

Synthesis and Characterization of PbTe Quantum Dots

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Table of Contents

1. Introduction	3
1.2_Metal Chalcogenides and Synthesis_	6
1.3_Physical -Chemical Synthesis:	8
1.4 Lead Telluride (PbTe)- Physical and Chemical properties.	13
1.5 Experimental Summary- Chemicals	14
1.6 Experimental Set Up:	15
2.Instrumental Analysis:	17
2.1 TEM:	18
2.2 UV-VIS-NIR:	19
3. Experimental	20
3.1 _Materials	21
3.2 Method	21
4. Results-Discussion- Future work	25
4.1_Results-Discussion_	26
4.2 Future work	28
5. References:	29

CHAPTER ONE:

INTRODUCTION

1. INTRODUCTION

In the past few decades, extensive research has been done in the field of nanotechnology. Great attention has been given in fabricating nanomaterials such as nano-wells, wires, tubes, films, rods, disks and semiconductor quantum dots (QDs). Semiconductor QDs are most studied due to their optical and electronic properties.¹²³ Having several applications such as in light-emitting diodes (LEDs), life sciences, thermoelectrics, photonics, telecommunications, security inks, solar cells and photovoltaic devices makes semiconductor QDs important elements in technological advancements. Semiconductor QDs can be made from binary, and ternary metal alloys.

Semiconductor quantum dots have intermediate electronic properties of both conductors and insulators. In a semiconducting QD, the material size is reduced in all three (x,y,z) dimensions having the exciton (electron-hole pair) confined in all directions. This characteristic of quantum confinement allows the formation of discrete energy states. Conversely, the allowed energy levels in a bulk semiconductor are continuous. The dependence on energy levels of the electrons confined in the quantum dot can be approximated using the particle in a box theory, whose potential is zero ($V=0$), and increases to infinity outside. The electronic wavefunction of a such particle can only have discrete energy levels, corresponding to certain standing wave pattern, and hence the energy levels in this potential well are quantized. Due to three dimensional confinements, semiconductor QDs offer large surface to volume ratio with size dependence control. Confined structures of QDs make them good candidates for developing high-performance optoelectronic devices such as light-emitting diodes and laser diodes. The difference in

energy between the valence and conduction band is expressed as a band gap. Engineering semiconductors with diverse band gaps allows control of the electronic properties in applications. For example wide band gap semiconductors (e.g. higher than 1eV) have high temperature applications such as optoelectronic and power devices. For most semiconductor QDs, the exciton spatial difference is calculated between 1- 10 nanometers. The Bohr equation (Eq. 1) can be used calculate the exciton spatial difference.²⁻³ Strong quantum confinement is observed when materials are smaller than the Bohr radius.

$$r = \frac{\epsilon h^2}{\pi m_r e^2} \quad \text{Eq (1)}$$

Where:

r = radius of the sphere

e = dielectric constant of the semiconductor

h= Planks constant

m_r = reduced mass of the electron-hole pair.

e= charge on the electron

Most QD's include binary or ternary materials such as II/VI or III/V compound semiconductors. II/VI QDs consist of combining metal cations from group 12 with chalcogens anions from group 16 to generate specialized semiconducting QDs. Some of II/VI semiconductors include: ZnO, ZnS, CdS, CdSe, PbSe, and PbTe QDs. III/V QDs are combination of elements in group 13 with elements in group 15. Examples of a few semiconductors include: GaN, GaP, GaAs, InP, and InAs.

1.2 Metal Chalcogenides and Synthesis:

Metal chalcogenides SQDs have significant properties. A lot of progress has been made in synthesizing and characterizing II/VI materials. These nanocrystals have a large size distribution allowing flexibility and control.^{1,3} Metal chalcogenide semiconductors tend to be ionic and have direct band gaps allowing them to have light emitting applications. II-VI compounds have wide range of band gaps. Chart 1 shows the different band gaps of II-VI and III/V bulk materials.^{1,3} The focus of this research mainly involves the study of PbTe- II/VI quantum dots metal chalcogenide semiconductor QDs.

<u>Compound</u>	<u>Band Gap eV - at 300K</u>	<u>Exciton Bohr Radii- nm</u>
III/V Materials		
GaP	2.25	5
GaAs	1.43	12
GaSb	.69	20.46
InP	1.28	11.3
InAs	.36	37
InSb	.17	65.6
II/VI Materials		
CdS	2.53	5.8
CdSe	1.74	4.9
CdTe	1.50	7.3
ZnS	3.6/3.8	2.5
ZnSe	2.58	3.8
ZnTe	2.28	5.2
PbS	.37	18
PbSe	.26	46
PbTe	.29	46

Chart1. III/V and II/VI compounds with their band gap energies in eV at 300K and exciton Bohr radius.

