which shows the phase of the particles to be predominantly hexagonal. The high resolution transmission electron microscopy images also confirm the crystalline nature of the particles with distinct lattice fringes observed. The optical absorption of the as-prepared nanoparticles is obvious blue shifted in relation to the bulk band-gap of CdS which is due to the quantum-confinement effect of CdS nanoparticles.

2.3 Zinc sulfide (ZnS)

2.3.1 Background

ZnS is an important inorganic semiconducting material occurring in nature as cubic and hexagonal wurtzite phase. At room temperature, hexagonal wurtzite and cubic has a wide band gap around 3.5–3.8 eV [84, 85]. The applications of ZnS are numerous to its credit. It has been used as base material for cathode-ray tube luminescent materials, as efficient phosphors in flat-panel displays, in thin film electroluminescent devices and infrared windows [86-91]. It is well known that the cubic phase (zinc blende) of ZnS is stable at room temperature, while the hexagonal phase (wurtzite) is a high temperature form. The equilibrium phase transformation between cubic and hexagonal phases occurs at about 1296 K [92]. Since the inherent crystal structures of ZnS have an important effect on its physical and chemical properties [93, 94], in view of its technological importance, the synthesis of ZnS nanoparticles has been a topic of interest to researchers. New synthetic routes are being explored to get phase pure material via an economically and technically viable method.

There have been many attempts in past to obtain good quality ZnS nanoaystallites by using various synthetic routes. However, most of the synthetic routes yield low quality nanoparticles having large size distribution. To obtain nanometer-sized particles, a variety of methods has been proposed, including precipitation in aqueous and organic media [95], sputtering [96], coevaporation [97], sol-gel [98, 99] solid state [100], micro-wave irradiation [101, 102], ultrasonic irradiation [103], thermal decomposition [104], hydrothermal synthesis [105], and microemulsion method [106]. Wilhemly and Matijevic [104] employed thermal decomposition of thioacetamide to prepare micrometer-sized spherical zinc sulfide particles by aging the reaction mixture several hours, using a two-step procedure in solution. Wang and Hong

have prepared ZnS nanoparticles by a solid-state reaction of zinc acetate and thioacetamide at low temperature. ZnS nanoparticles of different sizes were prepared and the particle size were varies by adjusted the reaction temperature [107]. Microwave and -irradiation techniques have also been applied to prepare ZnS nanoparticles from zinc salts using thioacetamide and thiourea as sulfur source [108, 109]. Zhao, *et al.* [110] have reported the synthesis of ZnS nanorods by a surfactant assisted soft chemistry method. By electrically driven spray pyrolysis ZnS nanoparticles were prepared from zinc nitrate and thiourea using ethyl alcohol solutions [111]

As part of the continuing effort to synthesize monodispersed nanoparticles, zinc sulfide nanoparticles with varying morphologies have been synthesized through a facile and reproducible synthetic route. The influence of experimental parameters on the final properties of the nanocrystallites is also discussed.

2.3.2 Experimental

2.3.2.1 Chemicals

Zinc chloride, zinc acetate, zinc carbonate, zinc sulphate, zinc nitrate, sodium borohydride, methanol, toluene, acetone and sulfur were purchased from Saarchem, UnivAR, Merck chemicals. Hexadecylamine, tri-n-octylphosphine oxide and tri-n-octylphosphine were purchased from Sigma-Aldrich. All the chemicals were used as purchased.

2.3.2.2 Synthesis of ZnS nanoparticles

Zinc sulfide nanoparticles were prepared as follows: In a typical reaction, sulfur powder (0.64 mmol) was mixed with deionised water (20 mL) in a three neck flask. A solution of NaBH₄ (1.58 mmol) was carefully added to this reaction mixture and the flask was immediately purged

with nitrogen to facilitate an inert atmosphere. After 12 h, zinc salt (0.64 mmol) was added to the reaction mixture. The suspension was stirred for 30 min followed by the addition of excess methanol. The resultant suspension was then centrifuged. The precipitate was dispersed in tri-noctylphosphine (6.0 mL) and injected into hot HDA (6.0 g) at 190 °C, and the reaction was allowed to continue for 2 h. After heating excess anhydrous methanol was added to the solution resulting in HDA capped ZnS nanocrystals. Several experiments were repeated with the above reaction procedure. The injection temperature was changed to 230 °C and 270 °C.

2.3.3 Results and Discussion

2.3.3.1 Structural characterization

The shape and size of the HDA capped ZnS nanoparticles formed were found to depend on the growth temperatures and the zinc sources used in forming the bulk ZnS. The TEM analyses reveal interesting changes in the morphology of the ZnS nanoparticles formed from the various zinc sources. The shapes of the ZnS nanoparticles were rod-like for all the zinc sources used except for the ZnSO₄ in which close to spherical shape particles was obtained. Agglomerated spheres were formed when ZnSO₄ was used as the zinc source and the growth temperature was carried out at 190 °C as shown in Figure 2.27(a). The agglomerated spheres formed might have been as a result of the particles not properly capped. It was difficult to determine the particle size from the TEM image, as the particles tend to agglomerate rapidly. The TEM image (Figure 2.27(b)) shows that the ZnS nanoparticles obtained at 230 °C consists of a mixture of spheres and nanorods. The average diameter of rods is 10.15 ± 3.03 nm and the length is 14.37 ± 3.02 nm. The average diameter of the sphere estimated from the TEM image is 10.18 ± 3.27 nm.



Figure 2.27. (a-c) TEM images of HDA capped ZnS from $ZnSO_4$ source at 190 °C, 230 °C & 270 °C respectively

At 270 °C, agglomerated spherical shaped particles were also formed and the average diameter of the particles is 7.17 ± 1.09 nm as shown in Figure 2.20(c).

Figure 2.28 showed the TEM images of the well-defined nanoparticles of as-prepared ZnS when $Zn(NO_3)_2$ was used as zinc source. TEM images (Figure 2.28(a and b)) reveal that particles obtained at 190 °C and 230 °C consist of monodispersed nanorods.



Figure 2.28. (a-c) TEM images of HDA capped ZnS from $Zn(NO_3)_2$ source at 190 °C, 230 °C & 270 °C respectively

The average lengths of rods are 25.12 ± 3.35 nm and 34.16 ± 9.01 nm for the reaction temperature of 190 °C and 230 °C respectively. The average widths of these rods were in the range of 19-26 nm. Attempts to grow ZnS nanoparticles at 270 °C in the presence of HDA
resulted in large aggregated and isolated nanorods with average length and width of about 218.11 \pm 26.35 nm and 132.41 \pm 25.32 nm respectively

When $ZnCl_2$ was used as zinc source, the products obtained at the three different growth temperatures were predominately rod-like in shape with very few spheres in the domain.



