

Development of Ultrasmall Near Infrared Emitting Colloidal PbS and PbS/CdS Quantum Dots with Enhanced Stability in Liquid Petroleum Products

by

Emek Göksu Durmuşoğlu

**A Thesis Submitted to the
Graduate School of Sciences and Engineering
in Partial Fulfillment of the Requirements for
the Degree of**

**Doctor of Philosophy
in
Material Science and Engineering**

Koc University

January 2017
Koc University
Graduate School of Sciences and Engineering

This is to certify that I have examined this copy of a Ph.D. thesis by
Emek Göksu Durmuşoğlu
and have found that it is complete and satisfactory in all respects,
and that any and all revisions required by the final
examining committee have been made.

Committee Members:

Assoc. Prof. Dr. Havva F. Yağcı Acar, (Advisor)

Assoc. Prof. Dr. Uğur Ünal,

Prof. Dr. Hakan Ürey,

Asst. Dr. Fehmi Çivitci, Ph. D.

Asst. Dr. Fırat İlker, Ph. D.

Date:

ABSTRACT

Semiconductor nanocrystals (quantum dots) attract significant interest due to their size-dependent optical properties, that are not achievable with the bulk semiconductor materials. Strong luminescence, broad absorption and narrow emission allows excitation of different QDs at a single wavelength, hence allows detection of different QDs at the same time. This unique property is exploited for optical tagging, diagnostic imaging and optical barcode generation.

Lead sulfide (PbS) QDs are popular QDs for biological imaging, photovoltaics and LEDs, due to strong absorbance in the visible range and strong emission in the near infrared region (NIR). NIR QDs in biological applications are valuable since excitation can be done in the non-harmful visible wavelength range and emission in the NIR can eliminate the autofluorescence of the tissue. It is also possible to generate optical barcodes with NIR QDs, as well, which may be considered as invisible barcodes to the naked eye. In spite of the high popularity of PbS, its instability is a major problem. Most PbS QDs are large nanocrystals with emission above 1100 nm. Besides, there is only a limited amount of reports on small colloidal PbS in the literature.

The overall aim of this thesis is the economically viable synthesis of highly stable, monodisperse, strongly luminescent Pb-chalcogenides with emission between 800-1100 nm.

This range is critical to many applications since most available and inexpensive detectors, such as Si-detector, do not perform at longer wavelengths.

In order to achieve such a goal, first, a relatively green synthetic method was developed which produces PbS and PbSe QDs with strong luminescence in the desired range with the aid of strongly binding dodecanethiol and diluting toluene to otherwise highly viscous and heterogeneous Pb salt and elementals S (or Se) solution in oleylamine. In order to improve long term optical stability, PbS/CdS core/shell structures were prepared as a second action. Yet, in order to provide a robust, highly controllable and scalable shell growth, a room temperature cation exchange method with Cd-oleate was developed. Post-synthetic solid state, low temperature annealing (50 °C) was also developed for highly crystalline PbS/CdS structure which improved the long-term stability. As the third action, a polymeric coating, poly(methacrylic acid) was utilized in the synthesis of PbS, to prevent ligand desorption in dilute solutions which hampers stability. This provided further size tuning within the desired range, did not prevent shell formation and improved the stability of both PbS and PbS/CdS QDs. Post synthetic exchange of oleylamine with dodecanethiol was performed for each composition.

Targeted immediate use of such Pb-chalcogenides is optical tagging of liquid petroleum products, which has strong absorbance in the visible range and a strong and broad auto-fluorescence at 700 nm. So, developing QDs stable in liquid petroleum products at low concentrations (100 ppm) in a 1 month to 1 year, period is the major application goal of the

project. Stability means both optical and colloidal stability and maintenance of the spectral position and the intensity of the emission peak, throughout this thesis.

Overall, colloidally stable, ultrasmall PbX, PbS/CdS QDs were successfully prepared by newly developed inexpensive, scalable, reproducible method. Stability studies indicated DT ligand exchange is absolutely necessary for long term stability. Core/shell structure and polymer existence in the coating composition definitely improves the long-term optical stability as well. Yet, since all petroleum products contain different additives, best composition for each does differ.

ÖZET

Yarı-iletken nano kristaller (kuantum noktalar), bulk yarı-iletken malzemelerde mümkün olmayan boyuta bağlı optik özellikleri nedeniyle son yıllarda önemli bir ilgi odağı haline geldiler. Güçlü ışılda, geniş soğurma ve dar emisyon özellikleri farklı kuantum noktaların tek bir dalga boyunda uyarılmalarına olanak sağlar ki, böylece farklı kuantum noktaların aynı anda tespit edilebilmesi mümkün olur. Kuantum noktaların bu eşsiz özelliklerden optik işaretleyici, optik barkod ve tıbbi teşhis uygulamalarında yararlanılır.

Kurşun sülfür (PbS) kuantum noktaları, görünür bölgede güçlü soğurma ve yakın kızılötesi bölgede güçlü ışımaları nedeniyle, biyolojik görüntüleme, fotovoltailer ve LED'ler için kuantum noktalar arasında için popülerdirler. Yakın kızılötesi ışımaya sahip kuantum noktalar, uyarılmaları zararsız görünebilir dalgalı boylarında yapılabildiği ve ışımaları dokudan gelen floresansa ışımayı elimine ettiği için biyolojik uygulamalar için değerlidirler. Ayrıca yakın kızılötesi ışımaya sahip kuantum noktalarla, görünmez kabul edilebilir, optik barkodlar üretmek de mümkündür. Yakın kızılötesi ışımaya sahip PbS kuantum noktaların, yüksek popülerliklerine karşın, kararlılıkları en büyük problemleridir. PbS kuantum noktalarının büyük miktarı 1100 nm üzerinde emisyonu olan büyük parçalardır. Literatürde sadece az miktarda küçük kolloidal PbS kuantum nokta raporlanmıştır.

Bu tez çalışmasının amacı, 800-1100 nm arası ışımaya sahip, yüksek kararlılıklı, eş-boyutlu, parlak kurşun parçacıkların ekonomik olarak sentezlenmesidir. Bu dalgalı boyu

aralığı, birçok uygulama için kritiktir, çünkü yaygın kullanılan ve ucuz olan detektörler (örn: Si detektör) bu aralıkta çalışmaktadırlar.

Bu amaçla, ilk adım olarak dodekantiyolun güçlü bağlanabilme özelliğinin ve tolüen ile seyreltmenin yardımıyla (diğer türlü Pb tuzu ve element S'nin (veya Se) oyleylamine içerisindeki reaksiyonu çok derişik ve heterojendir) istenilen bölgede güçlü ışıması olan PbS ve PbSe kuantum noktaları üretiminde kullanılan görece doğa-dostu sentez yöntemi geliştirildi. İkinci adımda, uzun süreli optik dayanımın sağlanması için, PbS/CdS çekirdek/kabuk yapıların üretilmesiydi. Dirençli, kontrol edilebilir ve ölçeklendirebilir kabuk büyütme işlemi için, oda sıcaklığında katyon değişimi yöntemi geliştirildi. Uzun süreli dayanımı arttıran katı hal tavlama işlemi düşük sıcaklıkta (50 °C) uygulandı ve yüksek kristallğe sahip PbS/CdS yapısı elde edildi. Üçüncü adım olarak, dayanımı azaltan bir süreç olan seyreltik solüsyonlardaki ligand kopmasını engelleyen, Polymathakrilik polimer kaplamalarını PbS sentezinde kullandık. Bu kaplama, hedeflenen dalgaboyu aralığında daha çok boyutlanabilirlik sağladı. Bununla birlikte hem PbS hem de PbS/CdS kuantum noktalarının uzun süreli dayanımları arttı. Dayanımın arttırılması için, oyleylamine'nin, dodekantiyol ile değişimi işlemi her kompozisyon için uygulandı.

Hedeflenen uygulama, 700 nm dalgaboyunda güçlü ve geniş kendiliğinden ışımaları olan sıvı petrol ürünlerin işaretlenmesidir. Yani, sıvı petrol ürünlerin içerisinde bir yıla kadar düşük konsantrasyonlarda (100 ppm seviyesi) kararlı kalabilen kuantum noktalar geliştirmek bu çalışmanın hedefidir. Uygulama kuantum noktaların hem optik hem de kolloidal

kararlılıklarının gerektirmektedir. Kararlılık hem optik hem de kolloidal kararlılık ve ışıma dalgaboyunun ve şiddetinin korunması anlamına gelmektedir.