In the past, not only II/VI metal chalcogenides have been synthesized and characterized but attention has been given to their vibronic properties. Vibronic modes are essential to understand electron-phonon coupling in SQDs. Theoretical Raman calculations on the modes were done to understand the surface character of SQDs. To better characterize and understand molecule-molecule interaction, it has been shown that Surface Enhanced Raman Scattering (SERS) is a great technique that successfully shows enhancement at much higher orders of magnitude.⁴ Two methods have been reported^{5,6,7,8} to observe SERS. The first method is to coating the semiconductor surface with a silver film and the second method uses a chemical etching process. Surface roughness plays a crucial role in obtaining large enhancements of the Raman signal. SERS provides many of important advantages such as sensitivity, selectivity, non-destructive detection, and feasibility for *in-situ* studies. It also allows detailed information as to the nature and orientation of the adsorbed molecule. Surface enhancement has been also observed on II/VI QDs in colloidal suspensions such as CdS, ZnS, ZnO, CuO and CdTe.^{9, 10, 11, 12} These systems have displayed enhancement factors ranging from 10^2 to 10^4 . In this project colloidal lead telluride (PbTe) QDs were synthesized and characterized. SERS application remained for future work.

As opposed to most II/VI materials, lead salts (PbS, PbSe, PbTe) have shown strong quantum confinement due to their small electron hole masses.³ Lead salts have a rock salt crystalline structure making them useful for studying additional intrinsic properties such their quantized electronic states. Their narrow band gap and non-linear optical properties makes lead salts useful in technology applications.

1.3 Physical -Chemical Synthesis:

Many synthetic routes have been established in synthesizing QDs. QD's can be studied in gas phase, colloidal suspension or implanted on solid surfaces.^{13, 14,15, 16}

Physical methods use electrochemical methodologies. Chemical composites are lithographically formulated and deposited onto a substrate. Such techniques include Molecular Beam Epitaxy (MBE) and doping on glass matrices.^{17, 18}

In MBE, the chemical composites are vaporized one layer at a time. This technique allows the crystalline thin films to grow in ultrahigh vacuum with specific control of thickness, composition and morphology . The MBE technique allows spontaneous self-assembly of QD formation and fabrication. This technique led to a breakthrough in QD devices such as in laser applications. Glass matrices synthesis consists of solid crystalline and an aqueous matrices. Oxide based glass matrices make it feasible to characterize size distribution via optical spectroscopy. In solid matrices the crystals are grown via a diffusion process. In this process the solid undergoes steady state decomposition then recondenses when the nanocrystals have grown.

Compared to physical techniques, chemical routes are cost friendly, simple, time saving and give optimum shape and size control. Some chemical techniques include: preparation of colloidal QDs via precipitation, thermal decomposition solvolysis, and organometallic systems.

In a precipitation method, ionic compounds are mixed in aqueous solutions at room temperatures. Low temperatures solutions have been prepared in the past.¹⁹ QDs

preparation is dependent on parameters such as concentration, pH, and temperatures. Thermal decomposition solvolysis synthesis requires non aqueous solvents and high temperatures (100-350°C) for nucleation to occur under inert conditions. Addition of the hot injection precursor into the solvent makes this approach favorable.²⁰ Another thermal approach such as the hydrothermal decomposition method uses water as a solvent in an autoclave chamber for nanocrystal growth.

Organometallic methods are popular and more advantageous compared to the other chemical processes. In an organometallic approach, experiments necessitate high temperatures and precursors preparation. An airless apparatus is assembled such as a Schlenk Line. A Schlenk line is a convenient set up when a glove box is unavailable. Both air and water are evacuated from the system and reaction vessel. In this method the chalcogen precursor is rapidly injected into the hot solution medium. Size- tuning is achieved during the synthesis by adjusting parameters such as growth time (nucleation) ,temperature conditions, chemical composition ratios and surfactant to precursor ratio of the nanocrystals. Proper control of these parameters facilitates higher yield in narrow size distribution of QDs. Chemical routes allow control of the composition and morphology of the QDs.