Figure 2.29. (a-c) TEM images of HDA capped ZnS from $ZnCl_2$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped CdS from $ZnCl_2$ at 190 °C

The morphologies of the ZnS nanoparticles obtained at the different reaction temperatures are shown in Figure 2.29(a-c). At 190 °C, nanorods with average width of 6.14 ± 2.06 nm and average lengths of 27.38 ± 4.02 nm were obtained (Figure 2.29(a)). At 230 °C, nanorods with average length and width of 25.05 ± 7.13 nm and 5.24 ± 1.25 nm respectively were obtained (Figure 2.29(b)). Rod-like particles with a slight decrease in length were obtained at 270 °C. The average length and width of the particles as estimated form the TEM image are 22.07 ± 5.19 nm and 17.28 ± 4.04 nm respectively (Figure 2.22(c)). Figure 2.29(d) shows the HRTEM image of the particles formed at 190 °C. It shows the two primary nuclei combining together to form the nanorod particles.

The ZnS nanoparticles formed when Zn(CH₃COO)₂ was used as zinc source were nearly monodispersed and their average length given by the TEM analysis are 43.35 ± 17.23 , $272.16 \pm$ 72.08 and 113.24 ± 47.13 nm for the 190 °C, 230 °C and 270 °C respectively (Figure 2.30(a-c)). The average width of the particles from the different reaction temperatures are 35.07 ± 15.33 , 199.02 ± 48.26 and 73.37 ± 19.41 nm, respectively. There was an initial increase in the length and width of particles formed when the reaction temperature changes from 190 °C to 230 °C and decreases at 270 °C. It seems that the nucleation and growth processes were uncontrolled. The seeds (nuclei) formed during nucleation were highly active and had the tendency to combine with each other to grow into larger nanoparticles. In the HRTEM image, lattice fringes can be clearly observed, which indicates that the particles are crystalline (Figure 2.30(d)).



Figure 2.30. (a-c) TEM images of HDA capped ZnS from $Zn(CH_3COO)_2$ source at 190 °C, 230 °C & 270 °C respectively and (d) HRTEM image of HDA capped ZnS from $Zn(CH_3COO)_2$ at 230 °C

Attempts to synthesize ZnS nanoparticles from the preformed bulk ZnS in the presence of TOPO ended in particles which were unable to assemble on the carbon coated copper grid. This was also evident from the optical absorption spectra, which in all cases, are broad and featureless.

The XRD patterns of the ZnS nanoparticles prepared from the ZnCl₂ and Zn(NO₃)₂ sources in Figure 2.31, reveal the cubic zinc blende structure of ZnS. The three peaks correspond to the (111), (220), and (311) lattice planes, respectively. It is known that decrease in particle size results in a broadening of the diffraction peaks. The broadening of X-ray diffraction peaks is an indication of the nanosized particles. The XRD patterns of the ZnS nanoparticle synthesized from the ZnSO₄ and Zn(CH₃COO)₂ sources were also study. The XRD patterns are shown in Figure 2.32. The diffraction peaks match perfectly with the (111), (220) and (311) crystalline planes of cubic ZnS, indicating the formation of ZnS nanoparticles.



Figure 2.31. XRD patterns of the HDA capped ZnS nanocrystals from (a) ZnCl₂ and (b) $Zn(NO_3)_2$ at 230 $^{\circ}C$



Figure 2.32. XRD patterns of the HDA capped ZnS nanocrystals from: (a) ZnSO₄ and (b) $Zn(CH_3COO)_2$ at 230 $^{\circ}C$

2.3.4 Optical properties

The band gap energy in nanoparticles could be obtained from the absorption maxima. Electrons in the conduction band and holes in the valence band are spatially confined by the potential barrier of the surface according to quantum confinement theory. Due to confinement of both electrons and holes, the lowest energy optical transition from the valence to conduction band will increase in energy, effectively increasing the band gap. The shoulder or peak of the spectra corresponds to the fundamental absorption edges in the nanoparticles and could be used to estimate the band gap of the nanomaterial [112].



Figure 2.33. UV-Visible spectra of CdS nanoparticles synthesized from $Zn(CH_3COO)_2$ at 270 °C (i) 15 min (ii) 30 min (iii) 1 h and (iv) 2 h.

Measurements from the absorption peaks (Figure 2.33) gave the estimated band gap as 3.44 eV (361 nm), 3.45 eV (360 nm), 3.47 eV (358) and 3.48 eV (357 nm) for the 15 min, 30 min, 1 h and 2 h, respectively for aliquot samples from $Zn(CH_3COO)_2$ source. The excitonic feature of the 15 min and 30 min samples are not very pronounced compared to the 1 h and 2 h samples. A blue shift of the absorption edge of the samples from their bulk value of 3.71 eV (334 nm) of ZnS is clearly observed [113]. The blue shift in the band edge is a consequence of exciton confinement and confirms the presence of nanoparticulate materials.

Figure 2.34 shows the photoluminescence spectra of the as-prepared ZnS nanoparticles prepared from $Zn(CH_3COO)_2$ source at the three different reaction temperatures in toluene.



Figure 2.34. Photoluminescence spectra of as-prepared ZnS nanoparticles from Zn(CH₃COO)₂ source dispersed in toluene (i) 190 °C (ii) 230 °C (iii) 270 °C nanoparticles.

The photoluminescence peaks were narrow with emission maximum at 426 nm, markedly blue shifted relative to that of the bulk ZnS. This might be due to the quantum size effect of the ZnS The PL peak centered at 426 nm is attributed to the presence of sulfur vacancies in the lattice [113].

2.3.5 Conclusions

In summary, ZnS semiconductor nanoparticles were successfully synthesized varying the temperature and zinc sources. HDA showed moderately good capping ability for the nanoparticles. The morphology of the ZnS nanoparticles were mostly agglomerated spherical or rod-like shaped particles while some gave mixture of both shaped. The XRD patterns exhibited the cubic zinc blende structure of ZnS for the samples analysed and no other crystalline phase was detected. Optical absorption and photoluminescence spectra of the as-prepared nanoparticles were strongly blue-shifted due to quantum confinement effect.

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CHAPTER THREE

Synthesis and characterization of core-shell semiconductor nanoparticles

3.1 Background

The size-dependent optical properties of nanoparticless have been the focus of significant research over the past two decades. Currently, tailored and multifunctional nanostructured materials that comprise two or more different components are at the forefront of research on nanomaterials due to the possibility of the combination and integration of material properties together from the viewpoint of technique requirements, which are not usually attainable in single-component nanoparticles [1-9]. In particular, multicomponent nanoparticles with a coreshell structure have aroused special interest, due to their fascinating and tailored properties for various applications in the areas of electronics, photonics, catalysis, biotechnology, magnetics, luminescence, fluorescent biological labels and lithium-ion batteries [5-12]. Semiconductor core–shell system represents another interesting direction towards functional nanostructures with enhanced structural and property tunability.

