SYNTHESIS AND CHARACTERIZATION OF II-VI GROUP QUANTUM DOTS AND THEIR ANTIMICROBIAL STUDIES

Project report submitted in partial fulfilment of the requirement for the degree of

BACHELOR OF TECHNOLOGY

IN

BIOTECHNOLOGY

Under the supervision of

Dr. Ragini Raj Singh
Assistant Professor (Senior Grade)

By

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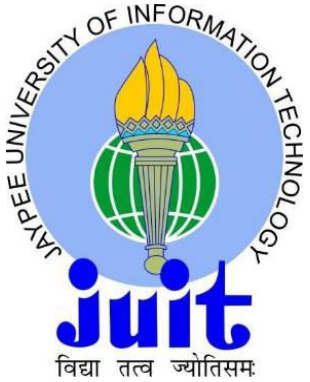

DEPARTMENT OF BIOTECHNOLOGY
Jaypee University of Information Technology Waknaghat, Solan-173234, Himachal Pradesh
May 2018

DECLARATION

I hereby declare that the work presented in this report entitled **"Synthesis and characterization of II-VI group quantum dots and their antimicrobial studies"** in partial fulfilment of the requirements for the award of the degree of **Bachelor of Technology** in **Biotechnology** submitted in the Department of Biotechnology and Bioinformtics**,** Jaypee University of Information Technology, Waknaghat is an authentic record of my own work carried out over a period from July 2017 to May 2018 under the supervision of **Dr. Ragini Raj Singh.**

The matter embodied in the report has not been submitted for the award of any other degree or diploma.

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CERTIFICATE

This is to certify that the work reported in the report entitled **"Synthesis and characterization of II-VI group quantum dots and their antimicrobial studies"** in partial fulfilment of the requirement for the award of the degree of **Bachelor of Technology** in **Biotechnology** submitted in the Department of Biotechnology and Bioinformatics**,** Jaypee University of Information Technology, Waknaghat is an authentic record of my own work carried out over a period from July 2017 to May 2018 under the supervision of **Dr. Ragini Raj Singh.**

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May 2018

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Abstract

This report work preferentially concerned with the synthesis of quantum dots of group II-VI through solution growth method and their characterisation followed by antimicrobial studies of the nano particles synthesised

The work has been systematically described in different chapters as follows:

Chapter 1 contains brief introduction of quantum dots, type of quantum dots synthesised ,applications, previous work done and objective of the research.

Chapter II describes the synthesis of quantum dots through solution growth method and their characterisation by employing X-ray diffraction, UV-vis spectroscopy Photoluminescence spectroscopy and Fourier transform infrared spectroscopy.

Chapter III results of characterisation techniques have been discussed.

Chapter IV describes antimicrobial studies on quantum dots and their interactions with them and disk diffusion test results are discussed.

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CHAPTER 1

1. Introduction

1.1 Background

Quantum dots (QDs) nanoparticles balanced of occasional gatherings of III-V or II-VI semiconductor assets, for example, ZnS, ZnSe, CdS, CdSe, CdTe, InP, and others. The diminished size of these QD incites a difference in the electronic excitations to higher vitality, focussed on the oscillator quality into only a couple of changes, presenting one of a kind quantum restricted photonic and electronic properties [1].

These nanocrystal that possess unique optical properties including broad-range excitation, size-tunable tapered emission spectra and high photostability, giving them considerable worth in various biomedical applications. The composition and size of QDs can be varied to obtain the desired emission properties and make them amenable to simultaneous detection of multiple targets. Furthermore, numerous surface functionalizations can be used to adapt QDs to the desired application The successful use of QDs has been reported in the areas of *in vitro* diagnostics and imaging. There is also possible for multimodal applications for concurrent imaging [2]. Quantum dots display properties that are intermediate between those of bulk semiconductor and those of discrete molecules.

They have numerous advantages over current fluorophores, such as organic dyes, fluorescent proteins and lanthanides chelates due to their unique optical and electronicproperties and also unlike organic fluorophores which bleach after only a few minutes on exposure to light [3]. QDs are extraordinarily steady and can experience rehashed cycles of excitation and fluorescence for quite a long time with a high level of brightness and photobeaching factors because of these properties quantum dots are suspected to be a best hotspot for antimicrobial examinations [4,5].

Including high volume ratio and surface area of QDs, which increases contact locale with target organisms ,small size which helps to easily pierce into the cell membrane needed for antimicrobial properties [6]. Polymer encapsulated QDs are found to be essentially nontoxic to cells and animals.In recent years, polymers with exceptional biocompatibility have been effectively and widely employed to modify QDs surface [7,8].

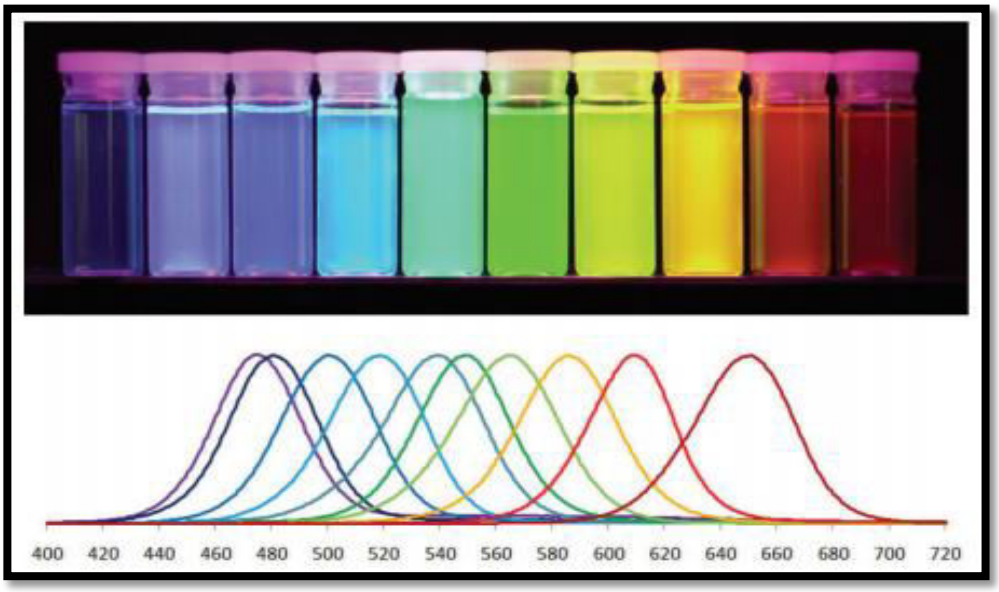

Figure1.1 : Colloidal semiconductor QDs with different emission colours related to different sizes of QDs

''Reprinted from Nano Today, 4, P. Zrazhevskiy, X. Gao. Multifunctional quantum dots for personalized medicine, 414-428 Copyright (2009), with permission from Elsevier''

1.2 Group II-VI semiconductors

Commonly used methods for the synthesis of the colloidal semiconductor QDs are the high temperature thermal breakdown of organic precursors of materials (Cd, Pb); in the presence of (nonaqueous) solvents and toxic chemicals as precursors, which are highly pyrophoric and must be handled under high vacuum conditions needing inert atmosphere and use of glove box in order to avoid risk of exposure. All these conditions are serious threat to safety issues. Also the toxicity of the materials limits the applications of these QDs in biology and home appliances. Recent regulations of the environment limit the use of toxic metals because of the threat to human health and environment.[9] New alternatives to Cd and Pb based QDs are being investigated. Doped QDs (d-dots), based on transition metal ion-doped QDs without heavy metal ions, such as ZnS and ZnSe,wide band gap semiconductors have attracted considerable attention as the new generation of luminescent NCs [10]. The synthesis of non-toxic QDs by means of "green chemical route" i.e. design of safer nanomaterials, reduced environmental shock and waste production, process safety, materials and energy competence is an approach receiving escalating consideration recently. There is a need to develop less toxic, low cost

[9,10].Quantum dots can be single section materials with uniform internal compositions, such as chalcogenide (selenides, sulfides or tellurides) of metals like cadmium, lead or zinc, example, CdTe or PbS. They arecomposed of elements from groups (IV, II–VI, III–V, or IV–VI) of the periodic table. They are important nanomaterials with unique physical and chemical properties owed to the "Quantum Confinement Effect" when the nanoparticle radius is below the exciton Bohr radius and have typical diameters of 2–20 nm [11].

1.3 Quantum confinement effect

Major feature of semiconductor nanocrystals is the '**quantum confinement effect"**, which leads to spatial inclusion of the electronic charge within the nano crystal. Because of this effect, researchers can use the size and shape of these "artificial atoms" to widely and accurately tune the energy of discrete electronic energy states and optical transitions. As a result, researchers can tune the light emission from these particles throughout the ultraviolet, visible, near-infrared, and mid-infrared spectral ranges. The decrease in the diameter of the QD and redistribution of its surface electronic density play different roles in the PL peak shifts [18].

"Quantum confinement" is related to the size of the quantum dots. When the size decreases the absorbance peak shift towards shorter wavelengths (blue shift), this means that energy gap increases. The diminishment in the size of the QD by ligand exchange causes a blue shift in the PL peak because of this impact, though the modification of surface electronic thickness of same QD by exchange of TOPO (capping specialist) with pyridine brought about (red shift) and a reduction in energy gap [19].

1.4 Biological applications:

The exceptional optical properties and multiplexing abilities of QDs give them a prime favorable position for fruitful utilitzation in different biomedical applications [12].Applications of QDs incorporate in vitro therapeutics diagnostics, and imaging. QDs are utilized as labels in immunoassays, immunohistochemical staining,cellular imaging and multiplex diagnostics [13,14].

(a) Biological imaging : The aim of molecular imaging is to make picture differentiate due to the molecular distinction in assorted tissues and organs. It

demonstrates the fluorescence pictures from Vero cells with inclusion of silicon quantum dots transfected into the cytosol. QDs are used to study intracellular processes, tumor targeting, cellular imaging at high resolution [15].

(b) Anticancer applications: One of the genuine difficulties in cancer is diagnosing the condition of a tumour and the potential for remedial treatment of that tumour. Near infrared QDs are recognized by good tissue penetration and lower background, which are suitable for the examination of lymph node "metastasis" [14].

(c) Gene technology: Gene therapy is a marvellous method to complement a deficient gene function. If there has been a possibility in some success with the delivery of particular genes using diverse methods, such as the use of liposomes and viral vectors, most of these methods have a limited yield and also carry a risk of oncogenesis [11].

(d)Bio sensing and energy transfer: Quantum dots act as solid fluorophores and are amicable with conventional bio detecting methods that apply fluorescence to create an extensive measurable signal.

(e) Anti microbial agents: Quantum dots are also being studied as Antimicrobial agents in a number of techniques like Antimicrobial Susceptibility Tests and Elisa [12].

1.5 Short review of work which has already been done on quantum dots and their antimicrobial properties

- The antimicrobial activity and system of CdTe quantum dots (QDs) against Escherichia coli was researched in a report. Colony forming capacity test and atomic force microscopy (AFM) images demonstrate that the QDs can effectively kill the microbes in a concentration dependant manner. Results of photoluminescence spectrophotometry, confocal microscopy, and antioxidative response tests recognize that the QDs bind with microorganisms and impair the functions of a cell's antioxidative framework, including down-directions of antioxidative qualities and reductions of antioxidative enzymes activities.Efforts have been put in the synthesizing the **ZnS** nanomaterials in order to reduce dimensions for high quantum efficiencies. The objective of this study was to synthesize ZnS nano particles, characterize them and test for antibacterial activities. The ZnS nanoparticles were

synthesized with and without CTAB capping agent and characterized using affinity FTIR and UV-Visible spectrophotometer. The disc diffusion method was used to study the antibacterial activity of the synthesized ZnS nanoparticles. *Streptococcus aureus, Pseudomonas aeruginosa, Escherichia coli* and *Candida albicans* were used as model test strains. The characterized peaks for ZnS stretching were absorbed at $354cm^{-3}$ and $964cm^{-3}$ for the capped ZnS. The ZnS were tested against oral pathogens and were found to exhibit anti-bacterial and anti-fungal activity.