Genel olarak, kolloidal dayanımlı, küçük boyutlu PbX, PbS/CdS kuantum noktalar, yeni geliştirilen ucuz, ölçeklenebilir sentez yöntemimizle başarıyla üretildiler. Dayanıklılık çalışmaları dodekantiyol ligand değişimi yönteminin uzun dayanım için kesinlikle gerekli olduğunu gösterdi. Çekirdek/kabuk yapılar ve polimer kaplamalar da uzun süreli optik dayanımı açık bir şekilde geliştirdiler. Ancak tüm petrol ürünleri farklı katkıları içerdikleri için, her birinde en iyi sonucu veren kuantum nokta kompozisyonu değişmektedir.

ACKNOWLEDGEMENTS

First of all, I would like to thank to my advisor Assoc. Funda Yağcı Acar for her guidance, trust, great support, motivation and encouragement for my academic career and in my life. Her positive and friendly attitude, sincerity, sympathy and endless energy provides to me confidence to overcome struggling challenges. I am deeply indebted to her for everything she made for me, for her great contributions to my research, to improve myself academically and personally.

I would like to thank to my thesis committee members Prof. Hakan Ürey, Assoc. Prof. Uğur Ünal, Asst. Prof. Fırat İlker and Asst. Prof. Fehmi Çivitci for support, contributions and suggestions to my PhD thesis. I would like to thank to Assoc. Prof. Oğuzhan Gürlü as a member of my thesis progress committee, for his contributions and suggestions.

I would like to thank to my qualifying exam members, Prof. Ali Serpengüzel, Assoc. Funda Yağcı Acar, Assoc. Prof. Uğur Ünal, Assoc. Prof. Özgür Birer and Assoc. Prof. Sarp Kaya for their contributions and suggestions to my PhD research studies.

I would like to thank Koc University Surface Technology Research Center (KUYTAM) for their help in characterization of QDs. I deeply appreciate the assistance and support of the KUTAM team, Dr. Barış Yağcı, Cansu Yıldırım, Assoc. Prof. Özgür Birer and Assoc. Prof. Uğur Ünal.

I would like to express my thanks to my co-researchers in our project: Dr. Emre Heves, Dr. Fehmi Çivitçi, Dr. İbrahim Hocaoglu, Dr. Yurdanur Türker, Dr. Pınar Dağtepe and Başarbatu Can for their collaboration, contribution and motivation to my research.

I would like to express my thanks to Koc University, OPET A.Ş. and Kuantag A.Ş. for funding to my PhD researches.

I would like to express my thanks to former and present members of our research group: Dr. Yurdanur Türker, Dr. İbrahim Hoccoğlu, Dr. Rouhullah Khodadust, Dr. Aydın Can, Özge Çavuşlar, Didar Aşık, Yasemin Yar, Özlem Ünal, Enes Buz, Gökay Avcı, İrem Ülkü, Fatma Demir Duman, Pelin Turhan and Emre Köken for their support and motivation.

I am deeply grateful to all faculty members of the Material Science and Engineering Program for their assistance.

Finally, I would like to express my sincere thanks to my family and my friends. I am very grateful to my mother Müzeyyen Durmuşoğlu, my father Haluk Durmuşoğlu, my brother Gökay Durmuşoğlu, his wife Melike Baş Durmuşoğlu, my aunt Saime Odabaş, my dear friends Seda Gönül, Çağlar Koca, Buket Kara, Emir Gürsel and Bülal Doğan for their everlasting support, trust, guidance, encouragement, motivation, financial and spiritual support. I would like to also thank the other members of my family for their support: my cousins, my nieces and my aunts.

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NOMENCLATURE

$(\text{TMS})_2\text{S}$	Bis(TriMethylSilyl)Sulfide
Ag_2S	Silver(I)sulfide
Ag_2Se	Silver(I)selenide
Ag_2Te	Silver(I)telluride
CB	Conduction Band
Cd^{+2}	Cadmium Ion
CdO	Cadmium Oxide
CdS	Cadmium Sulfide
CdSe	Cadmium Selenide
CE	Cation Exchange
CuInS_2	Copper Indium Sulfide
CuInSe	Copper Indium Selenide
D	Diameter
DLS	Dynamic Light Scattering
DOS	Density of States
DT	Dodecanethiol
E_0	Band gap energy
EDX	Electron Dispersive X-ray

EuS	Europium Sulfide
FFT	Fast Fourier Transform
FTIR	Fourier Transform Infrared Spectra
FWHM	Full Width at Half Maximum
GSH	Glutathione
InAs	Indium Arsenide
InGaAs	Indium Gallium Arsenide
InP	Indium Phosphide
IR	InfraRed
LE	Ligand Exchange
LED	Light Emitting Diodes
m_e	Effective mass of electron
m_h	Effective mass of hole
MPA	Mercapto Propionic Acid
MRI	Magnetic Resonance Imaging
Na ₂ S	Sodium sulfide
NC	Nano-Crystal
NIR	Near InfraRed
NIRQDs	Near Infrared Emitting Quantum Dots

OA	Oleic Acid
ODE	Octadecene
OLA	Oleylamine
Pb ⁺²	Lead Ion
PbCl ₂	Lead Chloride
PbO	Lead Oxide
PbS	Lead Sulfide
PbSe	Lead Selenide
PbTe	Lead Telluride
PL	PhotoLuminescence
PLQY	PhotoLuminescence Quantum Yield
PMAA	Poly Methacrylic Acid
PMT	PhotoMultiplier Tube
PV	PhotoVoltaic
QD	Quantum Dot
QY	Quantum Yield
RT	Room Temperature
SILAR	Successive Ionic Layer Adsorption Reaction
TAA	ThioAcetAmide

TCSPC	Time Correlated Single Photon Counting
TEM	Transmission Electron Microscopy
TOP	n-Tri-Octyl Phosphine
TOPO	n-Tri-Octyl Phosphine Oxide
UV	Ultra Violet
VB	Valence Band
Vis	Visible
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
ZnS	Zinc Sulfide

Chapter 1

1 Introduction

1.1 Quantum Dots

For more than 30 years now, colloidal semiconductor nanoparticles (QD) have been studied extensively in different disciplines of science and technology. With unique size-dependent electronic, chemical, magnetic and optical properties, QDs are important semiconductor materials. Particle sizes smaller than Bohr radius enable the discretization of the energy levels and widen the bandgap. If a nanoparticle has a dimension below its Bohr radius, electrons become confined. QDs are confined in all three spatial dimensions. This confinement regime allows tuning of optical and electronic properties by simply changing the size of QDs (Figure 1. 1). So, QDs have attracted significant attention due to their unique optical properties, which are dramatically different than the bulk crystals.

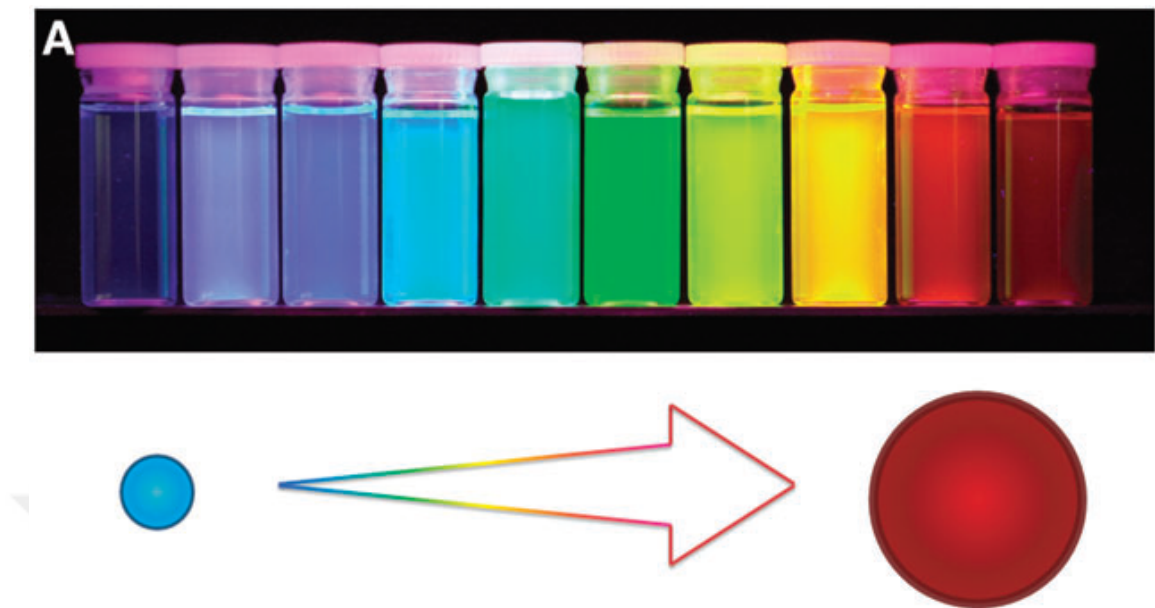


Figure 1. 1 Size-dependent luminescence of QDs [1]