Core-shell semiconductor nanomaterials are a group of nanoparticless that consist of the quantum dot core and a shell of a distinct semiconducting material. Their sizes fall within the range 20-200nm. They are unique because of their easily modular properties due to their size. Core-shell semiconductor nanomaterials came about when there was a need to improve the nanocrystals surface passivation by growing a second semiconductor on it. Nanoparticles also known as quantum dots are composed of an inorganic core, made up of between a few hundred and few thousands atoms, surrounded by an organic ligand bound to the surface. The small size of the nanoparticles makes them exhibit an increase in band gap accompanied by the quantization of energy levels to discrete values which are referred to as quantum confinement

effect. This effect brings about the exaltation of the couloumb interaction between charge carriers which modifies the processes of intraband and interband relaxation. The small size of the nanoparticles also results in a very high surface-to-volume ratio. But a significant part of the organically capped core nanoparticles exhibit surface related trap states acting as fast non-radiative de-excitation channels for photogenerated charge carriers, as a result reducing the fluorescence quantum yield. Core shell nanoparticles have improved fluorescence efficiency and stability against photo-oxidation. The use of the appropriate choice of the core and shell material makes it possible for the emission wavelength to be tuned in a larger spectral window than with both materials alone [1, 2].

Depending on the relative position of band gaps of the core and shell materials, there are three types of core/shell nanomaterial. The three types identified are namely type-I, reverse type-I, and type-II band alignment. In the type I, the band gap of the shell material is larger than that of the core and both electrons and holes are confined in the core. In the reserve type I, the band gap of the shell material is smaller than that of the core and, depending on the thickness of the shell, the holes and electrons is partially or completely confined in the shell. In the type II, either the valence-band edge or the conduction band edge of the shell material is located in the band gap of the core. Upon excitation of the nanoparticles, the resulting staggered band alignment leads to a spatial separation of the hole and the electron in different regions of the core-shell structure [13].

The shell is used to passivate the surface of the core in the type I core-shell system and the main aim is to improve its optical properties. The shell of the nanocrystals physically separates the surface of the optically active core from its surrounding medium. The consequence of this separation is that the sensitivity of the optical properties to changes in the local environment of the nanoparticles' surface, caused by the presence of oxygen or water molecules, is reduced. With respect to core nanoparticles, core-shell systems exhibit generally enhanced stability against photodegradation. At the same time, shell growth reduces the number of surface dangling bonds, which can act as trap states for charge carriers and thereby reduce the fluorescence quantum yield. The first published type of this system was CdSe/ZnS [14]. The ZnS shell significantly improves the fluorescence quantum yield and stability against photobleaching. The shell growth was accompanied by a small red shift of the excitonic peak in the UV-Vis absorption spectrum and the photoluminescence wavelength.

For reverse type I core-shell systems, a material with smaller band gap is overgrown onto the core with a larger band gap. The charge carriers are therefore partially delocalized in the shell and the emission wavelength can be tuned by the shell's thickness. A significant red-shift of the band gap with the shell thickness is generally observed. The most extensively analyzed systems of this type are CdS/HgS, CdS/CdSe and ZnSe/CdSe [15-17].

In type II core-shell systems, both band gap values and band offset allow one carrier to be localized in the shell while the other is localized in the core. The shell growth is aim at a significant redshift of the emission wavelength of the nanoparticles. This band alignment leads to a smaller effective band gap than each one of the constituting core and shell materials. The interest of these systems is the possibility to manipulate the shell thickness and thereby tune the emission colour towards spectral ranges, which are difficult to attain with other materials. Type II core-shell nanoparticles have been developed in particular for near-infrared emission. Examples of type II core-shell are CdTe/CdSe, CdSe/ZnTe, CdSe/CdS, CdS/ZnSe and ZnTe/CdSe [7, 18-20]. Both type I and type II materials have been the object of recent theoretical studies, giving further insight into the electronic structure of these systems [21–23].

The major challenge in synthesizing good crystalline quality of core-shell nanoparticles will required the understanding of how to form an interface between materials which may have different crystallographic structures, lattice dimensions, thermal stability as well as chemical reactivity. In this present chapter, we report the selective growth of two different core-shell nanoparticles produced by a two-step synthetic procedure which exclude the purification of core material before the deposition of the shell material. The procedure used in this work is simple and reproducible

3.2 Experimental

3.2.1 Chemicals

All reagents and solvents were analytical grade and used without further purification. Hexadecylamine (HDA), tri-*n*-octylphosphine (TOP), sulfur and selenium were purchased from Sigma-Aldrich. Methanol, cadmium nitrate, zinc chloride and acetone were purchased from Saarchem, UnivAR, Merck chemicals.

3.2.2 Preparation of CdS/ZnSe core-shell nanoparticles

The core-shell nanoparticles are typically synthesized in a two-step procedure. The preformed core and shell bulk samples are synthesized separately in the first procedure. In this reaction, selenium/sulphur powder (0.320 mmol) was mixed with deionised water (20.0 mL) in a three necked round bottom flask under a nitrogen atmosphere. The sulphur/selenium was reduced by the addition of a solution (20.0 mL) of sodium borohydride (0.030 g, 0.320 mmol). The reaction was allowed to proceed for 3 h and 12 h in order to allow the complete reduction of selenium and sulphur respectively. Then 0.64 mmol of the different metal chlorides dissolved in 20 mL deionised water was added to the sulphide ion solution to give a brownish-black solution.

The solution was stirred for 30 minutes followed by the addition of excess methanol. The resultant solution was then centrifuged and decanted to isolate the solid products which were dispersed into 6 mL TOP. In the second procedure, the preformed CdS core bulk sample is injected into hot HDA at 230 °C and thermolysed for 1 h or 2 h. Then the preformed ZnSe shell bulk sample is added to the reaction mixture and the reaction is allowed to continue for another 1 h or 2 h. The reaction was quenched by adding excess methanol to the solution. The flocculate was separated from the supernatant by centrifugation. The resultant CdS/ZnSe core-shell nanoparticles were dissolved in toluene for characterization.

3.2.3 Preparation of CdSe/CdS core-shell nanoparticles

Similarly, CdSe/CdS core-shell was prepared using the same procedure used for CdS/ZnSe nanoparticles. In a typical reaction, selenium/sulphur powder (0.320 mmol) was mixed with deionised water (20.0 mL) in a three necked round bottom flask under a nitrogen atmosphere and reduced by the addition of a solution (20.0 mL) of sodium borohydride (0.030 g, 0.320 mmol). The mixture was stirred at room temperature for 3 h and 12 h for the complete reduction of selenium and sulphur respectively. Then 0.64 mmol of cadmium chlorides dissolved in 20 mL deionised water was added to the selenide/sulphide ion solution to give reddish and brownish-black solution for CdSe and CdS respectively. The solution was stirred for 30 minutes followed by the addition of excess methanol. The resultant solution was then centrifuged and decanted to isolate the solid products which were dispersed into 6 mL TOP. The preformed bulk CdS sample is added to the reaction mixture and the reaction is allowed to continue for another 1 h or 2 h. The reaction was quenched by adding excess methanol to the

solution. The flocculate was separated from the supernatant by centrifugation. The synthesized CdSe/CdS core-shell nanoparticles were dispersed in toluene for further characterization.