- The green synthesis of cadmium sulfide (CdS) nanoparticles has been regarded as the most capable technique for their prospective applications in biological system. The bacterial strain *Bacillus licheniformis* has shown to be efficient in synthesizing cadmium sulfide nanoparticles [17]. The resultant CdS nanoparticles was tested for antimicrobial activity against a range of food borne bacteria *Ecoli*, *Bacillus licheniformis*, *Pseudomonas aeruginosa*, *Bacillus cereus* and *Staphylococcus aureus* and fungi *Fusarium oxysporum*, *Aspergillus flavus* and *Penicillium expansum.* The constancy of nanoparticles was due to protein interaction which may has played an important role as capping agents. This study explains a simple, Fcost effective way of nanoparticle synthesis suitable for large scale production. The green synthesis approach extends the horizon of applications to biological systems as an effective therapeutic agent.

1.6 Description of the work

We have synthesized QDs using group II-VI semiconductors.Group II-VI semiconductor QDs (ZnS, ZnSe, ZnO, CdSe, CdS) are most extensively applicable systems, having bandgap which can be engineered through the variation of the material composition and size. Nano crystals of this group semiconductors, are described by the uncommon optical properties, for example, broad absorption and sharp emission bands and in addition estimate size tunable photoluminescence in the noticeable visible range. The most prevalent quantum spots are CdS and ZnS QDs due to their bright and unique emission bandwidths. This group of QD have been found in adaptable photonic applications including solar cells, optical fiber enhanceers, probes

shows utilizing light-transmitting; diode clusters optical temperature tests and also in biology and drug [9].

1.7 Motivation behind the work

- It has been reported since the last 70 years, infectious diseases caused by microbes such as bacteria, viruses and parasites have been treated by drugs known as antimicrobial agents.
- Antimicrobial agents have now been used so widely that some of the micro-organisms targeted by the manufactured drugs have adapted and have become resistant to these drugs.
- Our aim was to test the antimicrobial properties of quantum dots , as they can be used as a substitute of antibiotics in future therefore protecting people from drug resistance.
- The quantum dots that did not show antimicrobial activity can be useful for the bio imaging of the pathogen as they are promising fluorescent labels for cellular imaging.
- It will also helped us to know about the bacterial or pathogenic behavior and there in vivo interactions.

1.8 Objectives

- We synthesised the quantum dots through aqueous method followed by their characterization and encapsulation.
- Antimicrobial testing of these quantum dots was successfully done thereafter using Disc Diffusion Method.
- This approach extended our horizon of applications of quantum dots to biological systems as they can be now used as an effective medicinal agent and will be able to replace with antibiotics in future.

CHAPTER 2

2. Materials and methods

2.1 Introduction

This chapter offers the detailed in sequence information about the synthesis procedure of poly ZnS, nano ZnS, poly CdSe nano ZnSe, poly CdTe and nano CdTe structures and encapsulated structures of CdS and CdTe nanoparticles. Basics of the methods used to study antimicrobial behaviour of QDs and encapsulated structures have also been discussed. Structural and optical properties of QDs were studied by X-ray diffraction (XRD), UV-Vis absorption spectroscopy (UV-Vis) and photoluminescence (PL) spectroscopy. Out of several available methods we have selected solution growth method for preparations of QDs. As better reproducibility, cost effectiveness, non toxic and environment friendly nature are the main features of the opted technique. Stabilization of the quantum dots (reduction in the particle size) attained in this method by using capping agent. Capping agent which have functional groups sulfhydryl and carboxyl are generally preferred. The experimental work is in thre main parts synthesis, characterization, encapsulation and antimicrobial studies .

(a)Quantum dots synthesisusing group II-VI.

Group II-VI semiconductor QDs (ZnS, ZnSe, ZnO, CdSe, CdS) are most extensively studied systems, having bandgap which can be engineered through the variation of the material composition and size.

Nano crystals of this group semiconductors, are characterized by the exceptional optical properties, such as broad absorption and sharp emission bands as well as size-tunable photoluminescence in the visible spectral range. The most popular are CdS and ZnS QDs due to their bright and unique emission with the wide excitation spectra and narrow emission bandwidths.This group QDs have been found in versatile photonic applications including solar cells optical fibre amplifiers, color displays using light-emitting diode arrays optical temperature probes as well as in biology and medicine [9].

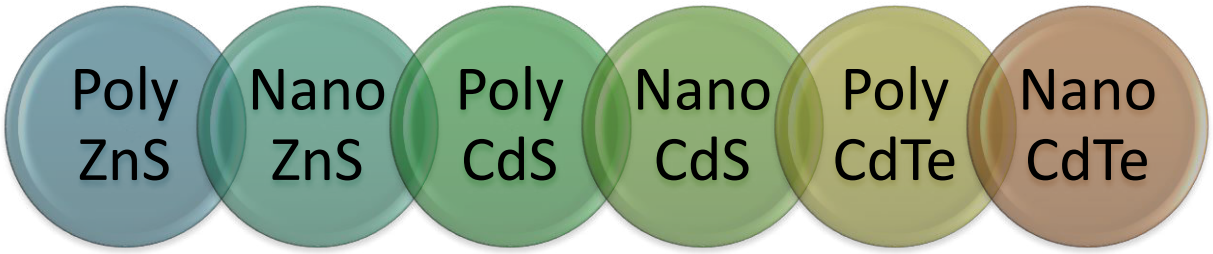

Figure 2.1: Types of semiconducting materials synthesized

(b) Characterization:

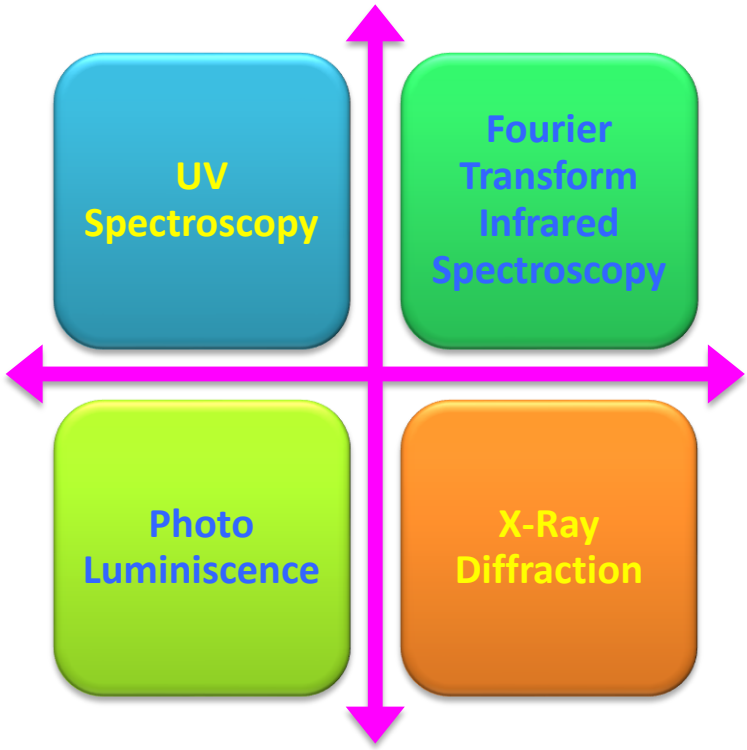

Figure 2.2: Characterization methods have been used to analyze prepared samples

(c) Encapsulation: It is the method to decrease the toxicity of the quantum dots and also makes them more stable by passivating the quantum dot's bare surface that is susceptible for the defect generation. The encapsulation has been done by coating these quantum dots using PEG (Poly ethyl glycol).

2.2 Synthesis of CdS, ZnS and CdTe

Synthesis of CdS : Figure 2.3 shows the process opted for synthesis of CdS quantum dots. Figure 2.4 shows the experimental setup of the solution growth method which has been opted for the synthesis in normal room conditions.

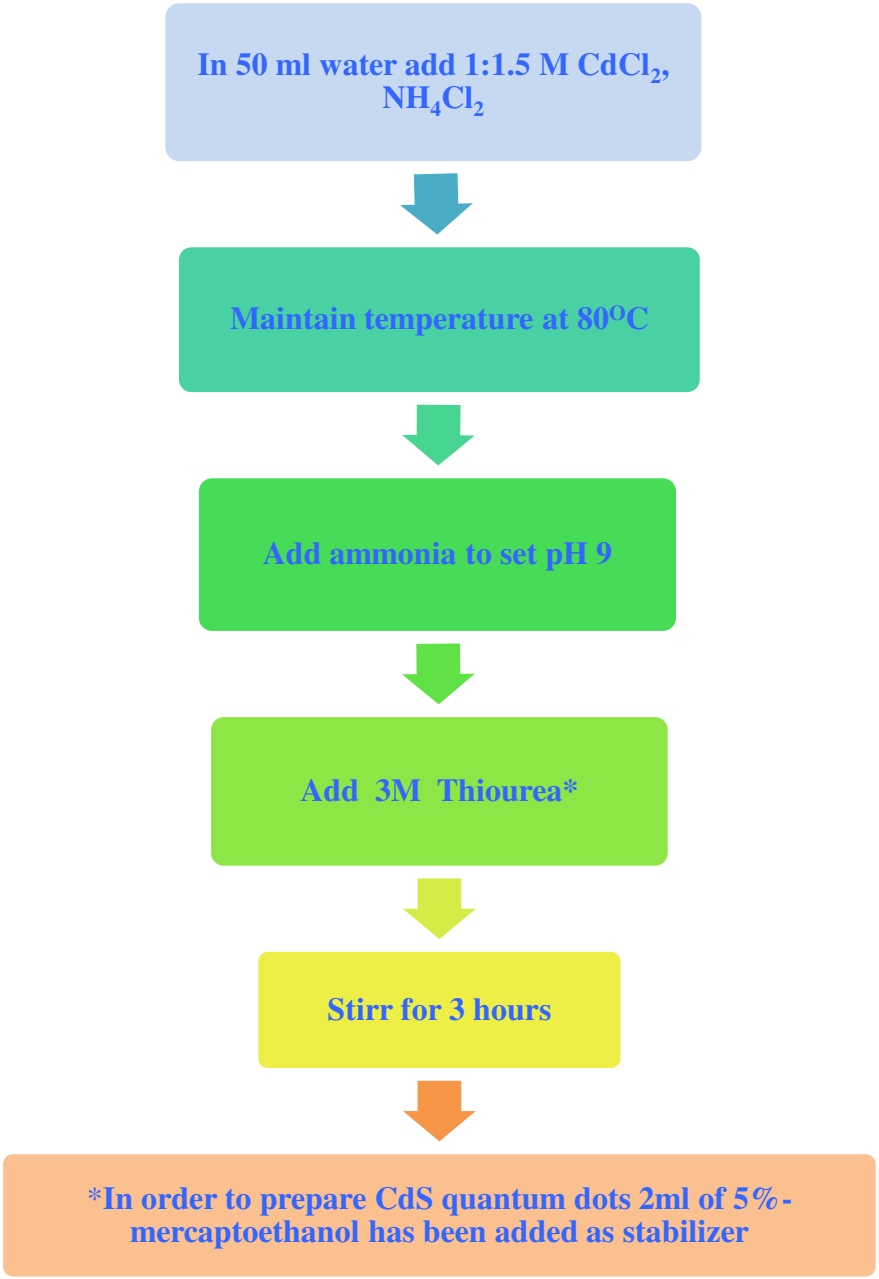

Figure 2.3: Process for synthesis of CdS

Figure 2.4: Experimental set up of Synthesis of CdS through solution growth method

Synthesis of ZnS: Figure 2.5 shows the process opted for synthesis of ZnS quantum dots. Figure 2.6 shows the experimental setup of solution growth method which has been opted for the synthesis in normal room conditions.