QDs usually have a diameter in the range of 2-10 nm and composed of group II-IV (ZnS, ZnSe, CdSe, CdTe, CdS, HgS), group III-V (GaAs, GaN, InP, InAs, InGaAs) and group IV-VI (PbS, PbSe) elements. Bandgap of QDs is material-specific bandgap which is larger than bulk semiconductors, and can be tuned by the crystal size (Table 1. 1). QDs are most famous with their luminescent properties. When excited with photons of appropriate energy, QDs fluoresce (as shown in Figure 1. 1). These unique properties of QDs enable wide-range of applications such as; biosensor[2], bio-imaging[3], optically trackable drug delivery[4], photodetector[5], LED[6, 7], photovoltaic[8], nanoprobe[9], optical fiber[10], laser[11], telecommunication[12] and labeling[13, 14] applications.

Table 1. 1 Properties of selected bulk semiconductors[15]

Material	Structure [300K]	Type	Bandgap [eV]	Lattice parameter [Å]
ZnS	Zinc blende	II–VI	3.61	5.41
ZnSe	Zinc blende	II–VI	2.69	5.668
ZnTe	Zinc blende	II–VI	2.39	6.104
CdS	Wurtzite	II–VI	2.49	4.136/6.714
CdSe	Wurtzite	II–VI	1.74	4.3/7.01
CdTe	Zinc blende	II–VI	1.43	6.482
GaN	Wurtzite	III–V	3.44	3.188/5.185
GaP	Zinc blende	III–V	2.27	5.45
GaAs	Zinc blende	III–V	1.42	5.653
GaSb	Zinc blende	III–V	0.75	6.096
InS	Wurtzite	III–V	0.8	3.545/5.703
InP	Zinc blende	III–V	1.35	5.869
InAs	Zinc blende	III–V	0.35	6.058
InSb	Zinc blende	III–V	0.23	6.479
PbS	Rocksalt	IV–VI	0.41	5.936
PbSe	Rocksalt	IV–VI	0.28	6.117
PbTe	Rocksalt	IV–VI	0.31	6.462

1.1.1 Exciton Bohr Radius and Quantum Confinement

According to their valance band (VB) and conduction band (CB) positions, materials are characterized as insulators, conductors and semiconductors. The energy difference between VB and CB is called as the bandgap and this region is prohibited to electrons. Semiconductors have a lower bandgap than insulators which can be jumped if sufficient energy is provided to the VB electrons with an external stimulus such as heat, radiation etc. If an external stimulus provides an energy, which is equal or higher than the bandgap energy, VB electrons get excited to the CB by leaving a hole in the VB (Figure 1. 2). At the CB, electrons climb down to the lowest level of CB by losing part of the gained energy to vibrational relaxation, then return to their steady-state in the VB by losing the remaining energy as non-radiative or radiative relaxation, and finally electron and hole recombination occurs. This radiative relaxation of electrons is called as luminescence.

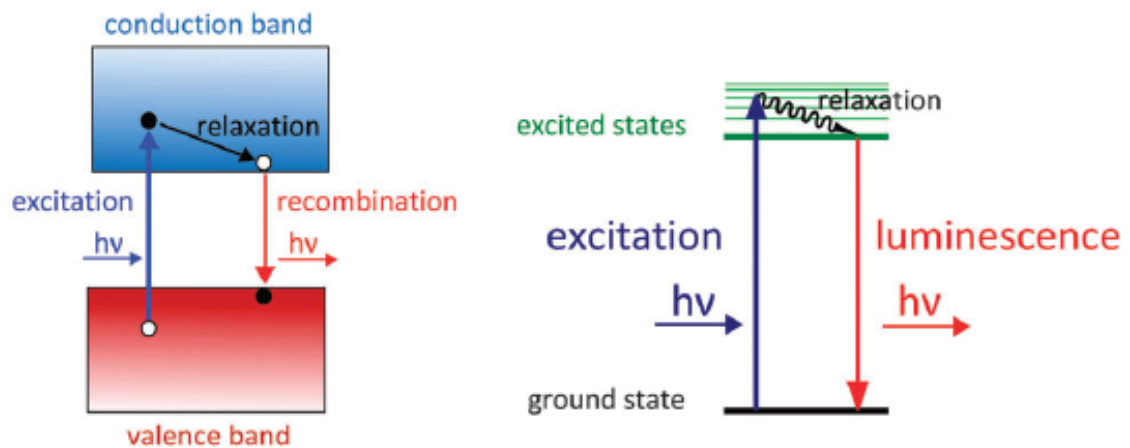


Figure 1. 2 Simplified presentation of excitation, relaxation and emission processes for electronic bands and discrete energy levels [16]

The “electron and hole pair” is called as the “exciton” and distance between them is called as the “exciton Bohr radius (EBR)”. EBR is material specific. If the size of the semiconductor crystal is between the range of 3-10 times of its EBR, particle is under a weak confinement regime. Strong confinement can be achieved by smaller dimensions than EBR. In a bulk semiconductor electrons are free to move in all directions and there is no confinement regime for electrons. If a dimension becomes small than EBR, electrons get confined. According to confined dimensions, semiconductors are grouped under 4 categories; confinement at one dimension is considered as quantum wells (2D), two dimensions as quantum wires (1D), three dimensions as quantum dots (0D) and no confinement as bulk materials (3D) (Figure 1. 2).

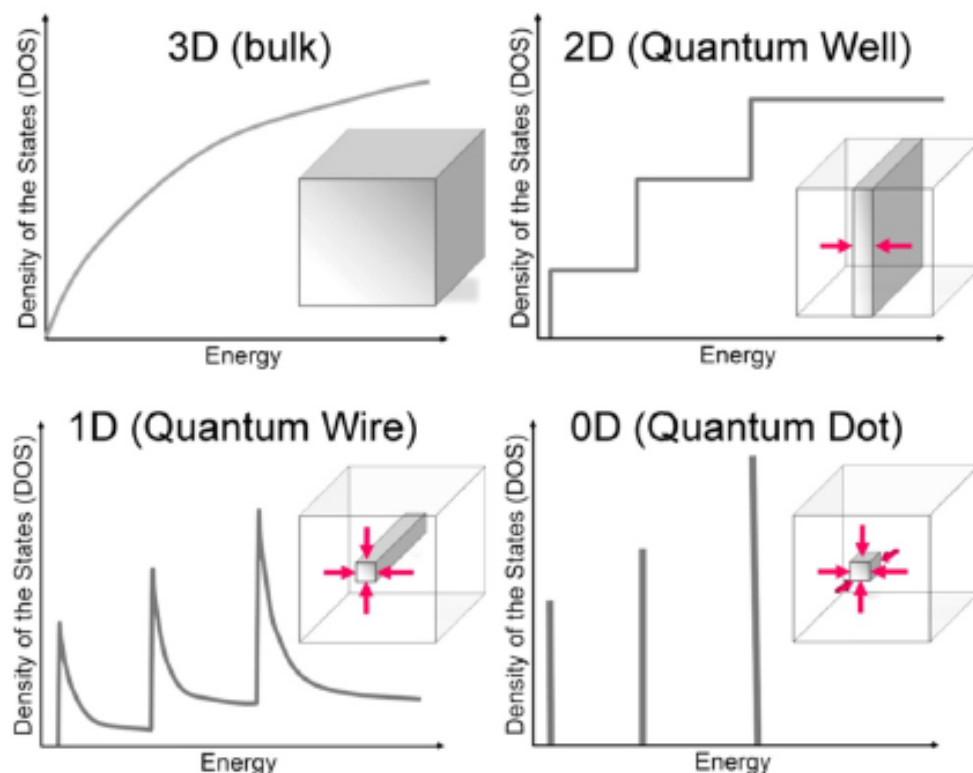


Figure 1. 3 Density of states for 0D, 1D, 2D and bulk materials.[17]

Figure 1. 3 shows the density of states (DOS) for different confinement regimes. Confinement of electrons causes discrete energy levels. Electronic properties or number of free electrons per unit volume, become more quantized as the dimensions get confined. This discrete energy levels and strong confinement regime enable unique size-dependent properties to QDs.