3.2.3 Characterization of core-shell nanoparticles

The synthesized core-shell nanoparticles were characterized using the same set of instruments used for organically soluble nanoparticles mentioned in Chapter 2 under sections 2.1.2.3 to 2.1.2.5.

3.3 Results and Discussion

3.3.1 CdS/ZnSe nanoparticles

The preformed core and shell bulk samples were prepared by a simple procedure, which involved the reduction of sulfur or selenium powder with NaBH₄ in water, followed by the addition of metal chlorides source as the metal precursors. The preformed bulk samples were dispersed in TOP ready to be injected to a hot coordinating solvent (HDA). The fabrication of the core-shell nanoparticles was achieved by a one-pot synthetic procedure. The preformed core bulk material was first themolyzed in hot HDA and the shell material is added to the mixture after 1h or 2 h reaction time and the reaction was allowed to continue for another 1 h or 2 h. Different morphologies were obtained by varying the time of reaction.

2.3.1.1 Structural characterization

The sizes and shapes of the core-shell nanoparticles were examined by TEM. Figure 3.1 shows TEM images of CdS/ZnSe core-shell nanoparticles prepared 1 h and 2 h after the addition of the shell material (ZnSe). All the particles are uniform and well dispersed on the copper grid

without any large aggregations. The core-shell nanoparticles formed after 1 h of the addition of ZnSe consist of close to spherical particles and the average diameter of the particles is 4.72 ± 1.54 nm (Figure 3.1a). The CdS/ZnSe core-shell obtained after growth time of 2 h was found to consist of a mixture of rod-like and close to spherical nanostructures (Figure 3.1c). The average diameter of the spherical core-shell particles estimated from the TEM image was about 5.94 ± 2.31 nm, indicating that the size increases as the reaction time is increased. The average length and width of the rod-like particles formed in the 2 h reaction time are 14.17 ± 3.18 nm and 4.30 ± 1.26 nm respectively. The crystallinity of the CdS/ZnSe core-shell nanoparticles is confirmed with clear lattice fringes observed in the HRTEM images as shown Figure 3.1b & d. They showed distinct lattice fringes and stacking faults extending throughout the entire nanoparticles which are an indication of epitaxial growth.

To prepare core-shell nanostructures by epitaxial growth, the existing nuclei should be able to withstand the conditions under which the second phase is being deposited and the surface energies of the two phases should be sufficiently similar so that the barrier for heterogeneous nucleation of the second phase is lower than the homogeneous nucleation. If the shell material exposes lower energy surfaces or attains good crystallographic matching with the core material, then its deposition will likely take place over the entire surface of the core, resulting in a uniform coverage. It is evident from the TEM images that the ZnSe shell uniformly covers the entire surface of the CdS core material. There was no evidence nor clear interface between the core and shell form the TEM images but the nanoparticles remained fully crystalline with some faceted shapes particles.



Figure 3.1 TEM and HRTEM images of the CdS/ZnSe core-shell nanoparticles prepared (a and b) 1 h and (c and d) 2 h reaction time after the addition of the ZnSe shell material.



Figure 3.2 XRD patterns of the nanoparticles (a) CdS core and (b) CdS/ZnSe core-shell for 2 h

Powder X-ray diffraction patterns of the core CdS and core-shell CdS/ZnSe nanoparticles are shown in Figure 3.2. The XRD patterns show broad peaks along the (111), (220) and (311) reflections which are assigned to the cubic phase structure. It is observed that both the core material and the core-shell nanoparticles are of the cubic zinc blended structure, suggesting that diffraction is predominantly due to the CdS core. A similar result has been previously reported [24]. The extra unlabelled peaks may be due to the unreacted starting materials. All the diffraction peaks showed similar broadening which is a characteristic of crystalline nature of the nanoparticles.

3.3.1.2 Optical properties

In the synthesis of core-shell nanoparticles, there is a possible for alloy nanomaterials to be formed. The optical properties of the nanoparticles formed can be used to differentiate between the two components. The epitaxial growth of a shell around a core nanoparticle modifies the optical properties of the core-shell nanoparticles. It has been reported that the differences observe in the optical properties of the core-shell nanoparticles when compared with those of the core nanoparticles could provide evidence for shell growth.

Figure 3.3 and 3.4 show the absorption spectra of CdS core and the CdS/ZnSe core-shell nanoparticles for 1 h and 2 h reaction time respectively. The core absorption spectrum is characteristic of well-disperse nanoparticles with band edge significantly blue shifted from the bulk values (515 nm, 2.41 eV). The observed red shifts in the absorption spectra of CdS/ZnSe nanoparticles of 164 nm compare to the core CdS (432 nm, 2.87 eV) for 1 h reaction time and 125 nm compared to the CdS (484 nm, 2.56 eV) for 2 h reaction time are strong indication for the formation of core-shell nanoparticles. These results corroborate with the estimated size from

the TEM images of the CdS/ZnSe nanoparticles. The decrease in the band edge of CdS/ZnSe nanoparticles from 1 h to 2 h reaction time corresponds to the increase observed in thieir sizes. This is due to quantum confinement in the nanoparticles synthesized.

The photoluminescence spectrum of the CdS/ZnSe core/shell nanoparticles synthesized at 2 h reaction time shows emission close to the absorption band edge. The emission maximum of the CdS/ZnSe is centered at 614 nm, with that of the CdS at 435 nm (Figure 3.5). The emission maximum of CdS/ZnSe shows red shift in relation to the emission maximum of CdS, which is consistent with the red shifts observed in the absorption spectra. The core/shell nanoparticles also show enhanced emission peak compared with CdS core. The strong luminescence demonstrated the influence of surface improvement and the sharpness of the emission peak showed the monodispersed nature of the core-shell nanoparticles.



Figure 3.3 UV-Vis spectra of nanoparticles (a) CdS core and (b) CdS/ZnSe core-shell for 1 h



Figure 3.4 UV-Vis spectra of nanoparticles (a) CdS core and (b) CdS/ZnSe core-shell for 2 h



Figure 3.5 PL spectra of nanoparticles (a) CdS core and (b) CdS/ZnSe core-shell

3.3.2 CdSe/CdS nanoparticles

3.3.2.1 Structural Characterisation

Figure 3.6 shows the TEM images of CdSe/CdS core-shell nanoparticles prepared 1h and 2 h after the addition of the shell material (CdS). The TEM images clearly indicate that the asprepared CdSe/CdS show spherical morphology with good monodispersity of nanoparticles. The formation of crystalline CdSe/CdS nanocrystals with uniform sizes is also observed from the TEM images. The particles sizes of these spherical are 4.91 ± 1.50 nm and 7.53 ± 2.46 nm for 1 h and 2 h samples respectively (Figure 3.6a & c). The epitaxial growth of CdS on the surface of the CdSe has been reported in the literature [22]. Purification of the core material was necessary to facilitate the growth of the shell material. In this present study, the CdSe core material do not require any post-purification to facilitate the growth of the CdS shell unto the core material to form the core-shell nanoparticles. The HRTEM images in Figure 3.5b & d showed that the CdSe/CdS core-shell nanoparticles were well-defined with observable lattice fringes. The lattice fringes stretch through the entire nanoparticles, indicating that the CdS shell material did not disturb the crystallinity of the nanoparticles. These observations indicate high degree of extended structural order resulting from epitaxial growth. The XRD pattern of the CdSe (core particles) correspond to that of bulk cubic CdSe without any indication of the hexagonal phase formation (Figure 3.7a). The CdSe/CdS core-shell nanoparticles diffraction patterns were similar to that of the CdSe core patterns (Figure 3.7a). The unreacted starting materials may account for the extra peaks observed in the XRD patterns of the core and core-shell nanoparticles.