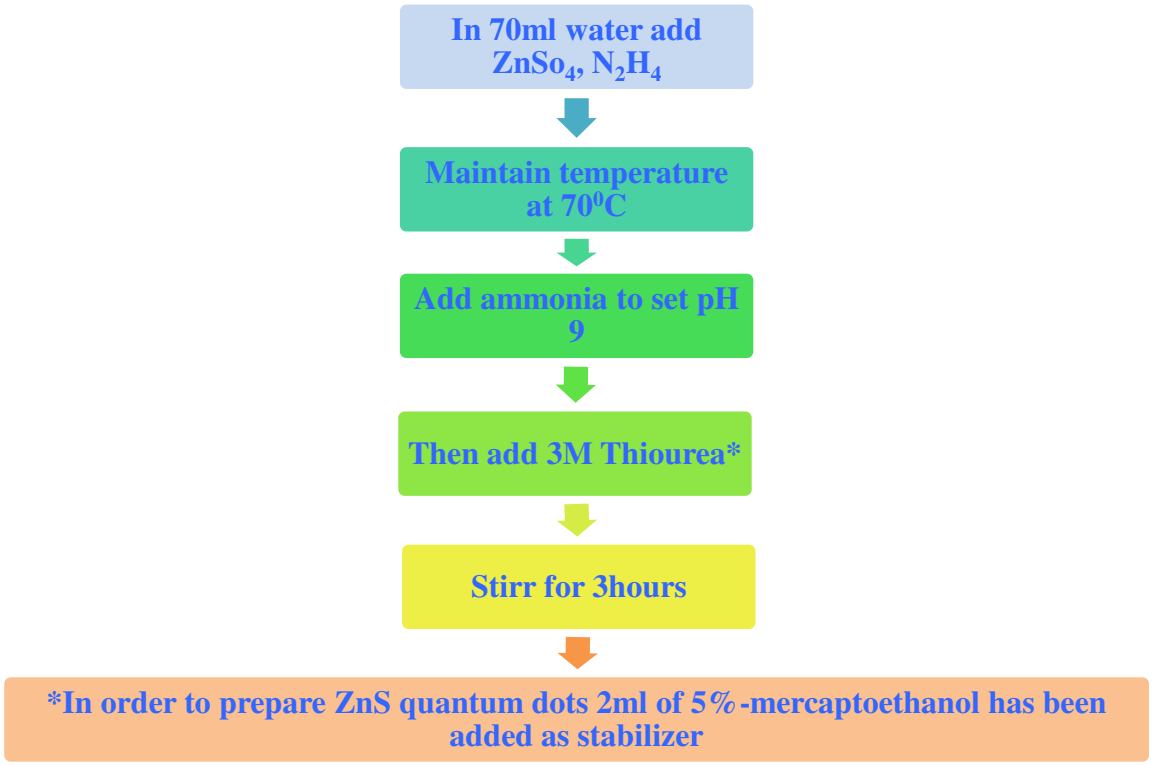

Figure 2.5: Process for synthesis of ZnS

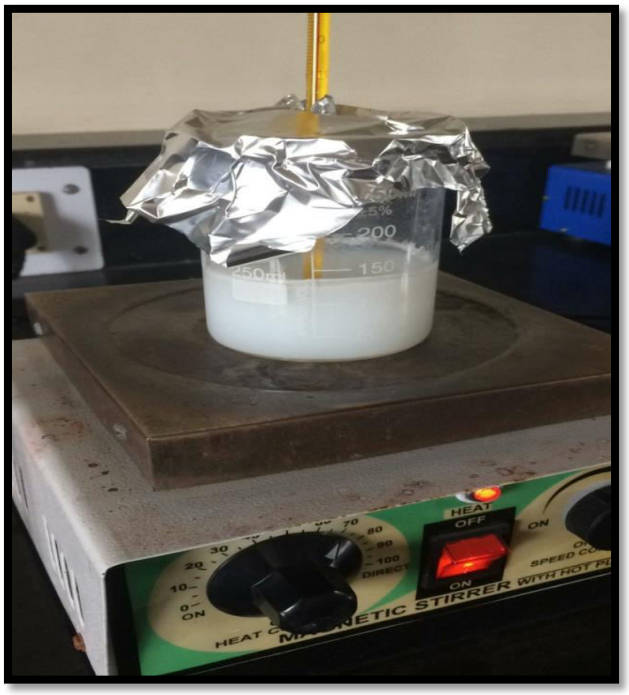

Figure 2.6: Experimetal set up of Synthesis of Poly ZnS through solution growth method

Synthesis of Poly CdTe: Figure 2.7 shows the process opted for synthesis of CdTe quantum dots. Solution growth method has been opted for the synthesis in normal room conditions.

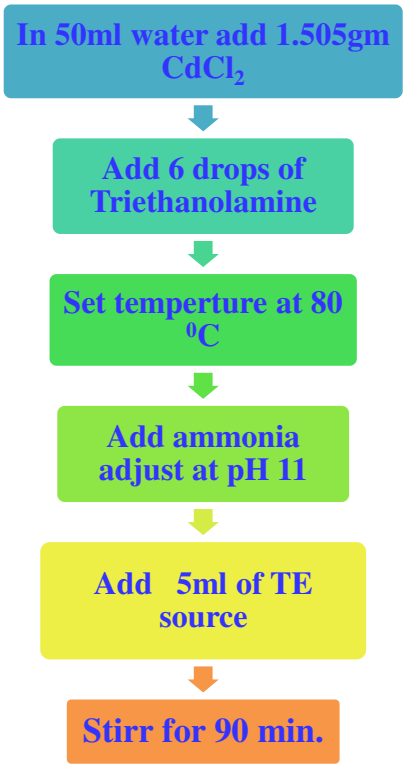

Figure 2.7: Process for synthesis of CdTe

All the samples were then washed and centrifuged. Figure 2.8 shows nano and poly ZnS , nano and poly CdS , nano and poly CdTe for further drying and characterization.

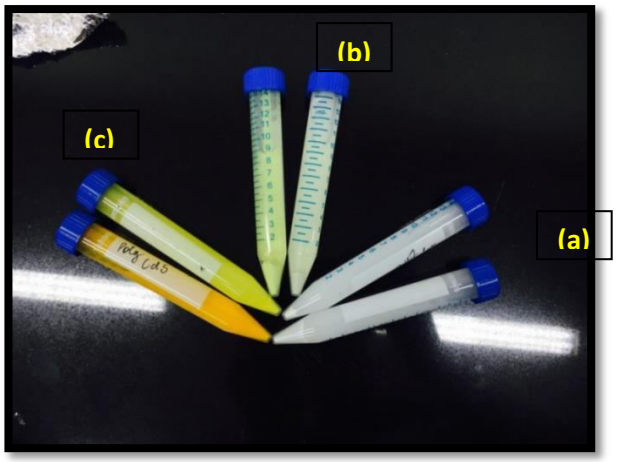

Figure 2.8: Samples of (a) Nano and Poly ZnS(2 from right) (b) Nano and Poly CdTe (2 in the midde) (c) Nano and Poly CdS (2 from Left)

2.3 Characterization

(a)Ultraviolet–visible spectroscopy

The instrument used in ultraviolet−visible spectroscopy is called a UV−Vis−NIR Spectrophotometer. It provides a means for analyzing liquids, gases and solids through the use of radiant energy in the far and near ultraviolet, visible and near infrared regions of the electromagnetic spectrum [17]. Accordingly, the predetermined electromagnetic radiation wavelengths for ultra−violet (UV), visible (Vis) and near infra−red (NIR) radiation are defined as follows:

- UV radiation : 300 to 400 nm
- Vis radiation: 400 to 765 nm
- NIR radiation: 765 to 3200 nm

Spectrophotometer works by passing a beam of light through a sample and measuring wavelength of light reaching a detector. The wavelength gives valuable information about the chemical structure and the intensity is related to the number of molecules, means quantity or concentration. Analytical information can be revealed in terms of transmittance, absorbance or reflectance of energy in the

wavelength range between 160 and 3500 mill microns. “Constraining electrons to smaller dimensions leads to quantum confinement.”As a consequence, the energy gap between the levels increases leading to blue shift in the spectrum.

(b) Photoluminescence (PL)

Photoluminescence spectroscopy is a contactless, versatile, non destructive, powerful optical method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo−excitation. This light can be collected and analyzed spectrally, spatially and also temporally. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties. Photo excitation makes electrons inside the material move into reasonable energized states. When these electrons return to their equllibrium states, the excess energy is; released and may incorporate the emission of light ("a radiative procedure") or may not "(a non radiative process").

(c)Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is an easyway to identify the presence of certain functional groups in a molecule. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Analysis by infrared spectroscopy is based on the fact that molecules have specific frequenciesof internal vibrations. These frequencies occur in the infrared region of the electromagnetic spectrum: ~ 4000 cm^{-1} to ~ 200 cm^{-1}.When a sample is placed in a beam of infrared radiation, the sample will absorb radiation at frequencies corresponding to molecular vibrational frequencies, but will transmit all other frequencies.

(d) X−ray Diffraction (XRD)

X−ray Powder Diffraction (XRD) is an efficient analytical technique used determination of grain size, composition of solid solution, lattice constants, and degree of crystalline in a mixture of amorphous and crystalline substances. It is a common technique for the study of crystal structures, atomic spacing, crystallite sizes, stress analysis, lattice parameters, quantitative phase analysis

and can provide information on unit cell dimensions. These X−rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin\theta$).

UV, PL , FTIR and XRD of the dried Quantum dots was carried out further. Figure 2.9 shows samples shows nano and poly ZnS , nano and poly CdS , nano and poly CdTe for characterization.

Figure 2.9: Dried samples ready for characterization

(d) Methodology for antimicrobial testing

The test conducted in our studies for Antimicrobial Susceptibility of our synthesized QDs (ZnS (Nano , Poly); CdS (Nano , Poly) and CdTe(Nano, Poly) was Disk diffusion test using both Gram positive (Bacillus Subtilis) and Gram negative (Escherichia coli) strains of bacteria.The disk diffusion susceptibility method is easy and sensible and has been well-standardized for antimicrobial testing. The test is performed by applying a bacterial inoculum of approximately $1–2\times10^{8}$CFU/mL to the surface of a large (150 mm diameter) Mueller-Hinton agar plate. Figure 2.10 shows the process opted for Antimicrobial Susceptibility Testing of the synthesized quantum dots.