1.1.2 Size-Dependent Optical properties of QDs

$$Eg_{QD} = Eg_b + \left(\frac{h^2}{8R^2}\right)\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \left(\frac{1.8e^2}{4\pi\epsilon_0\epsilon R}\right) \text{ (Eq. 1. 1)}$$

Eq. 1.1 shows the relation between the bandgap and the size of QD, where Eg_b and Eg_{QD} are the bandgap energies of the bulk material and QD, respectively, R is the radius of quantum dot, m_e is the effective mass of the electron in the bulk, m_h is the effective mass of the hole in the bulk, 'e' is the charge of an electron, 'h' is the Planck's constant and 'ε' is the dielectric constant of the bulk. E_g is indirectly proportional to the size of QD. So, smaller size QD has larger bandgap energy. Therefore, the relaxation of excited electrons emits more energetic photons for smaller QDs compared to larger ones. This allows tuning of optical and electronic properties by simply changing the size of QDs (Figure 1. 4). With the increasing crystal size of the QD, emission shifts to longer wavelengths due to smaller bandgap energy. Energy of the photon is inversely proportional with the wavelength. Shift to longer wavelength (lower energy) is considered as a red shift.

Photoluminescence (PL) describes the phenomenon of light emission from any form of excited material after the absorption of photons. Two types of luminescence are described; the fast one is considered as fluorescence and the slow one as phosphorescence. QDs show strong fluorescence, which is critical for many labeling and imaging applications. For the fluorescence, QDs should be excited with an external stimulus, which is usually a photon current (Figure 1. 5). If a VB electron absorbs a photon, which has a same or more energy than the bandgap of QD, electron jumps to the excited states (excitation). If electron returns to its ground state from single state, it loses its energy (relaxation) by light emission, called as fluorescence. If relaxation occurs from a triplet state, electrons lose their energy via phosphorescence. Due to energy loss at the excited state, the emitted photon is usually less energetic than the absorbed one, which is called as “stokes shift”.

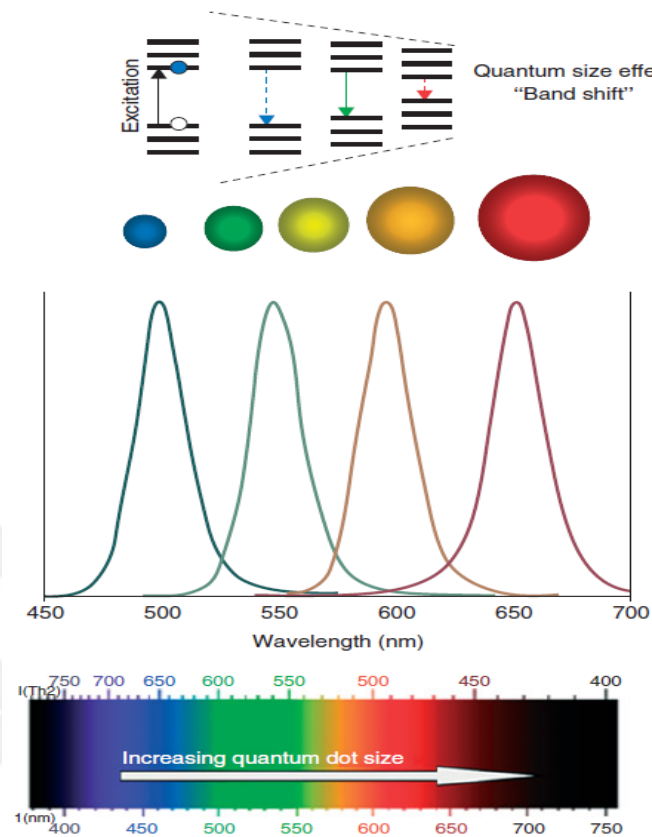


Figure 1. 4 Relationship between the crystal size, band gap and the emission wavelength of QDs.[1]

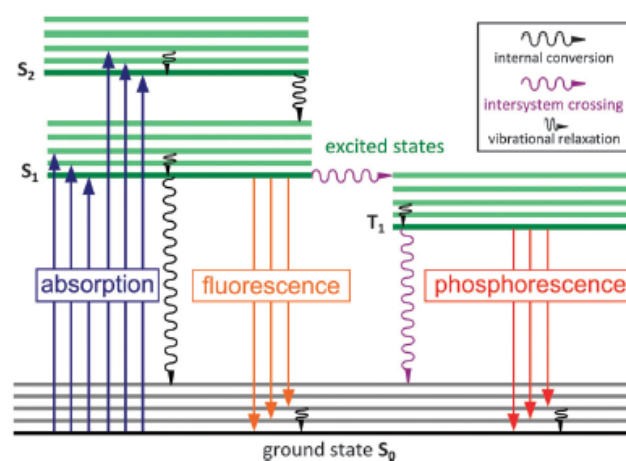


Figure 1. 5 Jablonski diagram[16]

Figure 1. 6 clearly shows the Stokes Shift with emission at longer wavelengths than absorption. The following two equations explain such energy difference between excitation and emission;

$$S_0 + h\nu_{ex} \rightarrow S_1 \text{ (excitation) (Eq. 1. 2)}$$

$$S_1 \rightarrow S_0 + h\nu_{em} + \text{loss energy} \text{ (emission) (Eq. 1. 3)}$$

where S_0 and S_1 are ground and excited states, respectively, $h\nu_{ex}$ and $h\nu_{em}$ are excitation and emission energies of photon, respectively. From the equations, emission have two components radiative and non-radiative (heat). Non-radiative event is the reason of Stokes shift between emission and absorption and it is also decreasing fluorescence quantum yield (QY) of QD.

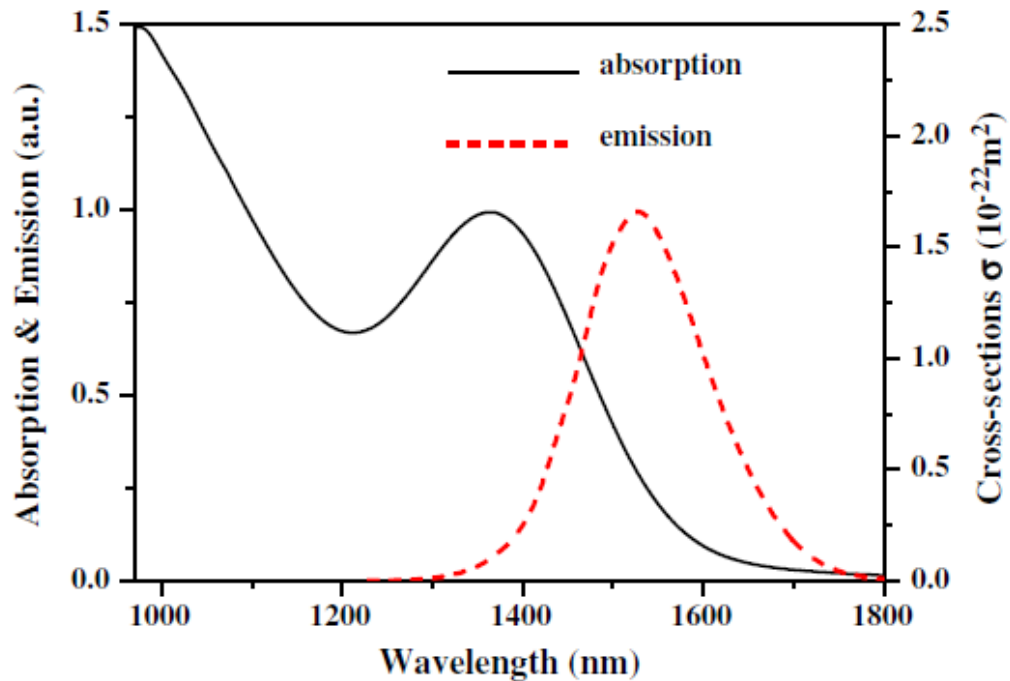


Figure 1. 6 Stokes shift between emission and absorption wavelengths [18]

$$\phi = \frac{\# \text{photons emitted}}{\# \text{photons absorbed}} \text{ (Eq. 1. 4)}$$

The QY quantifies the efficiency of the fluorescence process. It is defined as the ratio of the number of photons emitted to the number of photons absorbed (Eq. 1. 4). Non-radiative events reduce QY, hence emitted photons are always less than absorbed ones. In a way, high QY indicates high quality.