Many articles have been published on the synthesis of lead salts such as PbS, PbSe and PbTe. Past work has shown that lead salts, capping agents and temperature gave narrow size distribution of QDs below the Bohr Radius. In earlier work, 1-octadecene (ODE) and oleic acid (OA) were widely used for their chemical properties. ODE is mainly

used as a non-coordinating solvent. ODE is an inexpensive, nonpolar, eco-friendly and stable solvent.^{1,21, 22} OA was used as a capping agent to stabilize the NCs and maintaining acidic environments. OA is soluble in aqueous alkaline settings giving salts due to its alkene properties. OA is used for its oxidative and reducing properties.

In Murphy et al¹ and Yu et al^{21,22}, used a similar approach for synthesizing different metal chalcogenide NCs. ODE and OA was used in the lead precursor by varying the chemical composition ratios between ODE-OA-Pb. PbO was used as their source of lead. The first PbTe QD were synthesized in doped glass by Reynose et al¹⁸. Later, an organometallic approach was used to synthesize PbTe NCs in Cho et al²³ in 2003 and Lu et al²⁴ in 2004.

Murphy et al¹ used an organometallic route via one pot rapid injection approach to synthesize the PbTe NCs. The synthesis was set up under vacuum conditions and diphenyl ether¹ was substituted with ODE. Two precursors were prepared varying the molar ratios of lead oleate and ODE solution- ranging from 2.25(smallest nanocrystal)-6(largest nanocrystal). In addition to the precursor, a .5 M Trioctylphosphine (TOP)-Te solution was previously prepared and stirred overnight. The mixture was stirred vigorously under Ar to 170°C for 30mins and resulted to a clear solution. Nucleation occurred immediately upon rapid injection of TOP-Te into the lead oleate mixture keeping a 2:1 PbTe ratio. The NCs were characterized using TEM images, photoluminescence quantum yield measurements and multiple exciton generation (MEG) quantum yield measurements.

Yu et al²⁴ used a similar approach as Murphy et al¹ in synthesizing CdTe NCs. Again, varying different ranges of molar ratios; the CdO-OA-ODE precursor solution was prepared and heated to 180 °C. The .05mmol TOP-Te solution was rapidly injected into the clear solution and nucleation occurred immediately. The entire experiment was performed under Ar conditions. The QDs were then characterized using Cary 500 UV-VIS-NIR spectrophotometer, XRD Diffraction, photoluminescence spectra and TEM images.

In this project, a new method for synthesizing PbTe SQDs was developed. An organometallic phase synthesis of PbTe via one pot injection method under vacuum conditions was prepared. Using a three manifold-Shlenk line, a three-neck round bottom flask was used as the reaction medium. The entire set-up was done under N₂ atmosphere to dehydrate and removal of air. Lead chloride and lead acetate was replaced with PbO. We demonstrated a new method by substituting OA with oleylamine (OLA) to have alkaline environments opposed to acidic as in Murphy¹ and Yu²⁴. The presence of OLA in the synthesis showed ligand exchange, strong reducing properties and represented immediate nucleation upon injection. Most importantly, OLA played a crucial role in controlling the size of the NCs^{25,26}. ODE was used as a noncoordinating solvent.^{1,24} A .5 M TOP-Te solution was continuously stirred and prepared in a glovebox 24hrs prior to experimental set up. All trials were carried out by altering the molar ratios of the PbCl₂/PbAc-OLA-ODE solutions.

The lead precursor solution was gradually heated to 170-180°C for 30 min using a thermocouple device until stable temperatures were achieved and the compounds have

been fully dissolved. PbCl_2 based solution resulted in an opaque white mixture where as the PbAc was fully dissolved to a transparent solution. The Top-Te was rapidly injected into the reaction vessel for nucleation to occur. The NC growth time (nucleation process) was dependant on the molar ratio of the lead precursor used in each trial. The PbTe product was removed and immediately cooled in an ice bath to room temperature. The cooled product was purified by centrifugation and washed several times with hexane to collect the PbTe NCs. The final QDs were then characterized using Cary 500 UV-VIS-NIR spectrophotometer, TEM images and XRD Diffraction(to be done). All parameters such as; growth time (nucleation) of the NCs, temperature conditions, chemical composition ratios and surfactant to precursor ratio of the NCs were altered in the following trials.