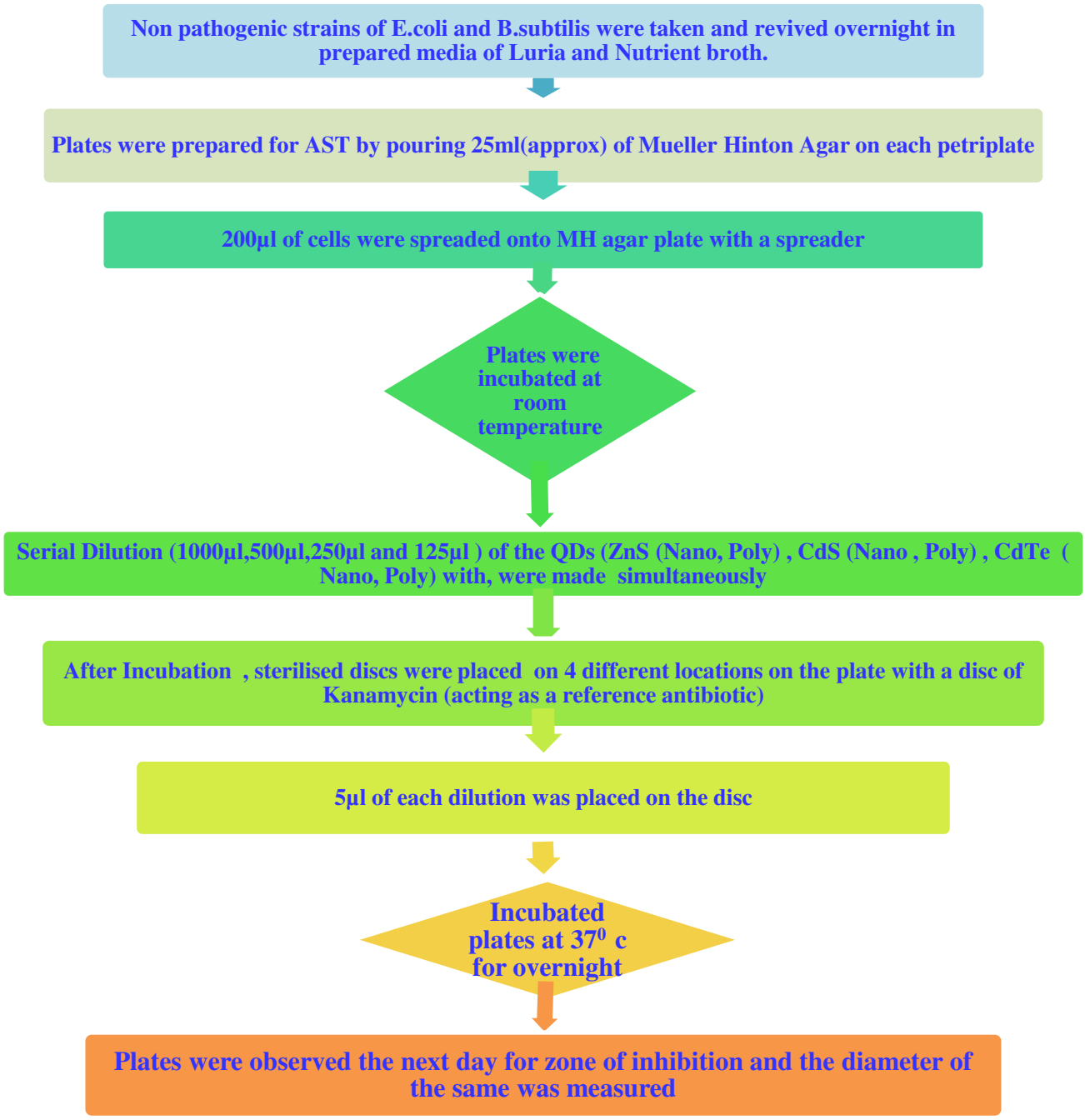

Figure 2.10: Procedure for antimicrobial testing

CHAPTER 3

3. Results and discussions

3.0 X-Ray Diffraction

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions and grain size. The analyzed material is finely ground, homogenized, and with average composition. X-ray diffraction spectra of bulk ZnS, CdTe ,CdS and capped with 2-mercptoethanol ZnS, CdTe, CdS QDs have been shown in Figure 3.1 – figure 3.6