The fluorescence lifetime measures the average time that the electron stays in its excited state before returning to ground state.[19]

$$[S1] = [S1]_0 e^{-\Gamma t} \text{ (Eq. 1.5)}$$

where $[S1]$ is the concentration of excited state molecules at time (t), $[S1]_0$ is the initial concentration and Γ is the decay rate or the inverse of the fluorescence lifetime. Most of the time, luminescence lifetime provides information about the relaxation paths and hence is an important characteristic of a QD, just like QY. The fluorescence lifetime is also called as photoluminescence decay time.

1.2 Near Infra-Red Emitting Quantum Dots (NIRQDs)

1.2.1 NIRQDs in Literature

QDs with emission in the near-infrared (NIR) region gained considerable attention in the last decade due to additional advantages in various applications.[20] As well as simple structures such as lead chalcogenides,[21-23] silver chalcogenides,[24-26] InAs,[27] InP,[28] a lot of binary or ternary alloys such as CuInS₂,[29] CuInSe₂,[30] core/shell

and core/shell/shell structures such as PbS/CdS,[31] PbSe/PbS,[32] PbS/EuS,[33] PbS/CdS/ZnS,[34] are described as NIR QDs in the literature. Some of these can be found commercially, as well. Strong absorbance in the visible spectrum, multiple exciton generation[35] and luminescence in the NIR region make simple NIR QDs an attractive candidate for wide range of applications, including bio-imaging,[36, 37] LEDs,[38] photovoltaics[39, 40] and photodetectors.[41]

1.2.2 Properties of PbX (X= S, Se) QDs

From the IV–VI group semiconductors, lead chalcogenides (PbX, X = S, Se, or Te) are most studied near infrared (NIR) emitting QDs due to their bulk bandgap, which is 0.41 eV for PbS, 0.28 eV for PbSe, and 0.31 eV for PbTe at 300 K, and large exciton Bohr radius (18 nm for PbS).[42] This strong confinement of PbS QDs enables up to 90 % quantum yield (QY) in solution.[43] However, long term instability (photo-degradation) is one of the most important drawbacks of lead chalcogenides.[44-46]

With tunable bandgaps and inter-dot spacing, high absorbance and carrier mobility NIR emitting PbS QD popular for epically photovoltaics as absorber layer.[47] Recently, Sargent et. al., achieved 10.6% efficiency by using PbS QDs in solar cells.[48] But PbS QDs used in photovoltaic applications have emission above 1200 nm and they are used as dispersed phase in thin films.[49-51] There was only a limited amount of colloidal PbS QDs, these have emission below 1100 nm, before our thesis work.

As discussed previously, bandgap of QDs are tunable by change of size. So, many studies were carried out to calculate theoretically and experimentally the size of QD from

the optical properties of QD.[52-54] Between these studies the relation of Cademartiri et. al., is one of the most used as a size curve for PbS QDs [35];

$$D(nm) = 0.85 + \sqrt{0.7225 + \left(\frac{1243}{\lambda(nm)} - 0.41\right) * 3.84} / \left(\frac{1243}{\lambda(nm)} - 0.41\right) \text{ (Eq. 1. 5)}$$

where D is the diameter of PbS crystal, 0.41 is E_{gb} of PbS QD. Therefore, with known size of PbS QD, the following formulas can be used to calculate the valance band energy (E_{vb}) conduction band energy (E_{cb}) and the bandgap (E_g);

$$E_{vb}(Ev) = -4.76 - 0.64 * D(nm)^{-0.9} \text{ (Eq. 1. 6) [55]}$$

$$E_{cb}(Ev) = -4.35 + 5.12 * D(nm)^{-1.27} \text{ (Eq. 1. 7) [55]}$$

$$E_g(Ev) = E_{cb}(Ev) - E_{vb}(Ev) \text{ (Eq. 1. 8)}$$

1.3 Core-Shell Quantum Dots

1.3.1 Core-Shell QDs in Literature

Colloidal core-shell QDs consists from at least two different semiconductor materials grown on each other. A semiconductor shell is usually used to tune optical properties of the core QD and to increase stability of the core QD. Optical properties such as emission and absorbance wavelength, QY and lifetime can be tuned by the shell growth. Due to the large surface/volume ratio of QDs, surface chemistry plays an important role on the optical properties.[56] As defects on the surface of the QDs behaves as surface traps for an electron or hole, they cause non-radiative coupling events. [57] These reduce the quantum yield of QDs. Hence, complete surfaced coverage, defect free crystal surface is needed for both colloidal and optical stability as well as high QY. Photo-oxidation is an

important problem, especially for Pb-chalcogenides. Poor surface quality enhances this degradation, as well.[58, 59] Organic long-hydrocarbon chain ligands usually used to passivate surface and provide colloidal stability. But, remaining dangling bonds on QD surface can act as charge trap sites and are prone to oxidation.[57] Passivation of core QD with another inorganic shell material is a useful method to improve the resistance to photodegradation, improve colloidal stability and improve QY.[60]

According to the alignment of the VB and CB positions of the core and the shell, three types of core/shell QDs may be considered (Figure 1. 7): type-I, quasi-type-II, and type-II. In the type-I, the bandgap of the core semiconductor is smaller than the bandgap of the shell, with both CB and VB of the core located within the band gap of the shell. Therefore, both electrons and holes are confined in the core region, significantly enhancing luminescence intensity. In the type-II, the VB and CB of the core is either higher or lower than the VB- CB of the shell, hence the hole and the excited electron would be at the VB of one material and CB of the other, based on the lowest possible distance, which is smaller than the bandgap of the core. Therefore, excitons are partially or completely confined in the shell. This usually causes a significant shift in the emission wavelength. Quasi-type-II, is an intermediate alignment similar to type-I but VB and CB of each material are close to each other. Such an alignment enables the delocalization of the exciton over the entire core/shell structure.[15, 61] PbX/CdX (X = S, Se, or Te),[62-64] CdS/ZnS,[65] CuInS₂/ZnS,[66] and InP/GaP/ZnS[67] are examples to such core-shell QDs frequently found in literature. This type of core/shell structures are usually providing better charge separation and higher QY, hence becoming more popular.

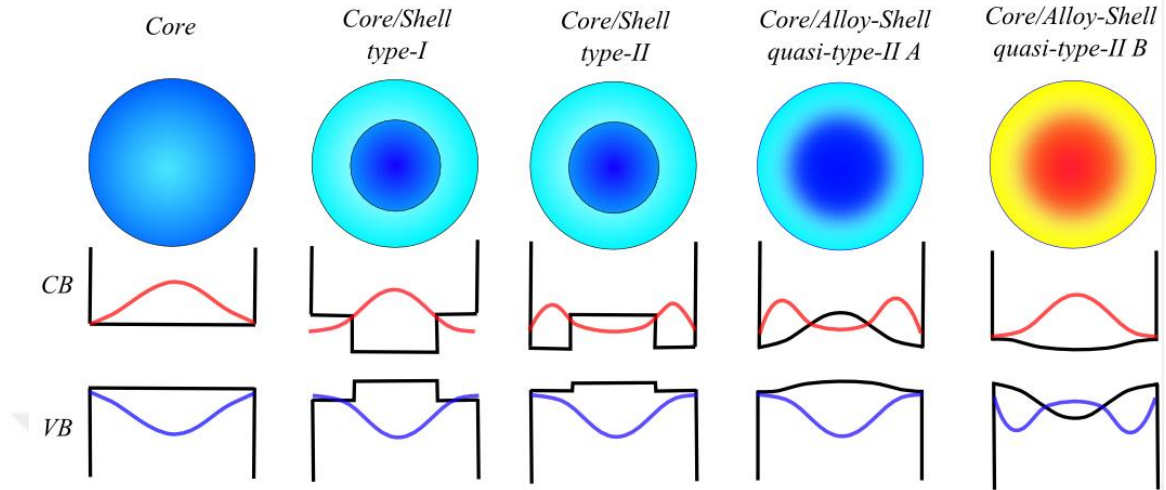


Figure 1. 7 Core-shell semiconductor QDs types [61]