Figure 3.6 TEM and HRTEM images of the CdSe/CdS core-shell nanoparticles prepared (a and b) 1 h and (c and d) 2 h reaction time after the addition of the CdS shell material.



Figure 3.7 XRD patterns of the nanoparticles (a) CdS core and (b) CdSe/CdS core-shell for 2 h

3.3.2.2 Optical properties

The absorption spectra for CdSe and CdSe/CdS nanoparticles synthesized at 1 h reaction time are shown in Figure 3.8. The band edge of CdSe/CdS is at 586 nm (2.12 eV), a red shift of 8 nm compared to that of CdSe (578 nm, 2.15 eV). A red shift in band edge was also observed for the particles synthesized at 2 h reaction time. The band edge of CdSe/CdS for 2 h reaction time is at 650 nm (1.91 eV), a red shift of 38 nm compared to that of CdSe (612 nm, 2.03 eV) as shown in Figure 3.9. This red shift at both reaction times indicates the formation of core-shell nanoparticle. Delocalization of the electron and hole wave functions into CdS results in a red shift of excitonic peaks in the CdSe/CdS nanoparticles.

The luminescence characteristics of the CdSe core and the CdSe/CdS core-shell nanoparticles for 2 h reaction time were also studied. Figure 3.10 shows the room temperature photoluminescence spectra of both the CdSe and the CdSe/CdS nanoparticles. It is obvious from the spectra that the intensity of the emission maximum is considerably increased in the core-shell nanoparticles as compared to the core material. The emission maximum of the CdSe/CdS is at 647 nm and that of CdSe is at 594 nm. A red shift observed in the emission maximum of the core-shell nanocrystals in relation to the emission maximum of core, which is in good agreement with the observation from absorption spectra; confirm the formation of core-shell nanocrystals. Therefore, based on the above optical properties, it can be confirmed that the as-synthesized nanocrystals in this study belong to the core-shell structure and not alloy structure. In alloy nanostructure, a linear blue shift in the absorption edge and emission maximum will occur with the gradual incorporation of the shell material.



Figure 3.8 UV-Vis spectra of nanoparticles (a) CdSe core and (b) CdSe/CdS core-shell for 1 h







Figure 3.10 PL spectra of nanoparticles (a) CdSe core and (b) CdSe/CdS core-shell for 2 h

3.4 Conclusions

A synthetic procedure has been developed for the fabrication of highly luminescent colloidal types I and type II core-shell nanoparticles without the purification of the core material. The X-ray diffraction patterns confirm cubic structure for both core and core-shell semiconductor nanoparticles. The observed red shift in the absorption and photoluminescence spectra of the core-shell nanoparticles compared to the core materials is a strong indication for the formation of core-shell nanoparticles. From the PL spectra, the intensities of the emission maximum are considerably increased in the core-shell nanoparticles as compared to the core materials.

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CHAPTER FOUR

Synthesis and characterization of water soluble semiconductor nanoparticles 4.1 Background

The ability to have a control over the reaction parameters to synthesize nanoparticles in order to tailor their size, morphology and properties has captured the attention of material chemists. The remarkable advances made in the field of nanoscience have enable scientists to develop nanomaterials with better properties, more functionality and at low cost than the existing ones. Progress made in the synthesis of fluorescent semiconductor nanoparticles, together with a better understanding of their photophysical properties and the development of biocompatible surface chemistries for their solubilization, have provided new imaging probes with enormous potential for scientists in the biological sciences. Researchers in the life sciences have started to use these nanomaterials in different applications such as diagnosis of diseases, gene therapies and biotechnology [1-7].

However, for nanoparticles to be useful in a biological system, they must be water soluble and stable at various pH values ranging from 5 to 9. Water solubilisation of nanoparticles is essential for many biological applications. It may be carried out either as the final stage of the functionalisation process of nanoparticles, or as an intermediate stage. Traditionally, colloidal synthetic methods for producing semiconductor nanoparticles have been based on the use of organic stabilizers to cap the surface atoms of nanoparticles in order to control the growth process [8, 9]. These methods generally use surfactants such as trioctylphosphine oxide, long-chain amines or long-chain carboxylic acid as capping agents, which produce hydrophobic nanoparticles which are not compatible with the biological environment or the biomolecules to which the nanoparticles are to be linked. The most common methods for producing water-soluble without affecting key properties are mostly based on exchange of the original hydrophobic surfactant layer with a hydrophilic one or the addition of a second layer such as the amphiphilic molecules, which may also contain another functional group [10, 11]. Other methods that have been used to increase water solubility of nanocrystals include encapsulation in phospholipid micelles [12], addition of dithiothreitol [13], organic dendron [14, 15] and oligomeric ligands [16]. Silica and mercaptopropionic acid (MPA) have also been used [10, 17] and they allow bioconjugation to ligands of interest. Mercaptopropionic acid achieves this through free carboxylic group (-COOH) and silica through the presence of thiol groups (-SH) on its surface. It has been reported that the TOPO ligand on semiconductor nanoparticles surface may be replaced with heterobifunctional linker molecules, which provides both hydrophilic character and functional groups for further bioconjugation [17, 18]. This method was found to be applicable to a wide range of bifunctional compounds containing sulf-hydryl groups [19–21] and for linker molecules such mercaptoacetic acid, mercaptosuccinic acid, glutathione, dithiothreitol, and histidine.

Gaponik, et al. [22] have studied the effect of 3-mercaptopropionic acid and thioglycolic acid on the quantum yield of semiconductor nanocrystal after ligand exchange. They showed that CdTe nanoparticles had better quantum yields with thioglycolic acid as capping agent than with 3-mercaptopropionic acid as the capping agent. Deng, et al. [23] have synthesised water soluble PbS nanoparticles using dihydrolipoic acid, a non-toxic biocompatible capping agent as a stabilizer. Zhao, et al. [24] have also reported the synthesis of water-soluble thiol-capped PbS nanoparticles stabilized with 1-thioglycerol, dithioglycerol, or а mixture of 1thioglycerol/dithioglycerol (TGL/DTG) via a one-pot synthesis at room temperature. The growth of colloidal ZnS nanoparticles in aqueous solution has been extensively investigated in presence

of two water-soluble thiols, cysteine and mercaptoethanol as biostabilizers. The growth rate was found to vary linearly with the average radius of growing nanoparticles [25]. Peng and coworkers have described a one pot synthetic method for preparing water soluble CdTe/CdS nanoparticles using thioglycolic acid as the capping agent [26]. It has been shown that ligand exchange improves the quantum yields of oleic acid capped CdS nanoparticles [28].