Particle size: 8nm (Bulk ZnS) **Particle size: 2.5nm (Nano ZnS)**

Particle Size: 17nm (Bulk CdS) **Particle Size: 1.8nm (Nano CdS)**

Particle Size : 24nm Bulk CdTe) **Particle Size : 5nm (nano CdTe)**

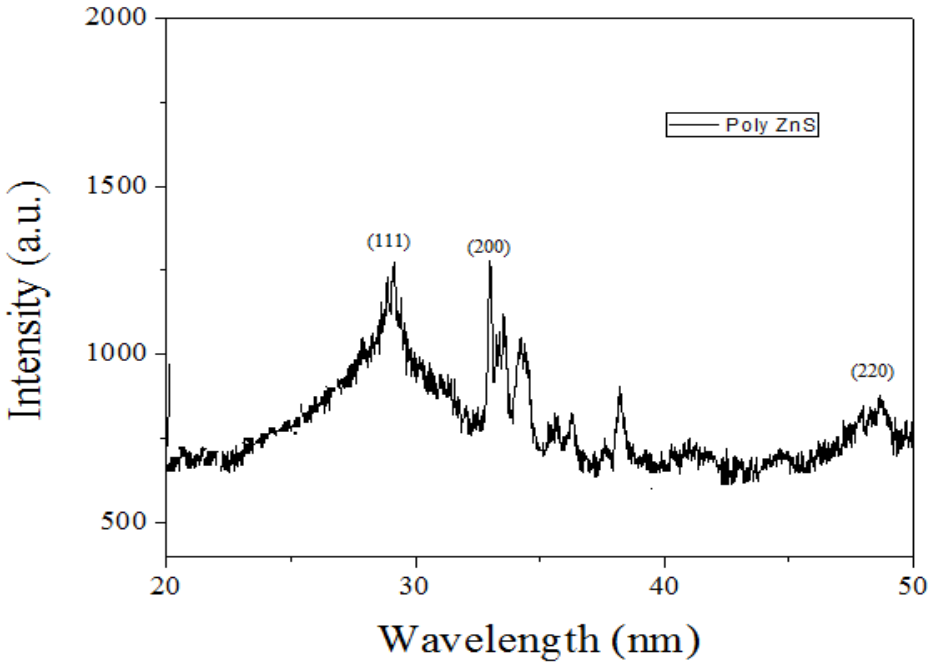

Figure 3.1: X-ray diffraction spectra of poly ZnS

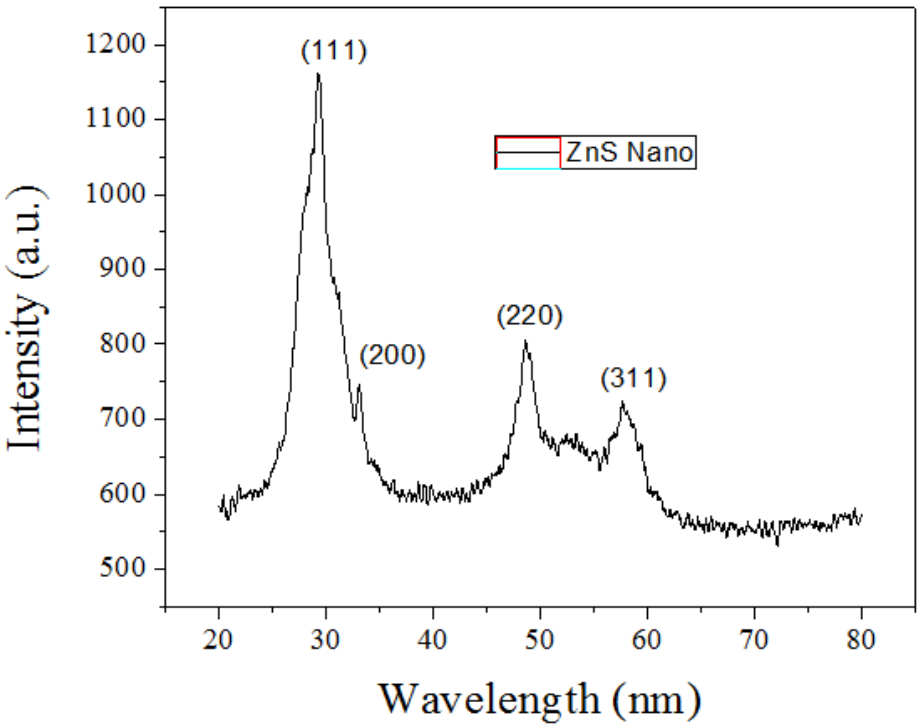

Figure 3.2: X-ray diffraction spectra of nano ZnS

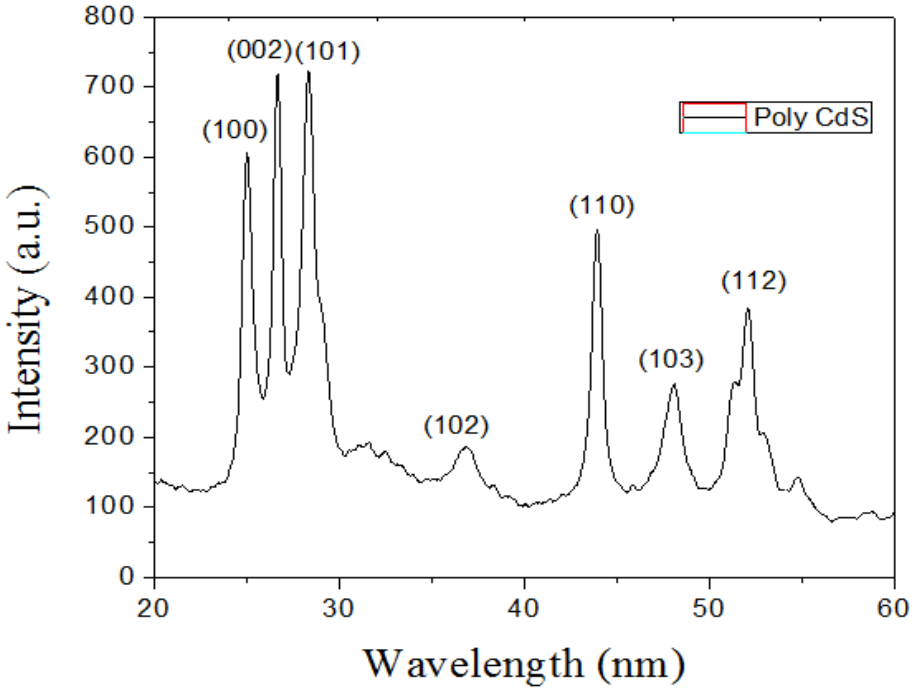

Figure 3.3: X-ray diffraction spectra of poly CdS

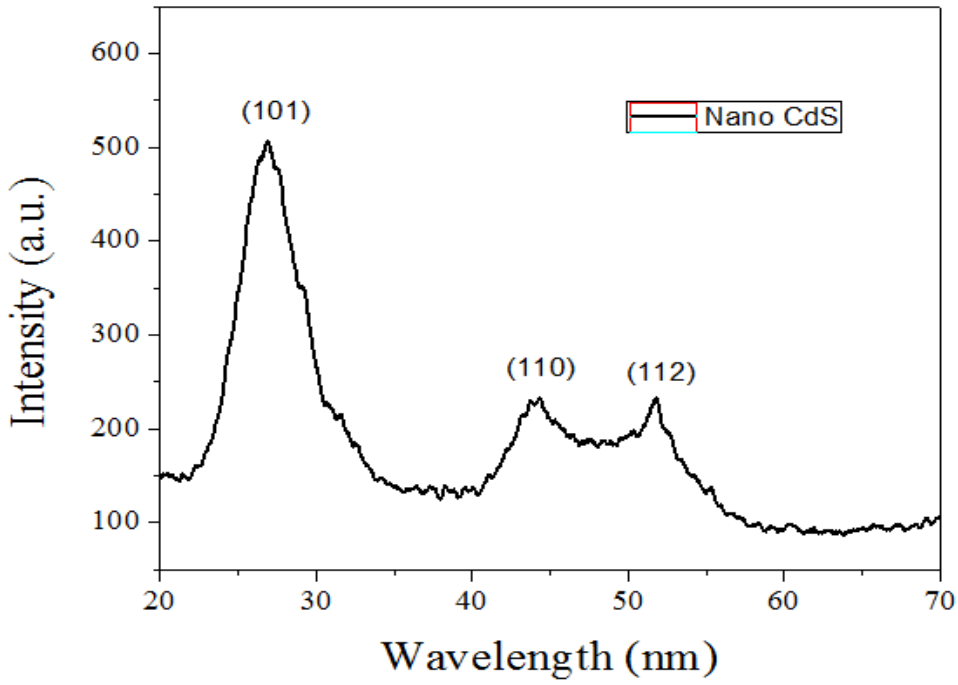

Figure 3.4: X-ray diffraction spectra of nano CdS

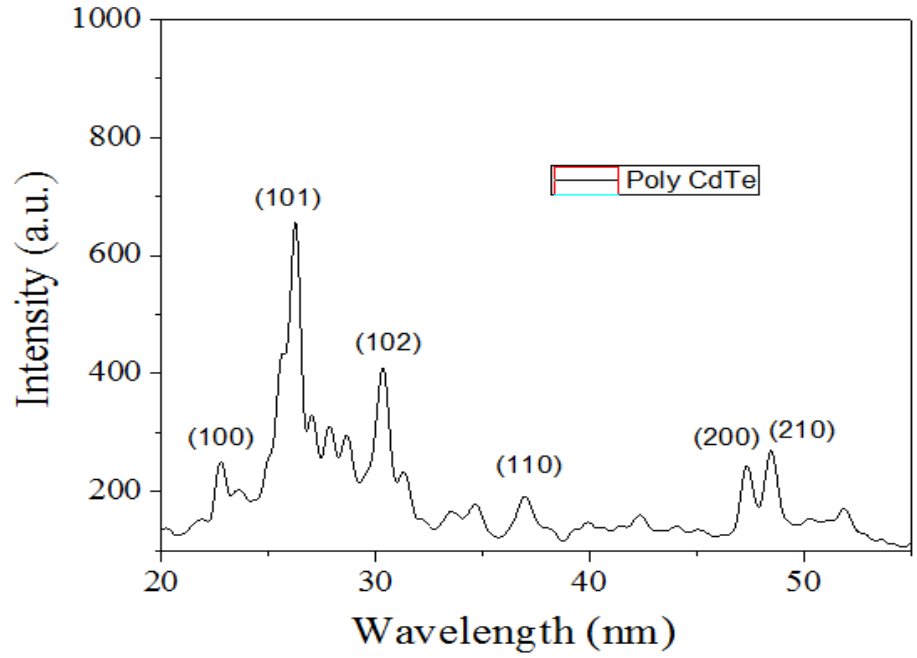

Figure 3.5: X-ray diffraction spectra of poly CdTe

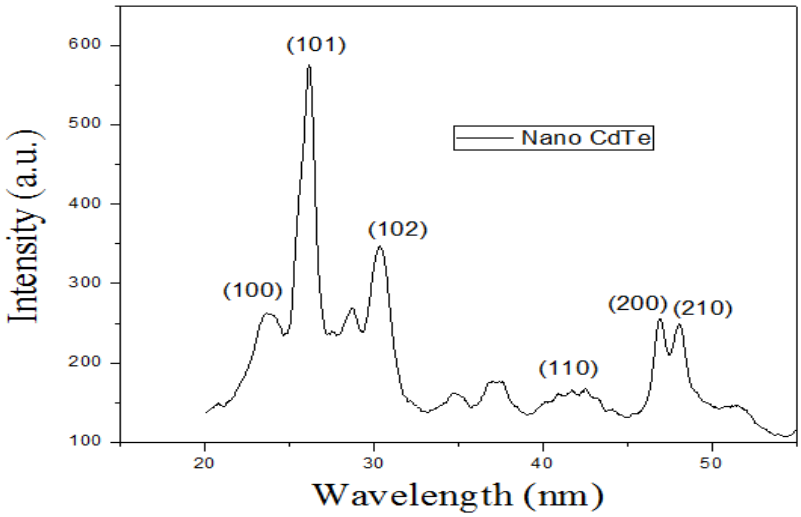

Figure 3.6: X-ray diffraction spectra of nano CdTe

Using Scherer's formula crystalline size (D) of the QDs has been calculated. Highly crystalline products are indicated by strong and sharp reflection peaks. Small size of the synthesized material is reflected by broadening of peak. Result clearly shows that from poly to nano form of QDs size of the quantum dots have been decreased an QDs become less ordered and more hardened because of which strength of materials increases due to decrease in grain size.

3.1 Optical Studies

3.1.1 Absorbance spectroscopy

It shows the absorbance peak of the quantum dots prepared and help us to identify that the desired quantum dots are prepared or not. UV-Visible absorption spectra of ZnS, CdS, CdTe both poly and nano quantum dots have been presented. As the band gap and surface area is increased there is decrease in size of the particle and therefore, absorption threshold shifts to shorter wavelengths because of quantum confinement effect. At nano sizes ,quantum confinement effect plays an important role. When the size decreases, surface states absorption becomes strong and absorption peaks shifts toward blue which shows that size decreases as surface state increases.

The plots having absorption maximum corresponding to 320nm for poly ZnS and 310 nm for nano ZnS . Band gap for Poly ZnS from absorbance received is 3.8 eV and for Nano ZnS band gap is 4 eV. There is shift of 0.2eV from poly ZnS to Nano ZnS

which shows that the quantum dots synthesized are blue shifted which tells us that the particle size of nano particles have decreased [20].

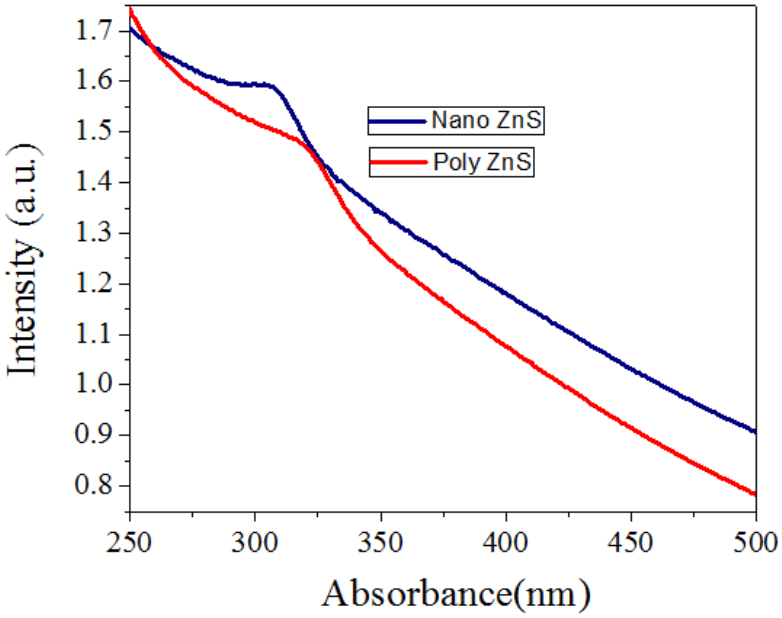

Figure 3.7: Absorbance spectra of Poly ZnS and Nano ZnS

The plots having absorption maximum corresponding to 477 nm for poly CdS and 425 nm for nano CdS. Band gap for poly CdS from absorbance calculated is 2.5 eV and for nano CdS band gap is 2.9 eV. it shows that there is shift of 0.4 eV from poly CdS to nano CdS and shows blue shift [22].

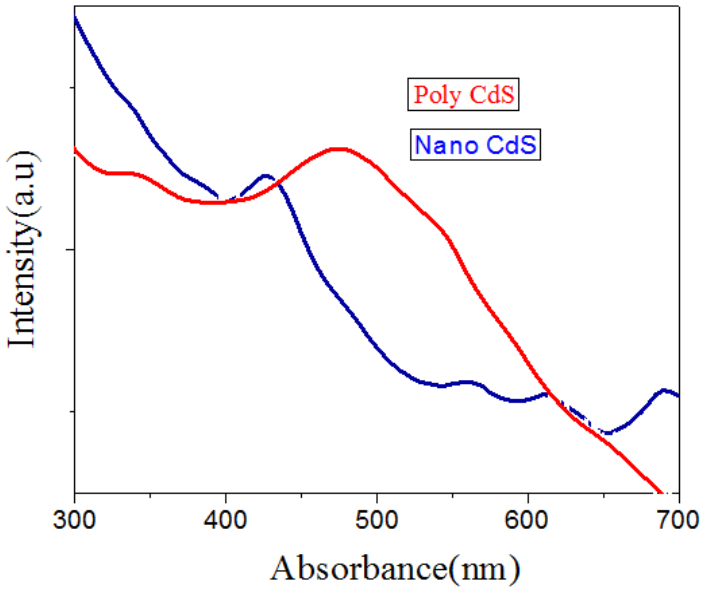

Figure 3.8: Absorbance spectra of poly CdS and nano CdS

The plots have maximum absorption corresponding to 850 nm for poly CdTe and 422 nm for nano CdTe . Band gap for poly CdTe is 1.45 eV and nano CdTe from absorbance received is 2.93 eV. There is blue shift of 1.48 which shows that the nano quantum dots synthesized have decreased particle size.