1.4 Lead Telluride (PbTe)- Physical and Chemical properties.

Lead Telluride (PbTe) is a black-blue crystalline solid with a rock salt- halite crystal structure. In a rock salt structure, the atoms are arranged in a face center cubic (FCC) unit cell with a Fm3m space group²⁴ The unit cell expresses the structure of the solid. In a crystal, the unit cell is repeated numerous times to fully assemble at a larger scale. It has been reported that nanocrystals with rock salt unit cells have high surface energies.²⁴

In the FCC unit cell there is one atom at each corner and one atom in each face (Fig. 1). Each corner atom participates one eighth of its volume and each face atom participates one half of its volume to the unit cell. The formula used to calculate the number of atoms in the FCC unit cell is as follows:

$$\text{FCC} = 8 (\text{atoms at corners}) \times \frac{1}{8} + 6(\text{atoms at face centers}) \times \frac{1}{2} = 4 \text{ atoms.}$$

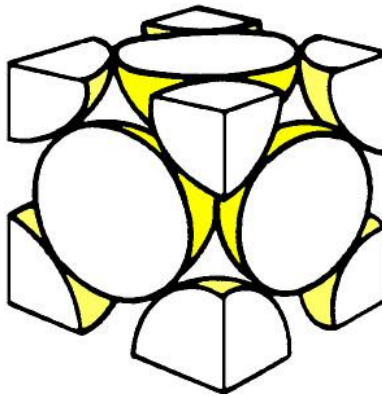


Fig. 1 : Shows the unit cell diagram of a Rock Salt structure. Rock Salt structure has a face centered cubic (FCC) unit cell. PbTe has indirect band gap of 0.25 eV at 0K and 0.31 eV at 300 K.

1.5 Experimental Summary- Chemicals

The aim of this study was to utilize an organometallic phase synthesis of PbTe via one pot injection method under vacuum conditions. Reactions were between a metal containing precursor mixture (e.g. lead chloride (PbCl_2) and a chalcogen containing precursor (Trioctylphosphine telluride (TOP-Te)). The chalcogen lead precursor solution was gradually heated to 170-180°C for 30 min under inert conditions until stable temperatures were achieved and the compounds were fully dissolved. PbCl_2 based solution resulted in an opaque white mixture whereas the PbAc was fully dissolved to a transparent solution. The TOP-Te was rapidly injected into the reaction vessel for nucleation to occur.

A coordinating solvent such as oleylamine (OLA) was used as a capping agent. OLA's long hydrocarbon chain and primary amine group adheres to the nanocrystals surface during synthesis in the non-polar solvent aiding stability and preventing aggregation. The presence of OLA in the synthesis showed additional properties such as ligand exchange, strong reducing properties and represented immediate nucleation upon injection. Most importantly, OLA played a crucial role in controlling the size of the NCs.^{25,26} Previous work has reported^{21,22}, successful colloidal QDs have been obtained by solvents with long hydrocarbon chains ($\text{C}_8\text{-C}_{18}$) due to their ligand exchange properties.

A non- coordinating solvent such as 1-octadecene (ODE) was used in the lead precursor. ODE is an inexpensive, non-polar, eco-friendly and stable solvent.^{1,21,22} Its inert properties make the compounds soluble without reacting with the remaining chemical compounds.

1.6 Experimental Set Up:

A dual -3 manifold Schlenk line apparatus was assembled. One manifold was connected to a source of purified inert gas, while the other was connected to a high-vacuum pump. The nitrogen gas line is vented through an oil bubbler. The gaseous vapor products from the solvents reaction were also prevented from contaminating the vacuum pump and ports. The reaction medium was a three-neck round bottom flask where the colloids were synthesized (Fig. 2). The flask was fit into a heating mantle with a stirring bar. A thermocouple was submerged into the liquid to monitor temperature reading of the solution. The top of the flask was connected to a glass joint with a stopcock. The glass joint was connected to the manifold with an adapter such that during the evacuation of air and removal of water, the pressures were equalized. The remaining neck was sealed with a rubber septum to maintain an inert atmosphere and insertion of reactants. The transfer of all liquids was performed by using a syringe. The entire apparatus was properly sealed, evacuated and purged with nitrogen.