Recently, several articles have reported the progress made in the synthesis of fluorescent semiconductor nanoparticles with a better understanding of their photophysical properties. The unique optical properties of these colloidal semiconductor nanocrystals have made them exceptional biological markers. Beato-López, et al. [29] has optimized a synthetic process to obtain glutathione-capped fluorescent CdS nanoparticles which are used to specifically detect glutathione S-transference(GST)- tagged proteins. An aqueous phase synthesis of highly luminescent glutathione-capped CdS nanocrystals by the reaction of Cd²⁺ and thiourea has been investigated by Zhou, et al. [30]. The pH value and Cd-to-ligand molar ratio play a crucial role in determining luminescent properties of the obtained CdS nanoparticles. Xue, et al. [31] have successfully transferred oil-soluble oleic acid-capped NIR-emitting PbS nanoparticles into water using four different strategies ie. via micelles, nanohydrogels, amphiphilic polymers and watersoluble thiol small molecules. Among all these phase transfer agents, N-succinyl-N0-octyl chitosan micelles and glutathione (thiol) molecules were able to retain the optical property of the initial oil-soluble PbS nanoparticles (PL quantum yield was 30 % in water) while the nanohydrogel and amphiphilic polymers water-soluble ones display relatively weak fluorescence emission.

There have been serious concerns raised regarding the cytotoxicity of the semiconductor nanoparticles containing heavy-metal elements [32-34]. These heavy-metal elements can be

potent toxins and neurotoxins depending on the dosage, complexation, and accumulation in the liver and the nervous system. ZnS nanocrystals have been considered as a good candidate to replace the heavy metals contained in semiconductor nanoparticles. Zinc is not hazardous to human body and an average adult ingests 10-15 mg of zinc daily as a nutrient. It has been reported that ZnSe nanocrystals doped with manganese or copper can cover a similar emission range as that of CdSe nanocrystals [35-37]. The synthesized ZnSe nanocrystals were found to less sensitive to environmental changes such as thermal, chemical, and photochemical disturbances. Zhang, *et al.* [38] have successfully synthesized lysozyme-capped ZnS nanoparticles by a simple biomolecule-assisted biomimetic method at room temperature. Different template concentrations of lysozyme were used to investigate the influence of biomolecule on the formation of nanoparticles.

There remains a critical need to investigate a direct aqueous synthesis route that is benign to the environment, simple, cost-effective and friendly to human health, which will produce highly luminescent water-soluble nanoparticles that are well dispersed and ready for bioapplications. This chapter deals with the synthesis and characterization of cysteine-capped metal sulfide nanoparticles through a facile and cost-effective method. This method also compiled with green chemistry protocol. The synthesized cysteine-capped metal sulfide nanoparticles are stable to all environment factors over a long period of time.

4.2 Experimental

4.2.1 Chemicals

All reagents and solvents were analytical grade and used without further purification. Sulfur and selenium powder were purchased from Sigma-Aldrich. Methanol, Cadmium chloride, zinc chloride, lead chloride and acetone were purchased from Saarchem, UnivAR, Merck chemicals.

4.2.2 Preparation of cysteine-capped CdS nanoparticles

Cysteine-capped CdS nanoparticles were synthesized using one-pot synthetic approach directly in aqueous medium. In a typical room temperature reaction, 0.64 mmol of sulphur was mixed with 20ml of deionised water in a three necked round bottom flask. 1.58 mmol of sodium borohydride was added to this mixture under an inert atmosphere. This was followed by the addition of 20 ml aqueous solution molar ratio 1:20 (CdCl2: Cysteine) of metal salt and 40ml of L-cysteine ethyl ester hydrochloride after 12 h. The pH of the solution was varied just after the addition of the CdCl₂ and L-cysteine ethyl ester hydrochloride with either hydrochloric acid or ammonia to just the pH's to 4, 7 and 11. The solution was then heated at 90 °C for 6 h under nitrogen. The Cysteine-capped CdS was separated from the mixture by filtration and then acetone was added to precipitate out the particles.

4.2.3 Preparation of cysteine-capped ZnS nanoparticles

Following the same procedure described above, 0.64 mmol of sulphur was mixed with 20ml of deionised water in a three necked round bottom flask. 1.58 mmol of sodium borohydride was added to this mixture under nitrogen flow. Then 20 ml aqueous solution molar ratio 1:20 (ZnCl₂: Cysteine) was added after 12 h of reaction time. The pHs of the solution were adjusted with either hydrochloric acid or ammonia to pH's 4, 7 and 11 just after the addition of the ZnCl₂ and L-cysteine ethyl ester hydrochloride. The solution was then heated at 90 $^{\circ}$ C for 6 h under

nitrogen. The cysteine-capped ZnS was separated from the mixture by filtration and then acetone was added to precipitate out the particles.

4.2.4 Preparation of cysteine-capped PbS nanoparticles

Cysteine-capped PbS nanoparticles were synthesized using the same method described above. 0.64 mmol of sulphur was mixed with 20ml of deionised water in a three necked round bottom flask and 1.58 mmol of sodium borohydride in dissolved in 20 ml of water was added to this mixture under nitrogen atmosphere. 20 ml aqueous solution of molar ratio 1:20 (PbCl₂: Cysteine) was then added after 12 h of reaction time. The pHs of the solution were adjusted with either hydrochloric acid or ammonia to pH's 4, 7 and 11 just after the addition of the ZnCl₂ and L-cysteine ethyl ester hydrochloride. The solution was then heated at 90 °C for 6 h under nitrogen. The Cysteine-capped PbS was separated from the mixture by filtration and then acetone was added to precipitate out the particles.

4.2.5 Characterization of water soluble nanoparticles

The instruments used for the characterization of the as-synthesized water soluble nanoparticles have been described in chapter under the sessions 2.1.2.3 to 2.1.2.5.

4.3 Results and discussion

Cysteine-capped metal sulfide nanoparticles were produced by a simple, inexpensive and reproducible colloidal aqueous synthetic route. The pH of the cysteine-capped metal sulfide nanoparticles were varied to see the effect on the morphologies of the nanoparticles formed. The surfactant used has the ability to control the size and morphology of the growing nanoparticles through charge transfer and lowering of surface tension. It contains ionisable carboxylic and amine functional groups and this amino acid moiety is responsible for the water solubility nature of the nanoparticles formed.