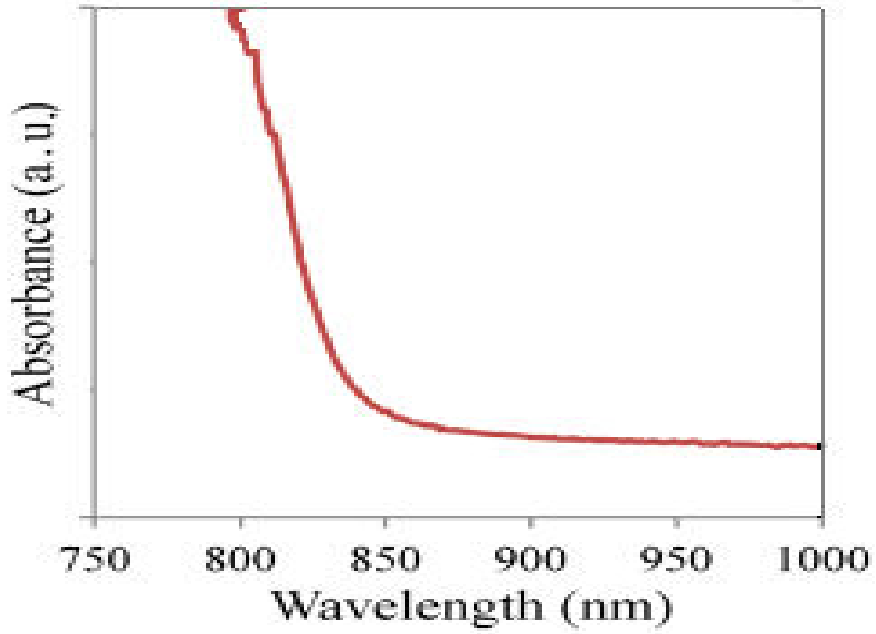

Figure 3.9: Absorbance spectra of poly CdTe

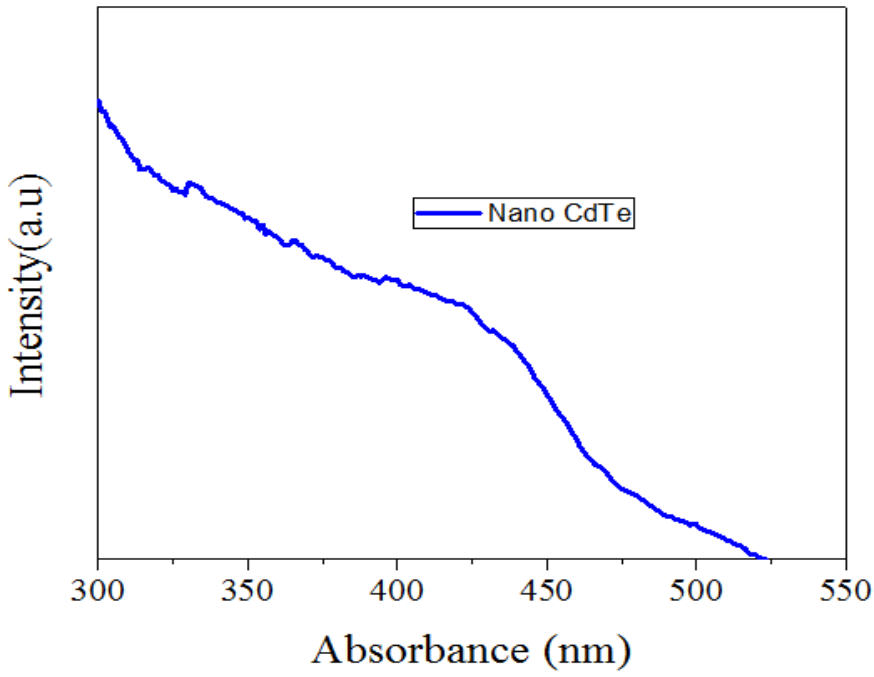

Figure 3.10: Absorbance spectra of nano CdTe

3.2 Photoluminescence Spectroscopy

To confirm whether the emission is band edge emission or generated from several defect states all the samples were excited at different excitation wavelengths within the range 300–450 nm and the emission spectra have been recorded. The emission spectra show no variance with respect to excitation wavelength and occurred at same wavelength in each scan. This confirms that prepared samples are emitting only the band edge luminescence or the luminescence due to surface traps. This also shows that QDs possess broad excitation and narrow emission spectra [21]. Photoluminescence spectra was recorded at room temperature for all the quantum dots synthesised.

Photoluminescence spectra of nano ZnS showing PL emission peak position at 328 nm whereas of Poly ZnS is 340 nm . Figure 3.11 shows that the poly ZnS with a single peak and for nano it shows double peaks, the first peak shows the band edge and second peak is due to defects which occurs due to zinc and sulphur vacancy, as size decreases there is defect in emission spectra because of surface to volume ratio increases and atoms comes out on surface because of which dangling bonds are formed which are unsaturated bonds and results in defects.

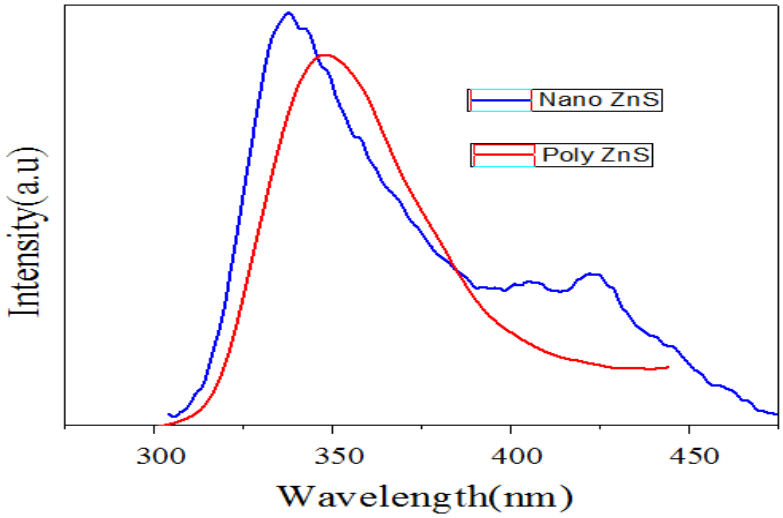

Figure 3.11: Photoluminescence spectra of Nano and Poly ZnS

Photoluminescence spectra of Nano CdS showing PL emission peak position at 444 nm whereas of Poly CdS is 532 nm. Figure 3.12 shows that the poly CdS with a single peak and for nano CdS it shows 4 peaks, the first peak shows the band edge and second ,third and fourth peaks are due to defects which occurs due to zinc and sulphur

vacancy ,as size decreases there is defect in emission spectra because of surface to volume ratio increases and atoms comes out on surface because of which dangling bonds are formed which are unsaturated bonds and results in defects.

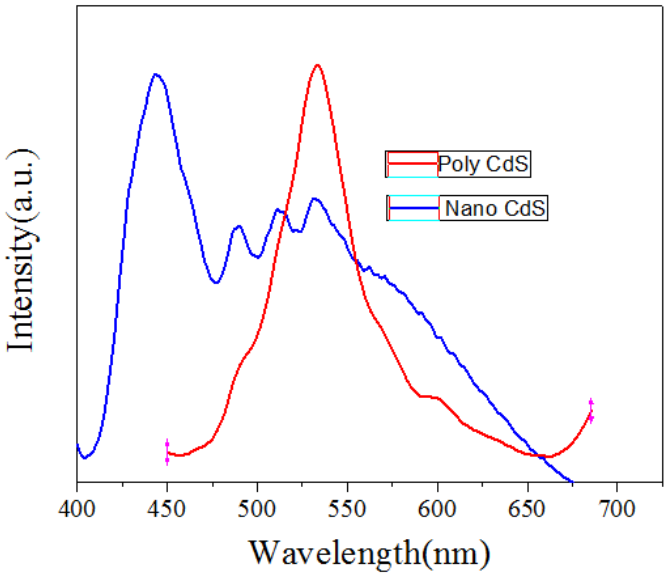

Figure 3.12: Photoluminescence spectra of Poly and nano CdS

Poly CdTe shows no luminescence and figure 3.13 shows photoluminescence spectra of Nano CdTe showing PL emission peak position at 600nm shows defect free luminescence.

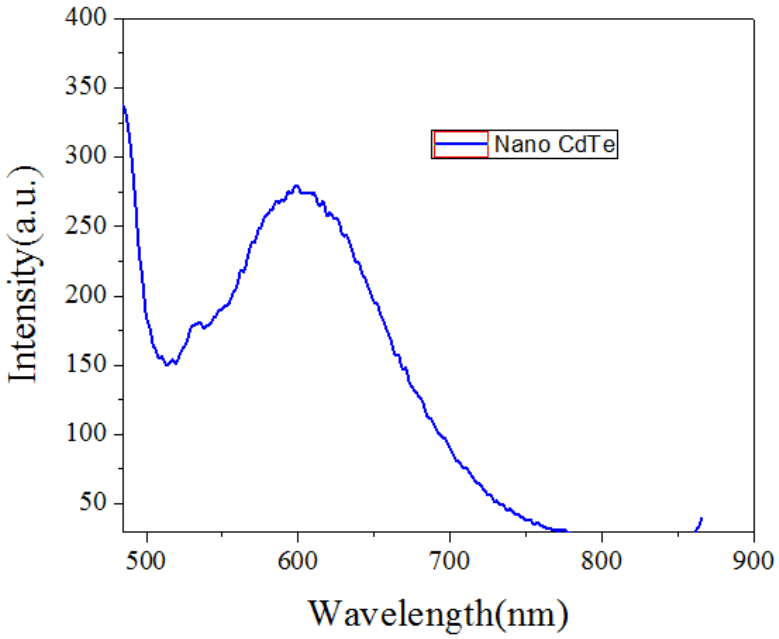

Figure 3.13: Photoluminescence spectra of Nano CdTe

3.3 Fourier Transform Infrared Spectroscopy

The most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency range are measured as wave numbers typically over the range 4000 – 600 cm^{-1} this have been shown in figure 3.14.

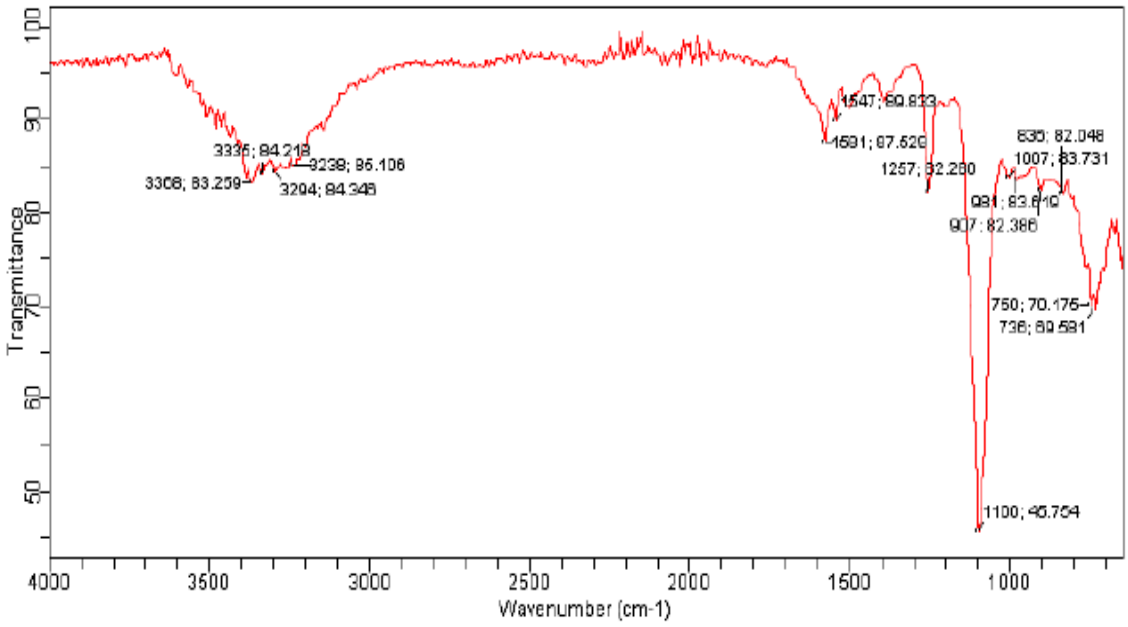

Figure 3.14 : FTIR spectra of Nano ZnS

1. C-O stretch most important, occurs at 1200-1000 cm^{-1}
2. O-H stretch occurs between 3650-3300 cm^{-1} - position and shape vary depending on amount of hydrogen bonding (a) free O-H: sharp peak between 3650-3600 cm-1 (b)H-bonded O-H: broad peak between 3500-3300 cm^{-1}
3. C=C stretching often occurs in pairs at 1600 cm-1 and 1475 cm^{-1}
4. Band at 700−899 corresponds to C-S stretching. Some extra peaks are present because of some impurities.
5. At 1465 cm^{-1} CH3 bending absorption at 1375 cm^{-1} CH2 (four or more CH2 groups) rocking at 720 cm^{-1}