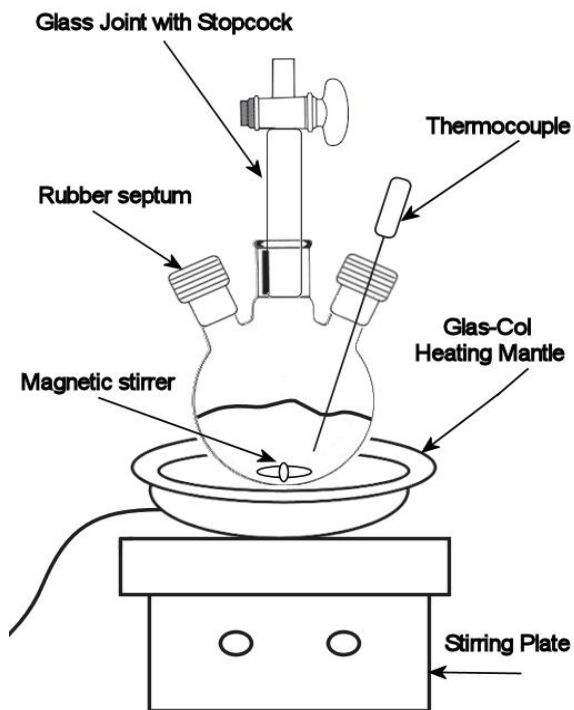


Fig. 2: General diagram of setup used during the synthesis of PbTe QDs. End of glass joint was attached to the Schlenk Line manifold via rubber tubes.

Upon completion of synthesis, the dark blue QDs solution was suspended in hexane to purify. The inorganic compound was fractionated via ThermoScientific megafuge 16 centrifuge. Once the pellet was formed, the supernatant was decanted and the pellet was again washed with hexane. This process of centrifugation to pellet, decanting of the supernatant and re-suspension in hexane was repeated an additional two times. The final purified product was sonicated for 30-45min. The QDs were characterized by using a Cary 500 UV-VIS-NIR spectrophotometer, Zeiss EM902 TEM images, and XRD patterns.

CHAPTER TWO

INSTRUMENTAL ANALYSIS:

UV-VIS-NIR and TEM

2. Characterization: UV-VIS-NIR and TEM

2.1 TEM:

A thermionic (tungsten) Carl Zeiss EM902, transmission electron microscope (TEM) was used to take images of the PbTe QDs. The TEM has a line resolution of 0.34 nm and a point resolution of 0.5 nm. It operates in three modes(normal, diffraction, and low dose modes) at 50 or 80 kV. Its magnification range is 150x to 400,000x. The samples were prepared on a copper-carbon coated grid for TEM imaging. In TEM, an electron gun produces a flow of monochromatic electrons into two lens focusing on the sample. The transmitted beam of electrons through with the specimen are focused by the objective lens and an image is produced. A simplified diagram of TEM is given in Fig. 3.^{27,28,29}

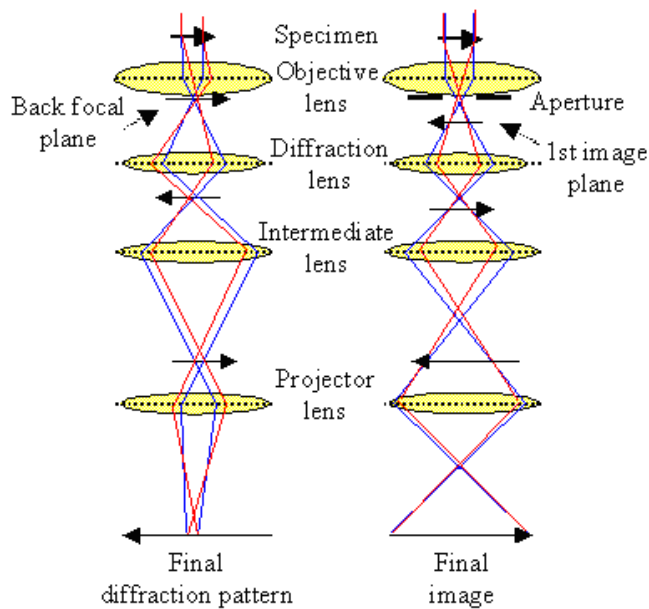


Fig 3. Shows the all (projector, intermediate, diffraction and objective) lens that play part during focusing and taking images of the specimen.²⁷⁻²⁹

2.2 UV-VIS-NIR:

Cary 500 spectrophotometer by Varian Instruments was used to obtain absorption spectra of the prepared PbTe QDs. A general schematic diagram is given below for UV-Vis spectrometer(Fig.4). This spectrophotometer contains a tungsten halogen visible source, a deuterium arc UV source, a R928 photomultiplier tube UV-Vis detector, and an electrothermally controlled lead sulfide photocell NIR detector allowing a broad range of wavelengths. The array of wavelength available is between 200- 3300nm. Solution samples were placed in a quartz cuvette for analysis.^{30, 31}