4.3.1 Cysteine-capped CdS nanoparticles

Cysteine-capped CdS nanoparticles were successfully synthesized by the addition of aqueous solutions of cadmium chloride and L-cysteine ethyl ester hydrochloride, to a freshly prepared NaHS solution. The reactions were refluxed at 90 °C for 6 h under nitrogen atmosphere. The formation of the Cysteine-capped CdS nanoparticles could be expressed as followed:

$$4\text{NaBH}_{4} + 2\text{S} + 7\text{H}_{2}0 \xrightarrow{\text{R.T}} 2\text{NaHS} + \text{Na}_{2}\text{B}_{4}\text{O}_{7} + 14\text{H}_{2} \qquad (4.1)$$

$$2\text{NaHS} + \text{CdCl}_{2} \xrightarrow{\text{Cysteine}} \text{Cysteine-capped CdS} + \text{NaCl} + \text{HCl} \qquad (4.2)$$

4.3.1.1 Structural Characterization

Figure 4.1(a–c) shows the TEM images of the cysteine-capped CdS nanoparticles synthesized at pH 4, 7 and 11. The TEM images show that spherical particles are obtained and the average diameters of the nanoparticles depend on the pH value used in the preparation. The cysteine-capped CdS nanoparticles formed at pH 4 and 7 were monodispersed with average sizes of 5.34 \pm 1.07 nm and 4.13 \pm 1.88 nm respectively.



Figure 4.1 TEM images of cysteine-capped CdS nanoparticles at (a) pH 4, (b) pH 7 and (c) pH 11

The TEM image in Figure 4.1c shows that the cysteine-capped CdS nanoparticles formed at pH 11 aggregated to some degree in the matrix of the biomolecule. This may be attributed to the fact that the carboxylic acid group of the cysteine molecule can be dehydrogenized more easily at this pH making the surface to become highly charged and resulting in the clustering of the nanoparticles as shown in Figure 4.1c. The size of the particles was difficult to be estimated from the TEM image due to aggregation of the nanoparticles. The HRTEM image provided further insight into the structural features of these cysteine-capped CdS nanoparticles. Figure 4.2 shows the HRTEM image of cysteine-capped CdS nanoparticles prepared at pH 7. The appearance of distinct lattice fringes in the HRTEM image indicates that the nanoparticles are single crystals rather than poly-crystalline aggregates.



Figure 4.2 HRTEM image of cysteine-capped CdS nanoparticles at pH 7



Figure 4.3 XRD patterns of cysteine-capped CdS nanoparticles at pH 7

The obtained XRD pattern of the cysteine-capped CdS nanoparticles is shown in Figure 4.3. It is indicated that the present cysteine-capped CdS nanoparticles have a cubic zinc blend crystalline structure with the (111), (220), (311) planes visible.

4.3.1.2 Optical properties

Figure 4.4(a-c) shows the UV-Vis absorption spectra of the cysteine capped CdS synthesized at different pH values. The optical band-gaps are located at approximately 449 nm (2.76 eV), 421 nm (2.94 eV) and 413 nm (3.00 eV) for the pH 4, 7, and 11 respectively. For all the samples, the excitonic absorption onset clearly shows a blue shift in comparison with that of bulk CdS at 512 nm (2.42 eV) irrespectively of the pH values.



Figure 4.4 UV-Vis spectra of cysteine-capped CdS nanoparticles (a) pH 4 (b) pH 7 and (c) pH 11

This shift of the absorption band, which corresponds to an increase in the energy gap between the valence and conduction bands of the semiconductor, provides evidence for the quantum confinement in these nanoparticles. The existence of such quantum confinement is indicative of the cysteine efficiency as a capping agent for CdS nanoparticles. It's implied that cysteine constitutes an effective molecule for the passivation and functionalization of the surface of the as-grown CdS nanoparticles, avoiding aggregation and excessive growth. Figure 4.5(a-c) shows the photoluminescence emission spectra of the cysteine-capped CdS nanoparticles prepared at the different pH values. All the samples show a well-defined emission band with the same emission peak located 432 nm. The only noticeable differences in the PL spectra are in the intensity of the spectra which could be attributed to the different pH values used in their preparation. This finding is also indicative of the formation of CdS nanoparticles, promoted by a good passivation of those cysteine molecules used as surfactant. The photoluminescence emissions of these present cysteine-capped CdS nanoparticles were due to the trap-state emission, rather than the band-edge emission because emission peak wavelength is larger than the corresponding absorption edge. The trap-state emission is associated with electron transitions between the trap states and the conduction band or valence band.



Figure 4.5 PL spectra of cysteine-capped CdS nanoparticles (a) pH 4 (b) pH 7 and (c) pH 11

4.3.2 Cysteine capped ZnS nanoparticles

4.3.2.1 Structural Characterisation

An attempt was made to synthesize cysteine-capped ZnS nanoparticles at the different pH values following the same procedure used in the synthesis of cysteine-capped CdS nanoparticles and to investigate their optical properties. Cysteine-capped ZnS nanoparticles were successfully synthesized at the various pH values. The sizes and morphologies of the nanoparticles formed were confirmed by TEM. The TEM images shown in Figure 4.6 represent the cysteine-capped ZnS nanoparticles. It can be seen from the TEM images that the particles are spherical in shape with some degree of aggregation in chain-like form. The average sizes of the nanoparticles estimated from the TEM images are 7.47 ± 2.79 nm, 6.52 ± 3.04 nm and 6.17 ± 2.90 nm for cysteine-capped ZnS nanoparticles at pH 4, 7 and 11 respectively.



Figure 4.6 TEM images of cysteine-capped ZnS nanoparticles at (a) pH 4, (b) pH 7 and (c) pH 11



Figure 4.7 XRD patterns of cysteine-capped ZnS nanoparticles synthesized at pH 7

The crystalline nature of the as-prepared cysteine-capped ZnS nanoparticles was confirmed by powder X-ray diffractometry. A representative XRD pattern of the cysteine-capped ZnS nanoparticles is shown in Figure 4.7. It shows three diffraction peaks at 2 values corresponding to reflections from (1 1 1), (2 2 0), and (3 1 1) planes of the cubic zinc blend phase. No extra peaks were found, indicating the single phased nature of the nanoparticles.

4.3.2.2 Optical properties

The absorption spectra of the cysteine-capped ZnS nanoparticles at pH 4, 7 and 11, are shown in Figures 4.8. It is evident from the absorption spectra of cysteine-capped ZnS nanoparticles synthesized at the three different pH values were featureless. The shape of the absorption spectra gives no information about the shape of the cysteine-capped ZnS nanoparticles.



Figure 4.8. UV-Vis and spectra of cysteine-capped CdS nanoparticles at (a) pH 4, (b) pH 7 and (c) pH 11

Figure 4.9 shows representative photoluminescence spectrum of the cysteine-capped ZnS nanoparticles synthesize at pH 7. Figure 4.9 displays a narrow photoluminescence emission at 447 nm for the cysteine-capped ZnS nanoparticles synthesized at pH 7. The PL emission peak,

which is red-shifted, compared to the excitonic transition, is consistent with the observation in literature [39, 40].