1.3.2 Synthesis of Core/Shell QDs

There are two common method to grow a shell on a QD; SILAR (Successive ionic layer adsorption and reaction) and cation exchange. SILAR is the commonly used process to grow a shell upon a core in the photovoltaic applications.[68, 69] Generally, SILAR method performed by using spin-coating, dip-coating, drop-casting methods wherein the shell material was coated over the core QD layer by layer.[68, 70, 71] But, cation exchange method is emerging as a popular method, lately. This method requires only addition of the second cation which will grow the shell in the expanse of the initial core, more or less keeping the anion component untouched. So, for a successful cation exchange, lattice parameters, crystal type and bandgap positions (Figure 1. 8) of the core and the shell materials is important (Table 1. 1). It is fast, easy, safe and produces more defect free interface, hence provide a strong enhancement in the optical properties.[72-

74] So, cation exchange is becoming a useful method to obtain colloidal core/shell particles, which are often inaccessible by one-step synthetic routes.[72] Cation exchange is a diffusion controlled process and hence, typically performed at and above 100 °C, to ensure desorption of surface cation and adsorption of the new ones, to avoid defective grain boundary formation and remnant impurities of the outgoing cation.[72] But, such high temperatures generally leads to Ostwald ripening of QDs.[75] Also, many studies revealed that thicker shells formed at high temperatures causing a decrease in quantum yield due to defects at interfaces and the thick shell.[31, 76]

1.3.3 PbS/CdS Core-Shell QDs

CdS is one of the most widely used shell material on PbS QDs to enhance optical properties and stability. PbS/CdS heterostructure is a type-1 core-shell QD. CdS has a larger bandgap (bulk bandgap around 2.49 eV) than PbS (bulk bandgap around 0.41 eV), so acts as a potential wall confining both electrons and holes within the PbS core.[15] Also, the small lattice mismatch between CdS (zinc blende, with lattice parameter 5.82 Å) and PbS (rock salt, with lattice parameter 5.93 Å) crystals, allows sharing of a face-centered cubic sublattice of S atoms and provide a good compatibility at the interface.[62] CdS shell passivates surface of core PbS QD and increases optical properties such as QY, lifetime, emission intensity.[75, 77]

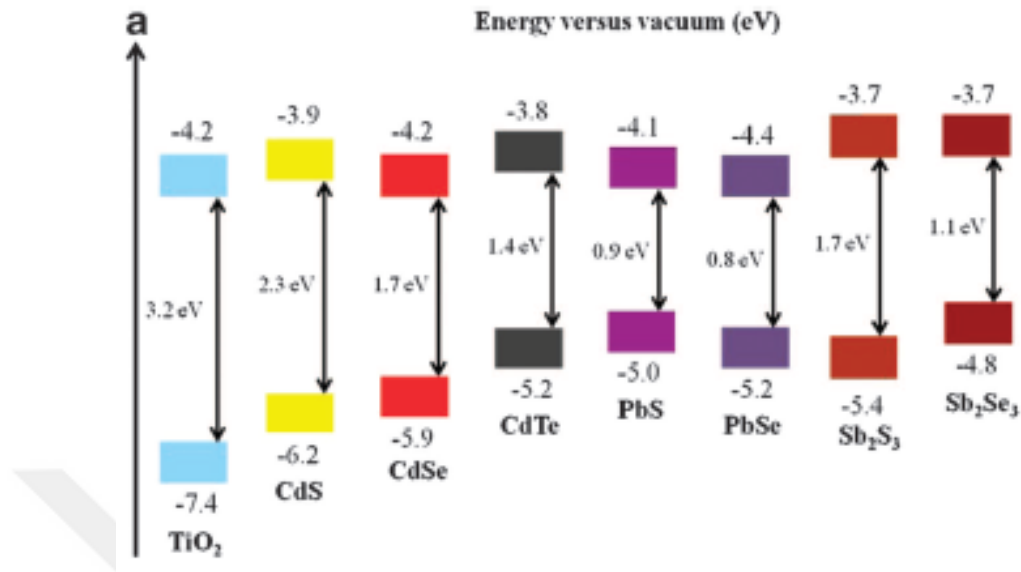


Figure 1. 8 Energy level (band position) versus vacuum of various QDs [78]

1.4 Synthesis of QDs

1.4.1 Synthesis of PbX (X:S and Se) QDs

There are different ways to produce PbX QDs: wet chemistry, gas phase and solid-state synthesis.[57] Among these methods, wet chemistry is more cost-effective, scalable and relatively an easier one. The wet-chemical synthesis is a widely used method to obtain highly monodisperse, stable and luminescent semiconductor nanocrystals (QDs).[6] Organometallic hot injection is a wet chemical synthesis method, which produces monodisperse QDs (little size variation of <4%) with high QY. [6] In organometallic hot injection method, precursors are usually added into a hot coordinating solvent for rapid nucleation and cooled down to a second temperature for the growth. This temperature range is usually between 120–360 °C.[79] Finally, the reaction is quenched by cooling to room temperature. In the synthesis of PbX QDs, organometallic hot injection method

developed by Hines-Scholes is the widely used solution synthesis method.[21] . By changing the reaction parameters, such as temperature, crystal growth time, stoichiometry and concentration, a fine control over the size of QDs can be achieved.[6, 80]

Highly monodispersed and scalable production of PbX QD was reported by organometallic hot injection method.[81] This method produces colloidal hydrophobic PbS QDs with tunable emission between 800-1800 nm and typically uses PbO, oleic acid (OA), octadecene (ODE) and highly toxic and air-sensitive bis(trimethylsilyl)sulfide ((TMS)₂S).[21] Although other S-sources can be used, quality of the particles were reported as poor.[21] One major drawback of PbS produced in this way is the instability of particles in ambient conditions due to oxidation which decreases with the decreasing crystal size.[82]

An alternative method was developed by Cademartiri et al.[81] This method is relatively green and less costly as reaction can be performed at lower temperatures and uses oleylamine as the coating and the solvent (OLA), lead chloride (PbCl₂) and elemental sulfur as the precursors. Gram-scale synthesis of PbS QDs with improved air stability were reported with this method.[81] Yet, particles are relatively large in size with tunable emission between 1200-1700 nm. Presence of an additional chloride passivation is suggested for better air-stability of PbS-OLA compared to PbS-OA.[83] Due to the nature of the growth kinetics of this method, it is difficult to synthesize smaller size nanoparticles with emission below 1200 nm. Recently, Moreels et al. incorporated tri-n-octylphosphine (TOP), which is also highly toxic and air-sensitive, to the standard formulation of this method and claimed production of PbS QDs in a broader size regime

(3-10 nm) with photoluminescence quantum yield (PL QY) up to 90 % for smaller size particles and air stability for over 6 six weeks.[43] Yet, no data on the luminescence behavior of the aged sample was provided. .

There are only few reports that mention the air-instability or the long-term instability of the optical properties of PbS QDs, clearly.[22, 59] Achieving stable PbS QDs becomes more difficult with the smaller size particles due to the increased surface energy. There are different known strategies to overcome the instability such as embedding QDs in polymeric beads,[44] growing an inorganic or semiconductor shell on the core QD,[31] halogen-treatment[84] and changing surface properties by ligand exchange.[85] Between these methods, the ligand exchange method, which is a post-synthetic process, is the easiest and commonly used one, both to enhance the stability and to change the surface chemistry (as an example from hydrophobic to hydrophilic). Enhanced stability of PbS was reported by exchanging OLA with oleic acid (OA) which binds more strongly to crystal surface.[54] Exchanging OLA or OA by thiolated ligands which binds even stronger than the carboxylic acid to PbS surface is another accepted way to improve the stability.[86] Yet, long term stability of small sized colloidal PbS QDs has not been reported, yet.