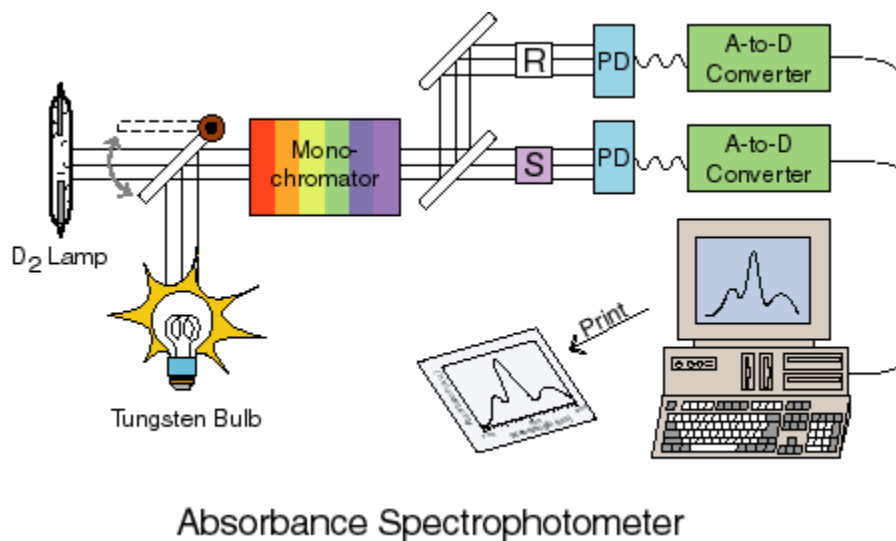


Fig 4: Basic schematic diagram showing absorbance spectrophotometer. A dual (visible and UV) source from the tungsten bulb and deuterium lamp used to create light which is then passed through a monochromator. Monochromator selects a single wavelength and passes through the sample for measurements. R and S represent reference and sample cells.

CHAPTER THREE

EXPERIMENTAL of PbTe QDs

3. Experimental: Materials and Method

3.1 MATERIALS:

Oleylamine (C_{18} , approx. 80-90%), Telluride (98.80 powder), Lead Chloride(99%), Methanol(99%) , Hexanes (99%), were purchased from Arcos Organics. 1-octadecene (90%) was purchased from Alfa Aesar). Trioctylphosphine (technical grade 90%) was purchased from Sigma Aldrich. Lead Acetate Trihydrate was purchased from Fisher Scientific.

3.2 METHOD:

In this project, PbTe QDs were synthesized using a similar approach as reported.^{1,21,22} PbTe QD's were characterized by obtaining transmission electron microscope (TEM) images and UV-VIS-NIR absorption spectra. The synthetic procedure was described below using lead chloride ($PbCl_2$) precursor. The apparatus was assembled using a dual 3-manifold Schlenk Line. An organometallic phase synthesis of PbTe via one pot injection method under vacuum conditions was prepared (Fig.5). A 100mL three neck round bottom flask was used as the reaction medium. The entire set up was under N_2 atmosphere to dehydrate and remove air since the chemical compounds used were both air and water sensitive.

For the synthesis of TOP-Te solution, .638grams of Te and to 10mL of TOP were added to a small vial. The .5M solution was prepared in a glovebox and continuously stirred 24hrs prior to experimental set up (Fig. 8) . A new method was demonstrated by

substituting OA with OLA to have alkaline environments as opposed to acidic[1,4]. The mixture was vigorously stirred under inert conditions. Initial lead precursor was prepared by combining .5562grams of PbCl₂ (2 mmol), 27.38 mL of ODE (78.08mmol) and 3.951ml of OLA (12.00mmol) (Chart 2). The whitish opaque mixture was stirred and heated to 100°C for 15min. The temperature was raised to 180°C for an additional 15min and upon temperature stabilization, 2mL of the yellow TOP-Te solution was rapidly injected into the hot lead precursor keeping a 2:1 PbTe ratio. The temperature reading was 170°C during 6 min nucleation (growth time) (Fig.6).