Figure 4.9 PL spectra of cysteine-capped CdS nanoparticles at pH 7

4.3.3 Cysteine-capped PbS nanoparticles

The TEM images of the cysteine-capped PbS nanoparticles at the different pH values are shown in Figure 4.10a-c. It can be seen from the TEM images that the cysteine-capped PbS nanoparticles are relatively monodispersed consisting of close spherically shaped nanocrystals in form of a network.



Figure 4.10 TEM images of cysteine-capped PbS crystals at (a) pH 4, (b) pH 7 and (c) pH 11

The average diameters of the particles estimated from the TEM images are 10.38 ± 3.65 nm, 8.15 ± 2.79 nm and 6.44 ± 2.35 nm for cysteine-capped PbS nanoparticles at pH 4, 7 and 11 respectively. Apart from the size differences of the nanoparticles, there were no other visible differences observed in the nature of the particles by varying the pH values used in the synthesis of the cysteine-capped PbS nanoparticles. The X-ray diffraction pattern shows peaks corresponding to the (111), (200), (220). (311), (222), (400), (331), (420) and (422) planes of cubic PbS bulk as shown in Figure 4.10.



Figure 4.10 XRD patterns of cysteine-capped PbS nanoparticles at pH 7

4.4 Conclusions

Metal sulfides nanoparticles have been synthesized by aqueous medium through a simple colloidal route. The use of cysteine as stabilizing agent and the pH values of reaction mixture are important parameters that determined the final morphology of cysteine capped metal sulfide nanoparticles. The TEM results shown that spherical shaped metal sulfide nanoparticles were obtained at the different pH values used and the sizes of the nanoparticle formed were decreasing as the pH values increases. It was also observed from the experimental results that effective balance between the binding ability of cysteine molecule and the growth rates determine the size of the nanoparticles formed. The smaller particle size is mainly caused by slow growth rate of cysteine at pH 11 in comparison with those at pH 4 or 7. X-ray diffraction measurement confirms the structure, single cubic phase for the sample. TEM studies of metal sulfides nanoparticles show that particles form crystalline aggregates. From optical absorption measurements it is found that the band gaps show some dependency of the pH values used in preparing the nanoparticles.

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CHAPTER FIVE

Conclusions and Future Prospects

5.0 Conclusions

The synthesis of organically and water soluble semiconductor nanoparticles using hybrid solution based high temperature and a related colloidal aqueous synthesis route yielded faceted shaped particles ranging from spheres to cubes and rods. The crystallinity of the particles was determined by X-ray diffraction while the details on the particle crystallinity, size and size distribution were investigated by transmission electron microscopy and high resolution transmission electron microscopy.

The PbS nanoparticles were grown by thermolysis in hot HDA or TOPO which act as the solvent and surface passivating agent. Size and shape evolutions of PbS nanoparticles were simply achieved by changing the lead precursor sources, reaction temperatures and organic surfactants. When the thermolysis was carried out in HDA, particles with morphologies ranging from close to spheres, elongated particles and perfect cubes were observed however when the capping group was changed to TOPO predominantly rod shaped particles were obtained. The crystallinity of the PbS nanoparticles was determined by X-ray diffraction which shows the phase of the particles to be cubic rock salt phase. The high resolution transmission electron microscopy images also confirm the crystalline nature of the particles with distinct lattice fringes observed.

HDA-capped CdS nanoparticles with spherical, triangular and rod-like shape were also successively synthesized. The as-prepared CdS nanoparticles have good crystallinity and a good surface chemical environment with a narrow size distribution. The morphology for most of the TOPO capped CdS nanoparticles formed from the various cadmium sources were closer to spherical, a result consistent with a preferential mode of arrangement of the CdS particles when they settle on the carbon coated copper grid. It was difficult to determine the shape of some of particle from the TEM images, as the particles tend to agglomerate rapidly. In some cases, the particles failed to assemble on the carbon coated copper grid. A possible explanation might be that the nanoparticles formed are poorly capped by the surfactant. The crystallinity of the particles was determined by X-ray diffraction which shows the phase of the particles to be predominantly hexagonal. The high resolution transmission electron microscopy images also confirm the crystalline nature of the particles with distinct lattice fringes observed on the images. The optical studies show the particles to be quantum confined and luminescent at room temperature.

The morphology of the HDA-capped ZnS nanoparticles were mostly agglomerated spherical or rod-like shaped particles while some gave mixture of both shaped. The shapes of the particles were rod-like for all the zinc sources used except for the ZnSO₄ in which close to spherical shape particles was obtained. Attempts to synthesize ZnS nanoparticles from the preformed bulk ZnS in the presence of TOPO ended in particles which were unable to assemble on the carbon coated copper grid. The XRD patterns exhibited the cubic zinc blende structure of ZnS for the samples analysed and no other crystalline phase was detected. The room temperature optical absorption and photoluminescence spectra of the as-prepared nanoparticles were strongly blue-shifted due to quantum confinement effect

A synthetic procedure has been developed for the fabrication of highly luminescent colloidal CdS/ZnSe and CdSe/CdS core-shell nanoparticles without the purification of the core materials. The X-ray diffraction patterns confirm cubic structure for both core and core-shell semiconductor nanoparticles. In the synthesis of core-shell nanoparticles, there is a possible for

alloy nanomaterials to be formed. The optical properties of the nanoparticles formed were used to differentiate between the two components. The observed red shift in the absorption and photoluminescence spectra of the core-shell nanoparticles compared to the core materials is a strong indication for the formation of core-shell nanoparticles. From the PL spectra, the intensities of the emission maximum are considerably increased in the core-shell nanoparticles as compared to the core materials.

Cysteine-capped CdS, ZnS and PbS nanoparticles were successfully synthesized by aqueous medium through a simple colloidal route. X-ray diffraction measurement confirms the structure, cubic zinc blende phases were obtained for CdS and ZnS while cubic rock salt was obtained for PbS nanoparticles. TEM studies of cysteine capped metal sulfides nanoparticles show that particles form crystalline aggregates. From optical absorption measurements it is found that the band gaps show some dependency of the pH values used in preparing the nanoparticles.

5.1 Suggestion for future work

Although great strides have been made in the syntheses and uses of nanoparticles, there is a serious lack of information about the impact of nanoparticles on human health and environment, especially the potential for nanoparticles-induced toxicity. High quality organically and water soluble semiconductor nanoparticles were successfully synthesized but there is great need for *in vitro* and *in vivo* toxicity studies to be carried out on these particles to fully understand their biodistribution and potential adverse effect. Since zinc is not hazardous to human body, cysteine-capped ZnS nanoparticles synthesized in this present study should be screened for its anti-microbial and antiviral properties using different strain of microorganisms.