1.4.2 Synthesis of Core-Shell PbS/CdS QDs

1.4.2.1 Common Synthetic Methods

There are two common method to grow a shell on a QD; SILAR (Successive ionic layer adsorption and reaction) and cation exchange. SILAR is the commonly used process to grow a shell upon a core in the photovoltaic applications.[68, 69] Generally, SILAR

method performed by using spin-coating, dip-coating, drop-casting methods wherein the shell material was coated over the core QD layer by layer.[68, 70, 71] But, cation exchange method is emerging as a popular method, lately. This method requires only addition of the second cation which will grow the shell in the expanse of the initial core, more or less keeping the anion component untouched. So, for a successful cation exchange, lattice parameters, crystal type and bandgap positions (Figure 1. 8) of the core and the shell materials is important (Table 1. 1). It is fast, easy, safe and produces more defect free interface, hence provide a strong enhancement in the optical properties.[72-74] So, cation exchange is becoming a useful method to obtain colloidal core/shell particles, which are often inaccessible by one-step synthetic routes.[72] Hollingsworth et. al., applied this method to the synthesis of PbS/CdS and PbSe/CdSe, successfully.[64] Cation exchange is a diffusion controlled process and hence, typically performed at and above 100 °C, to ensure desorption of surface cation and adsorption of the new ones, to avoid defective grain boundary formation and remnant impurities of the outgoing cation. [31, 53, 75] But, such high temperatures generally leads to Ostwald ripening of QDs.[75] Also, many studies revealed that thicker shells formed at high temperatures causing a decrease in quantum yield due to defects at interfaces and the thick shell.[31, 76] Hens et. al., reported that they obtained core-shell QDs with limited shell growth at room temperature cation exchange.[76] In addition Alivisatos et. al., investigated extensively the cation exchange mechanism and reported thermodynamically limitations for RTCE between Pb^{+2} and Cd^{+2} ions.²⁴

1.4.2.2 Heat Treatment

Annealing is a heat treatment process and applied at above materials recrystallization temperature to enable diffusion of atoms to defects. Defects between interface of QD and shell material is a common result of shell growth process. Defects act as electron or hole trap and reduce QY of QD. Annealing process is used frequently to increase crystallinity and reduce crystal and interface defects of the QD induced films in photovoltaics.[62, 68] Especially after SILAR process, annealing is used to reduce interfacial defects between PbS and CdS layers.[70, 87]

1.4.3 Stabilizing Ligands

1.4.3.1 Ligands for Synthesis

In QD synthesis, surface binding ligands play a crucial role because they control particle growth, stabilize the surface, render particles hydrophilic or hydrophobic and provide colloidal solutions in appropriate solvents/liquids.[80] They may form micellar structure and play an important role in nucleation and growth. So, ligands concentration, size and structure are important reaction parameters to control crystal growth and influence optical properties.[44, 88, 89] Ligands can bind to QD surface by covalent, dative, or ionic bonds and passivate QD surface which is crucial for both optical properties and colloidal stability.[44, 80] According to their chemical structures, ligands may provide hydrophobic (oil-soluble) or hydrophilic properties (water-soluble) QDs (Figure 1. 9). In the two most popular synthetic methods used for PbX QDs (Hines&Scholes or Cademartiri), organic soluble hydrophobic ligands, such as OLA, OA, TOPO, TOP, DT were used.[44] These all have long hydrocarbon chains and polar

head group with lone pair electrons. Most widely used hydrophobic ligands not only for PbX but for most QDs are fatty acids, in deed. In QD synthesis, the polar head group of the ligand (for oleic acid hydrophilic part) binds to QD surface and the tail part (hydrophobic part) extends into the solvent, provide colloidal structure and provide steric stabilization. A critical length of the tail is necessary to enable colloid formation.

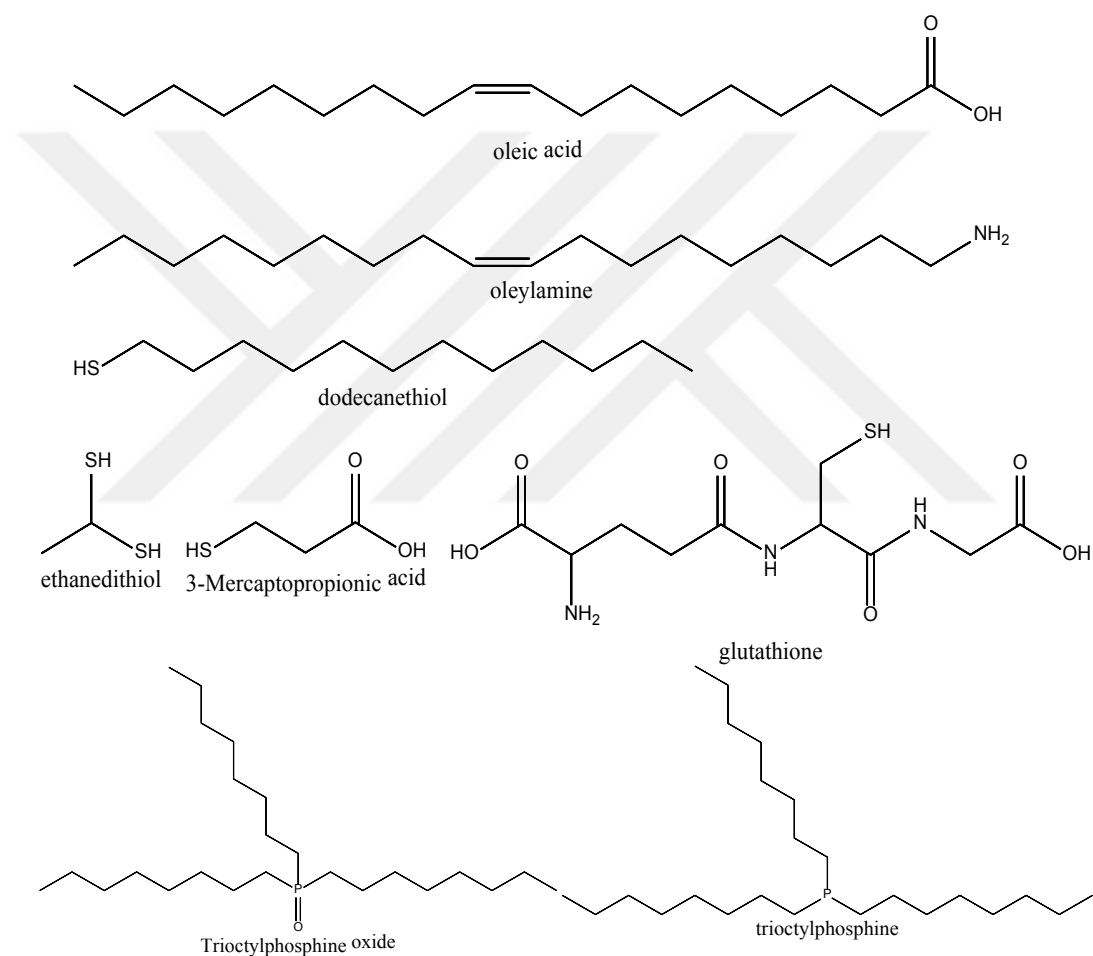


Figure 1. 9 Chemical structures of different ligands using to coat PbS QDs

1.4.3.2 Ligand Exchange

Ligands have different binding strengths to QD surface.[88] Those which are loosely bound may be exchanged with a more strongly binding ligand in a post-synthetic process to enhance stability or transfer QDs from for example hydrophobic solvent into a water. This exchange process is driven by the affinity between the ligand and the QD as well as concentration. This is actually based on the hard-soft acid-base interaction between the QD and ligand. As an example, Pb^{2+} is a borderline acid compared to soft Cd^{2+} and OA and DT is a harder base than OLA and sulfide. OLA ligands form weak bonds with Pb^{2+} atoms via amine units. DT is thiol containing ligand and has higher affinity to Pb^{2+} than OLA. Changing of OLA with thiolated ligands or OA is used commonly in the literature to increase stability of PbS QDs.[90-92]

By organometallic routes, organic soluble PbS QDs were obtained. For the biological applications, water soluble PbS QDs is needed. Ligand exchange process can provide hydrophilic PbS QDs by changing hydrophobic ligands with hydrophilic ones. [44, 93, 94]

Ligand type is also important for carrier mobility especially for photovoltaics. Shorter hydrocarbon tail reduces the inter-QD spacing and increases carrier mobility greatly. [89] Therefore, ligand exchange is used for changing long hydrocarbon ligands with smaller ones to increase efficiency in photovoltaics.[95, 96]

1.4.3.3 Polymer Coated Quantum Dots

Polymers as coating ligands offer many advantages and hence they are attractive ligands to encapsulate QD and passivate its surface.[44, 97-99] Desorption of the ligands

due to weak binding, oxidation or degradation reduces the stability of QDs and usually have a detrimental effect on both colloidal stability and luminescence stability. Unpassivated surface may undergo oxidation, dissolution or aggregation. Therefore, stable ligands are important to increase the stability of QDs. Ligands do stabilize nanoparticle against aggregation as well via electrostatic or steric stabilization. Long chain length of polymers offer multiple binding sites, hence full desorption is very difficult; steric stabilization due to long polymer chain and steric stabilization if ionic groups are available. Polymers may have the surface binding moieties such as thiol, amine or carboxylic acid just like the common ligands OLA, OA or DT, with the above mentioned additional benefits. [99, 100] Long chains of polymeric coatings contain a large number of repeat units which introduces a large number of surface binding functional groups which, can be controlled by the length of the polymer chain (molecular weight).[101] However, there is an important disadvantage of polymeric coatings, as well. Although they have a positive effect on the colloidal stability, they usually cause an inferior optical property. [101] They can reduce carrier mobility and QY. This is the main challenge of polymer coatings.