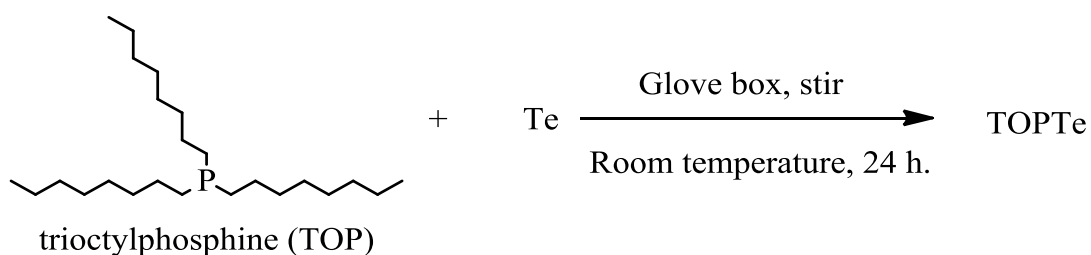


Fig. 5. Chemical reaction between TOP and Te.

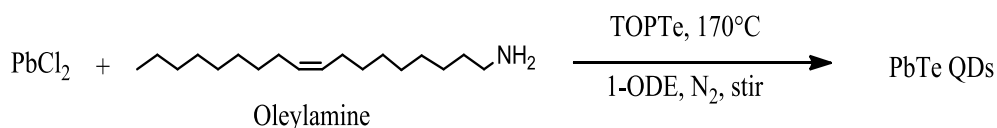


Fig 6. Generalized chemical reaction with lead salt, OLA, TOP-Te at 170°C giving PbTe QDs.

	<u>Tellurium (Te)</u>	<u>Oleylamine (OLA)</u>	<u>1-Octadecene (ODE)</u>
Molecular weight (g/mol)	127.6	267.5	252.48
Density (g/mL)		0.81	0.789
Purity		0.8	0.9
	<u>Trioctylphosphine (TOP)</u>	<u>Lead Chloride (PbCl₂)</u>	<u>PbTe</u>
Molecular weight (g/mol)	370.64	278.1	334.8

Chart 2: Physical properties of the chemicals used.

In order to achieve size selectivity, the solution was further purified. The fractionation procedure was as follows: The dark colored QDs solution was suspended in hexane to purify. The inorganic compound was fractionated via ThermoScientific megafuge 16 centrifuge for 5min. Once the pellet was formed, the supernatant was decanted and the pellet was again washed with hexane. This process of centrifugation to pellet, decanting of the supernatant and re-suspension in hexane was repeated an additional two times. The final centrifuged pellet was dissolved in TCE and sonicated for 30-45min. After sonication, the sample was prepped for taking an absorption spectra and TEM images.

For the absorption spectra, the Cary 500 UV-VIS-NIR spectrophotometer was turned on and warmed up for several minutes. A quartz cuvette was used to analyze the sample. TCE was used as the blank and placed into the holder for base line scanning. Then, the PbTe SQDs dissolved in TCE was scanned for the absorption process

For the TEM images, one drop of the PbTe solution was dropped onto a carbon grid. After drying (approximately one hour) the sample was taken for imaging .The QDs were characterized by using a, and a Zeiss Em902 transmission electron microscope (TEM).

CHAPTER FOUR

RESULTS, DISCUSSION and FUTURE WORK

4.1: RESULTS/DISCUSSION:

PbTe Quantum Dots- Synthesis:

It was found that adjusting the molar ratios of the OLA and injection time gave narrow size distribution of the PbTe QDs. As a typical synthesis approach, many trials were done to observe the changes. Unlike previous work showing acidic conditions in OA^{1,21-24}, This project reported successful PbTe SQDs synthesis in alkaline conditions. Increasing the amount of OLA and decreasing the growth time (one minute) resulted in smaller sized nanocrystals. The molar ratio of 12:2:1 of OLA:Pb:Te produced 11.8nm (diameter) of spherical PbTe QDs. It was also noted that the injection time was very important in synthesizing the PbTe QDs. Longer growth time gave large nanocrystals whereas shorter growth time (one minute) gave smaller sized nanocrystals. Besides controlling the size of nanocrystals, OLA has ligand exchange properties. This property is important for future SERS work. Raman sensitive molecules (4-MPY, pyridine, PATP etc) would be adsorbed on the PbTe QDs to observe charge-transfer.

PbTe Quantum Dots-Optical Properties

The samples dissolved in TCE showed successful synthesis of colloidal PbTe SQDs in alkaline environments. The absorption peak at 2357 nm NIR region shows presence of PbTe QDs (Fig 8). Figure 7 shows the lead chloride samples in TCE. The TEM image of the PbTe QDs capped with OLA is shown in figure 9.