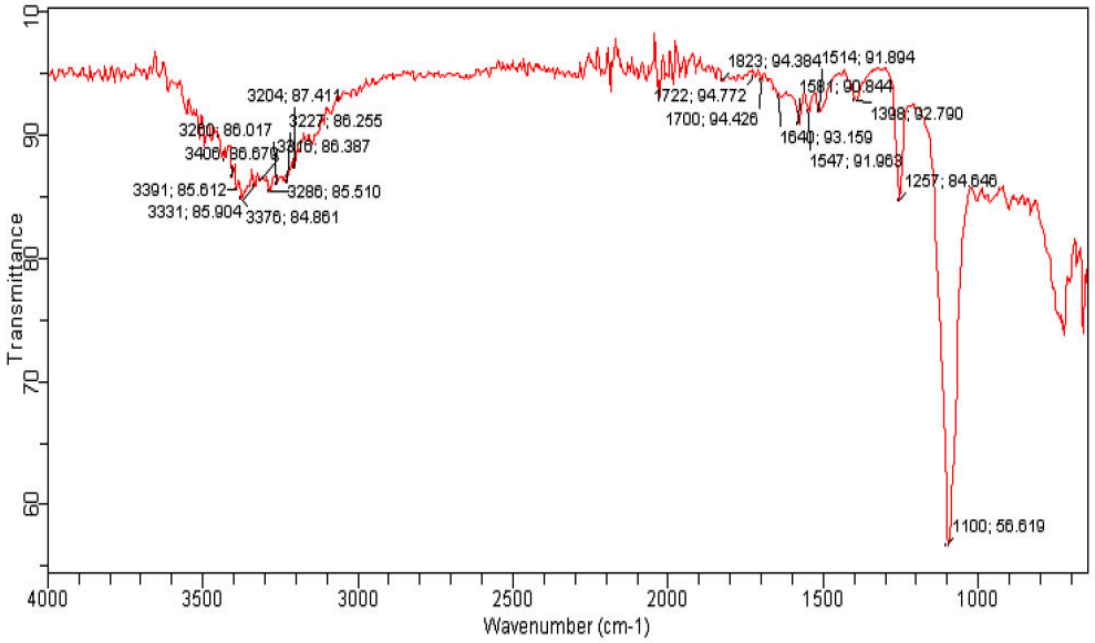

Figure 3.15: FTIR spectra of Poly ZnS

1. C-H stretch is most prominent around 3000 cm^{-1} – 2840 cm^{-1}
2. O-H stretch occurs between 3650-3300 cm^{-1} - position and shape vary depending on amount of hydrogen bonding (a) free O-H: sharp peak between 3650-3600 cm^{-1} (b)H-bonded O-H: broad peak between 3500-3300 cm^{-1}[18]
3. CH_2/CH_3 bending vibrations between 1475-1350 cm^{-1}
4. C=C stretching often occurs in pairs at 1600 cm^{-1} and 1475 cm^{-1}
5. C-O stretch between 1260-1000 cm^{-1}
6. Overtone/Combination bands appear between 2000-1667 cm^{-1}

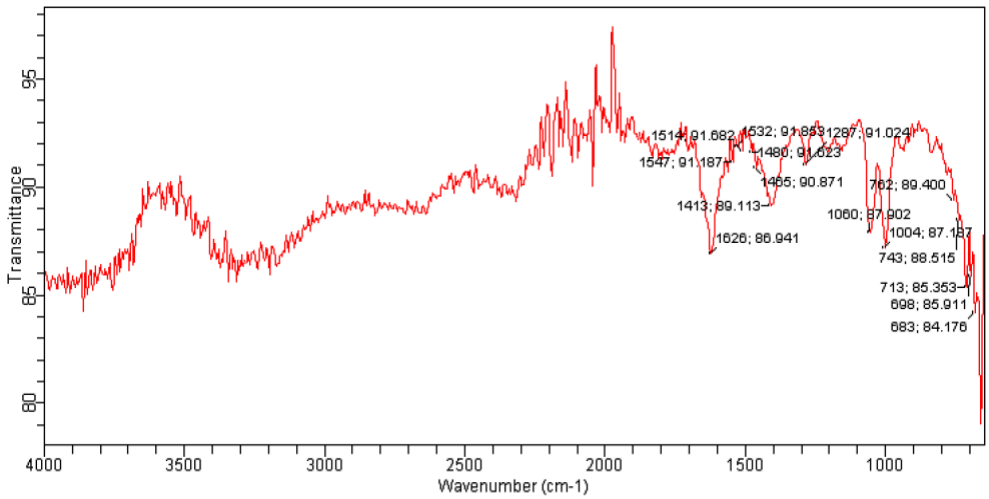

Figure 3.16: FTIR spectra of Nano CdS

1. Long chain (four or more) CH_2 groups in long chain may see a band at 720 cm^{-1} (weak, often obscured in more complex molecules)
2. C=C stretching often occurs in pairs at 1600 cm^{-1} and 1475 cm^{-1}
3. Overtone/Combination bands appear between 2000-1667 cm^{-1}

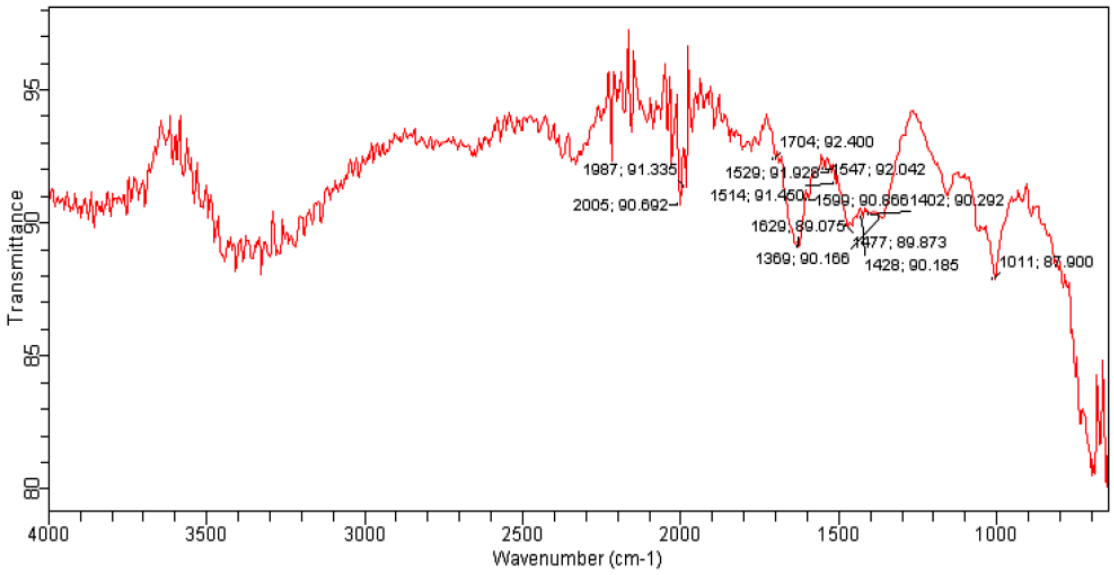

Figure 3.17 : FTIR spectra of Poly CdS

1. C=C stretch between 1500-1600 cm-1 - two to three peaks; often occur in pairs at 1660 and 1475 cm-1
2. Overtone/Combination bands appear between 2000-1667 cm-1
3. CH2/CH3 bending vibrations between 1475-1350 cm-1

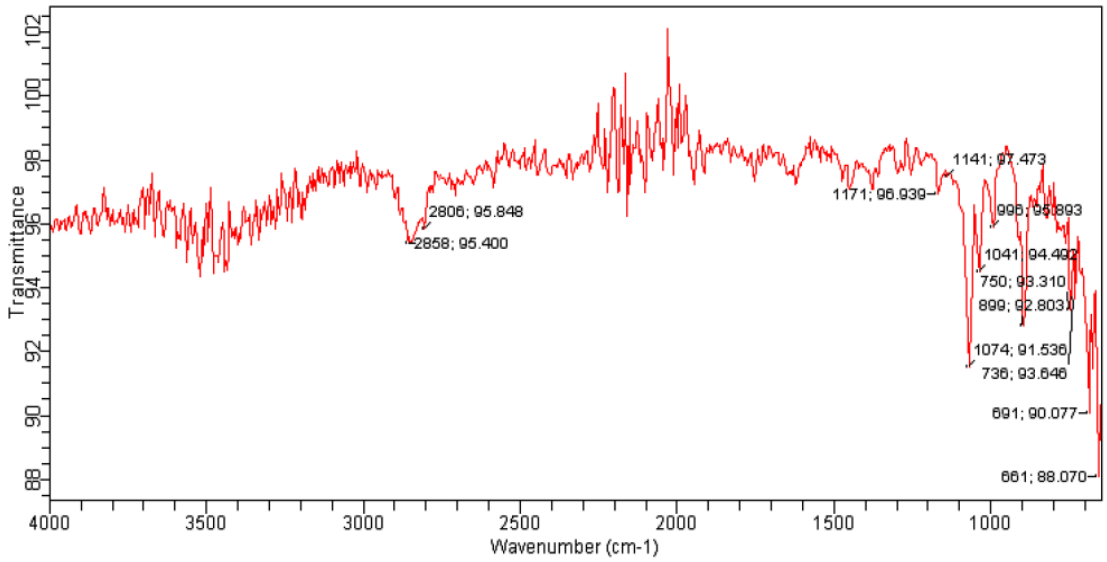

Figure 3.18: FTIR spectra of Poly CdTe

1. C-H stretch is most prominent around 3000 cm^{-1} – 2840 cm^{-1}
2. C-O stretch between 1260-1000 cm-1
3. CH_2/CH_3 bending vibrations between 1475-1350 cm^{-1}

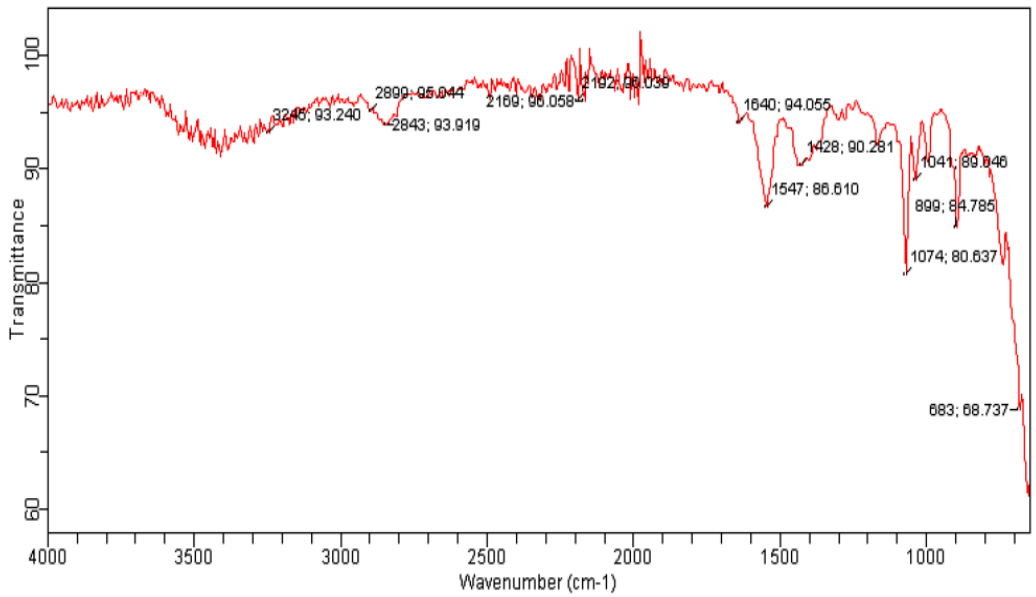

Figure 3.19: FTIR spectra of Nano CdTe

1. C-H out of plane bending vibrations between 900-680 cm^{-1}

2. C-O stretch between 1260-1000 cm^{-1}

3. C-H stretch is most prominent around 3000 cm^{-1} – 2840 cm^{-1}

4. C=C stretch between 1500-1600 cm^{-1} - two to three peaks; often occur in pairs at 1660 and 1475 cm^{-1}

CHAPTER 4

4. Antimicrobial behaviour of prepared Poly and Nano structures

4.1 Nanoparticles : Acting as good quality carriers of antibiotics

- NPs not exclusively can combat bacterial and microbial protection themselves, as specified prior, yet in addition can act as a "medium and carrier" of antibiotics. As a carrier of antibiotics, the major advantages of NPs compared with conventional delivery systems are as follows :

  Size: The ultra-small and convenient size of NPs is appropriate for conducting antimicrobial operations and skirmishing intracellular bacteria. Treatment of infections caused by intracellular pathogens and strains with drug resistance is more complex using antibiotics because of antibiotics poor membrane transport.