In conclusion, 11.8nm diameter PbTe QDs were synthesized much smaller than the PbTe Bohr Radius (50nm) resulting strong quantum confinement. UV-VIS-NIR spectra and TEM images show proper achievement of the PbTe QDs.



Fig. 7: PbTe SQRs dissolved in TCE suspension

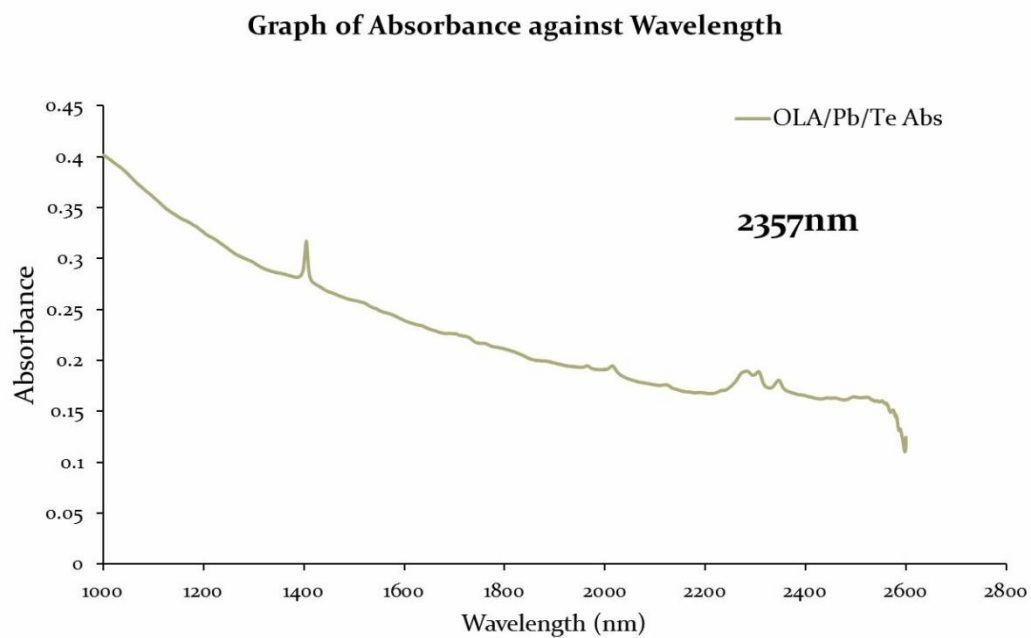


Figure 8.: The ratio of 12:2:1 has first exciton peak at 2357 nm

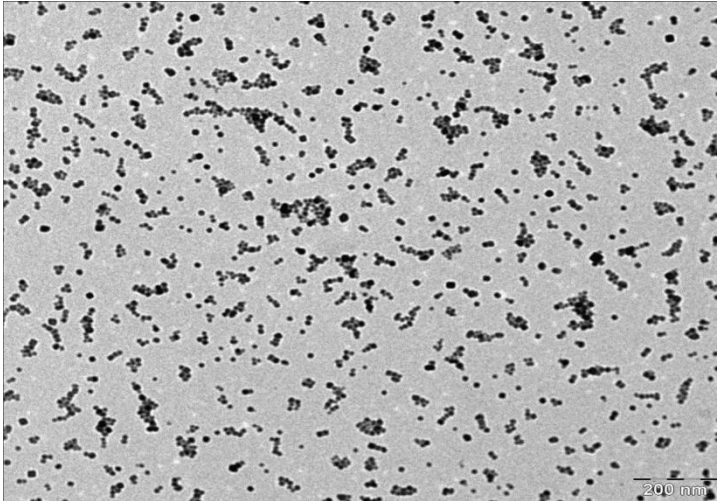


Figure 9: TEM image of PbTe SQDs with OLA capping using the Zeiss EM902. PbTe QD sample shows size of 11.8 nm in diameter.

4.2 Future Work:

In the future, detailed work will be done to observe surface-molecule interactions. SERS techniques will be employed to study charge transfer between the quantum dot and the adsorbed molecule. In addition to spectroscopy, a variety of QDs will be investigated by changing molar ratios of the parameters: coordinating solvents, temperature, growth time and surfactants to achieve various sizes. Presently, similar approach is being carried out by replacing lead chloride with lead acetate. An interesting feature of lead acetate was that it dissolved better in the lead precursor compared to PbCl_2 . Additional synthesis and optical measurements are in process to achieve size distribution nanocrystals.

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