- Drugs of average size thus have little effect on intracellular microbes. A modified treatment method using drug-loaded NPs as intermediaries has been proposed to overcome this limitation.

- The size of most types of NPs is so small that they are easily phagocytosed by host phagocytes. Moreover, the structures of many types of NPs are suitable for carrying drugs.

  Protection: NP carriers can assist to boost the serum levels of antibiotics and protect the drugs from resistance by target bacteria.

- Within NP carriers, drugs are protected from detrimental chemical reactions; thus, the potency of the drugs can be maintained.

- In addition, protection from the resistance mechanisms of the target bacteria is an significant mechanism.

  Precision and security: NP carriers can help to target antibiotics to an infection site and thereby minimize systemic side effects.

- It is difficult to encourage high-dose drug absorption at the desired site while preventing side effects (including drug toxicity) when using conventional antibiotics without a carrier. NP-based antibacterial drug delivery systems deliver the drug to the site of action and therefore reduce the side effects.
- The undesired adverse effects of antibiotics on the body are specifically weakened because of the higher dose delivered to the site of infection.
- Eg: Vancomycin powerfully restrains Gram-positive microorganisms. However, vancomycin has solid ear and kidney poisonous quality. One way to enhance treatment is to boost drug delivery to the desired location, hence constraining the amount of medication getting organs where it is unnecessary. With the assistance of NP carriers, vancomycin modified mesoporous silica NPs (MSNs is a subset of Van) were designed, which made it likely to see and kill pathogenic Gram-positive microorganisms specifically finished macrophage-like cells.
- A successful and crucial plan as often as possible being used to accomplish "target treatment" is to first target macrophages with NPs because most lively bacteria at infection sites can be beset and gulped by macrophages. The medications in the NPs are then discharged in the macrophages in which microbes are available.

Controllability: Persistent and handy release of antibiotics can be achieved flexibly.

- With a conventional delivery method, the blood drug level is maintained for a short time in a relatively large range that can exceed the maximal tolerated dose or fail to reach the lowest effective dose.
- Therefore, repeated dosing is key, with associated side effects. With the appropriate NP carrier or strategy for drug discharge the blood concentration of the drug at the infection site can be sustained at the required level for a long time, resulting in good constancy, reduced occurrence of medication, improved patient compliance, and condensed patient pain.

- Compared with free drug at the same concentration, drug delivered ia an NP carrier has a much more prominent inhibitory effect on cellular growth, along with prolonged drug release. Moreover, NPs can be activated by different types of controllable stimulatory factors (such as chemical agents, a magnetic field, light, pH, and heat).

  Combination: Multiple drugs or antimicrobials can be packaged within the same NP, and NPs can be combined with other constructs to improve the agents antibacterial properties.

- NPs are an unpredictable gelation tendency and inherent low incorporation rates. Hybrid NPs can maximize the strengths while minimizing the weaknesses of the individual types of NPs. For example, studies have shown that superior efficacy of in vivo cellular delivery can be achieved by lipid–polymer hybrid NPs compared with delivery without polymeric NPs or by liposomes.

- In addition a prolonged effective time can be achieved during the "combinatorial" method, which can effectively and considerably decrease the likelihood of the expansion of resistance in bacteria .

4.2 Antimicrobial Studies

Anti-biotic resistant bacterial pathogens are an overall wellbeing episode, spreading at a hurried rate. In the only us, these pathogens rate Millions dollars in human services, with 29 million hospitalizations and 23,0008 deaths yearly [23].This flare-up is Accelerated by boundless abuse of anti-microbials in clinics and farming in the course of the most recent couple of decades, enabling microscopic organisms to advance and create methods for resistance. [24,25]. Contradicting microorganisms are broadly set up in the general public and can likewise be obtained by means of nosocomial contaminations, post-medical procedure complications, and ruined sustenance [25,26]. Safe bacterial diseases can likewise reason sepsis, which has death rates extending from 30% to half . taking into account the extreme Condition of infected patient, a sort clinical task is recommending the patient with powerful anti-biotics, which requires quick finding of the rebellious contaminations and Anti-microbial susceptibility testing (AST) [27].

4.3 Antimicrobial susceptibility test

Antimicrobial susceptibility tests are used to determine which specific antibiotics a particular bacteria or fungus is sensitive to. Most often, this testing complements a Gram stain andculture, the results of which are obtained much sooner. Antimicrobial susceptibility tests can guide the physician in drug choice and dosage for difficult-to-treat infections [28].

Results are commonly reported as the "Minimal Inhibitory Concentration (MIC)" which is the lowest concentrationd of drug that inhibits the growth of the organism. Reports typically contains a quantitative result in µg/mL and a qualitative interpretation. The interpretation usually categorizes each result as susceptible (S), intermediate (I), resistant (R), sensitive-dose dependent (SD), or no interpretation (NI).

Figure 4.1 (a) and (b) shows test conducted in our studies and the results for antimicrobial susceptibility test of our synthesized QDs ZnS (Nano, Poly) CdS (Nano , Poly) with disk diffusion test using both Gram positive (Bacillus Subtilis) and Gram negative (Escherichia coli) strains of bacteria and using Kanamycin as a reference antibiotic. Figure 4.1 shows the presentation of the QDs with the respective diameter of the zone of inhibition with respect to the reference antibiotic Kanamycin.

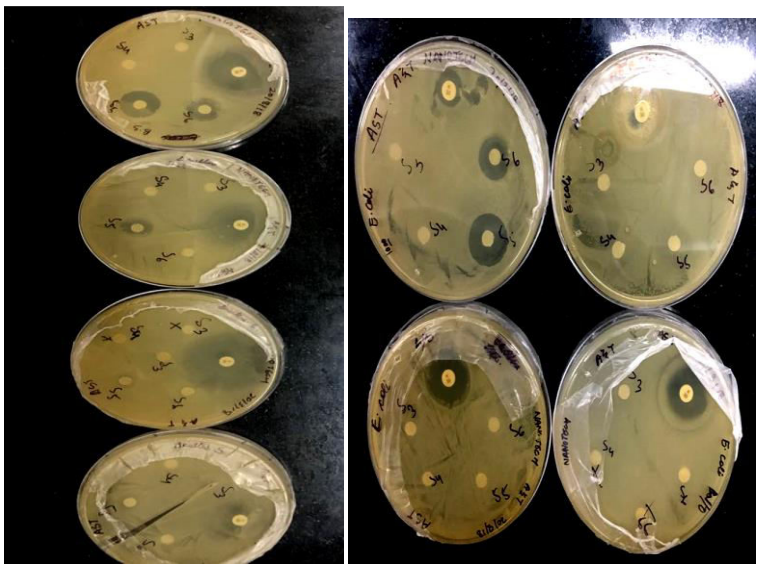

Figure 4.1: (a) Antimicrobial test results for S3 - Zns(poly), S4 - ZnS(nano), S5 – CdS(poly) S6 – CdS(nano) for gram positive bacteria (b) Antimicrobial test results for S3 - Zns(poly), S4 - ZnS(nano), S5 – CdS(poly) S6 – CdS(nano) for gram negative bacteria

Table 4.1: Presentation of the zone of inhibition data for ZnS poly, ZnS nano, CdS poly and CdS nano

Concentration (mg/ml)	Kanamycin (Diameter mm)	ZnS(Poly) S3 (Diameter mm)	ZnS(Nano) S4 (Diameter mm)	CdS(Poly) S5 (Diameter mm)	CdS(Nano) S6 (Diameter mm)
1000 µl	25 mm	--	--	17 mm	15 mm
500 µl	25 mm	--	--	9 mm	--
250 µl	25 mm	--	--	--	--
125 µl	25 mm	--	--	--	--

Figure 4.2 shows test conducted in our studies and the results for antimicrobial susceptibility test of our synthesized QDs CdTe(Nano, Poly) with disk diffusion test using both Gram positive (Bacillus Subtilis) and Gram negative (Escherichia coli) strains of bacteria and using Tetracycline as a reference antibiotic. Figure 4.2.1 shows the presentation of the QDs with the respective diameter of the zone of inhibition with respect to the reference antibiotic Tetracycline.

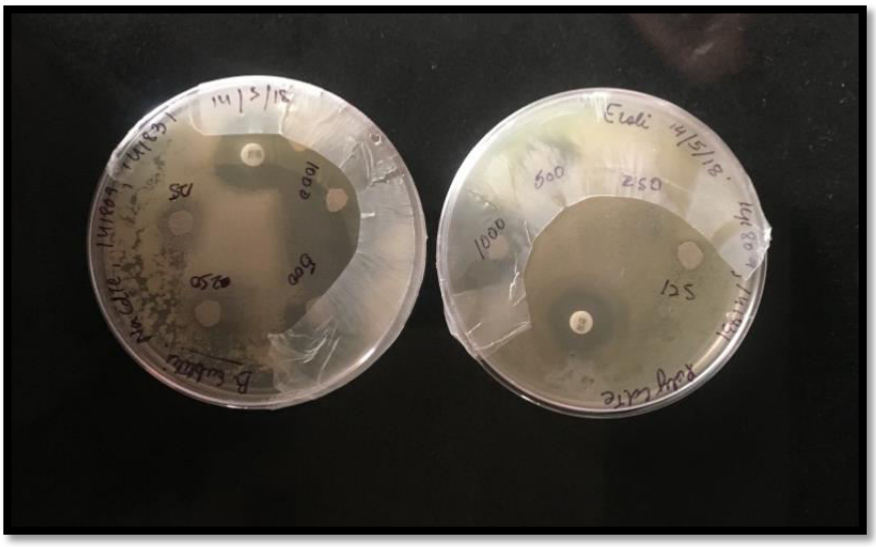

Figure 4.2: Antimicrobial test results for CdTe poly and CdTe nano

Table 4.2.1: Presentation of the zone of inhibition data for CdTe poly, CdTe nano,

Concentration (mg/ml)	Tetracycline (Diameter mm)	CdTe (Poly) (Diameter mm)	CdTe (Nano) (Diameter mm)
1000 µl	25mm	9mm	7mm
500 µl	25mm	5mm	5mm
250 µl	25mm	--	--
125 µl	25mm	--	--

5. Conclusion

It can be summarized from the study that the QDs are of very small size which can be synthesized using aqueous route. Quantum dots both Poly and Nano of ZnS, CdS and CdTe were successfully prepared and characterized. The QDs were characterized by XRD, absorbance spectroscopy, photoluminescence spectroscopy and FTIR [29]. These characterisation techniques helped us to know about the size, crystal structures, chemical groups present on the surface of the quantum dots and certain chemical and physical properties [29]. It was found that the structures prepared are found in good crsytallanity with appropriate grain size, exhibiting required optical properties in visible range and FTIR studies revealed the usability of these quantum dots in bio applications.

The QDs prepared by high temperature organic synthesis routes always possess hydrophobic surfaces and want post dealing for biocompatibility and bioconjugation purpose. There are most commonly found functional groups on bio molecules are -OH, -CHO, -C=O, -NH and –SH [30]. Due to the enhanced stability our synthesized quantum dots they were further studied and examined for their antimicrobial studies and various biocompatible properties.

Through the antimicrobial studies it was depicted that most of them showed prominent zone of inhibition which was comparable to the antibiotic whereas some of them showed no toxicity to both Gram positive and Gram negative bacteria. By checking the antimicrobial properties of quantum dots we can use them as a substitute of antibiotics and protect people from drug resistance in future .It can also help us to know about the bacterial or pathogenic behavior with their in vivo interactions.

6. References

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