Water soluble NIR QDs such as PbS, Ag₂S can be formed by using polymeric ligands as well.[102-104] Poly(methacrylic acid), polyethylene glycol, polyacrylic acid are some water soluble polymers used for QD passivation (Figure 1. 10)

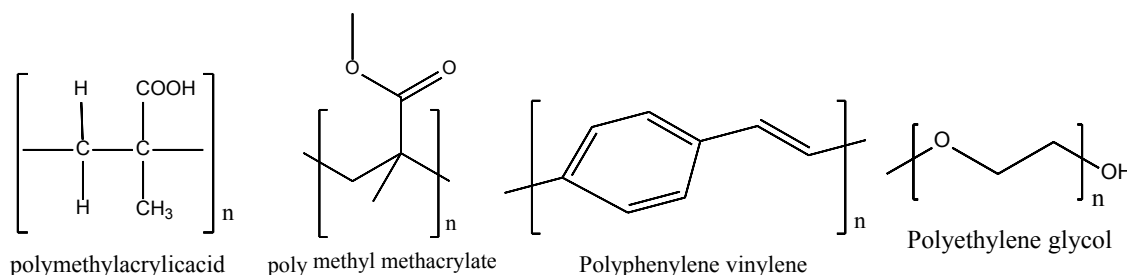


Figure 1. 10 Chemical structure of some polymers

1.5 Stability in Liquid Petroleum Products

The most important drawback of PbS QDs is the long-term instability. This instability is both colloidal and optical, meaning precipitation over time and/or loss of luminescence. Photo-corrosion, photo-oxidation, photodegradation, or photobleaching are possible sources. factors such as temperature, sunlight, oxidative environment and harsh solvents may enhance this stability. Generally, PbS QDs are stored in solvents such as chloroform and toluene at RT in ambient conditions.

Liquid petroleum products, such as engine oils, gasoline, diesel, etc. consist of long hydrocarbon chains and additives. There is an urgent need to tag some liquid petroleum products to track the liquids in distribution and in use, to identify and to ensure originality. This tag should be added in small amounts, should not hamper the functions of the liquid, should be relatively easily detected by an expert, should not be copied easily by non-experts and should be stable during the lifetime of the liquid petroleum product which means at least 1 month, up to 2 years. Another desired property is relatively cheap and mobile detection system. A possibility is to use fluorescent tags.[105] Yet, in order to tag multiple liquids a fluorescent barcode would be necessary and fluorescent dyes have

narrow absorbance and broad emission peaks which requires different excitation wavelength for each dye and not-well resolved emission peaks. Besides, they quench quickly. Therefore, just like in fluorescent labeling in biotechnology and medicine, quantum dots are great alternatives to fluorescent dyes. These additives create a harsh environment for QDs. Another important point is the strong auto-fluorescence of liquid petroleum products in the visible region (Figure 1. 11).[106]

Hence, they can be tagged either by high concentration of QDs which are luminescent in the visible range or with low concentrations of NIR QDs. QDs which will be developed for such products should be hydrophobic, colloidal, optically stable for long period of time (1 month-2years) and stable in the harsh environment of these petroleum products.

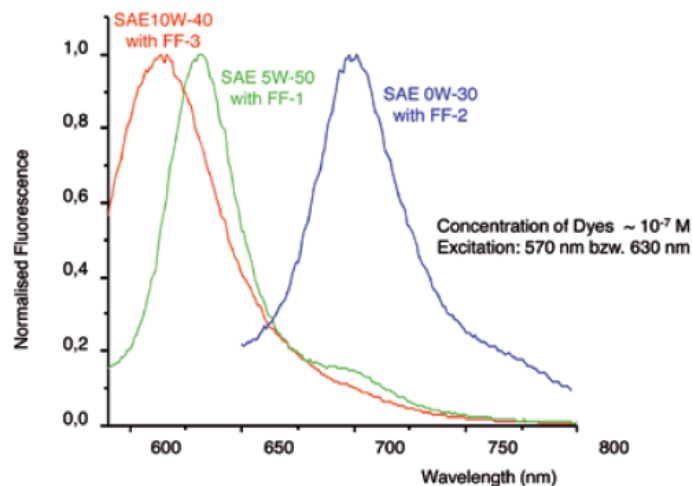


Figure 1. 11 Photoluminescence of different liquid petroleum products. [105]

1.6 Proposal and Aim of this Thesis Work

Despite of extraordinary optical properties of NIR PbS QD, their long-term instability is a major limitation in PV and optical tagging applications. Indeed, since the majority of

the PbX studies were directed to PV applications, there is only a limited amount of work on colloidal PbX QDs. The ultimate end use of the PbX QDs developed in this thesis is fluorescent tagging of liquid petroleum products, hence development of stable colloidal PbX is the major aim of this thesis. Most PbX NIRQDs have emission above 1200 nm. Detection of an optical signal above 1000-1100 nm requires relatively more expensive InGaAs detectors which is not standard in any spectrofluorometers, Elisa reader, FACS or fluorescent microscopes, limiting their practical use (Figure 1. 11). Highly stable, monodisperse PbX NIR QDs with strong and narrow band emission below 1100 nm which is detectable by Si detector or extended PMT is highly desirable for any realistic short term commercial use of such QDs in the field of fluorescent tagging. Emission within the 700-1000 nm range requires ultrasmall PbX QDs which are difficult to produce in large variety, stability and high QY with the existing methods. The most successful method, known as Hines&Scholes, uses toxic, oxidative, expensive precursors and solvents, in a difficult high temperature process which is not industrially viable. Existing 'green' syntheses method known as Cademartiri's, uses cheap, non-toxic and non-oxidative precursors at relatively lower temperatures but could not achieve ultrasmall colloidal PbX QDs. In addition, there are successful examples to size tuning in the NIR II window, but not in NIR I which is one of the main interests of this thesis. Expansion of the size-emission range within the NIR-I with improved quality offers great advantage in all applications of NIR QDs.

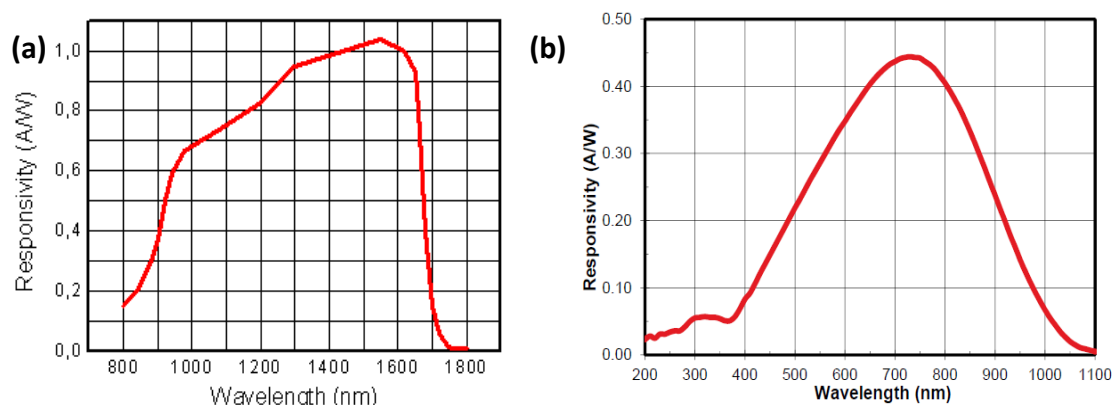


Figure 1. 12 Responsivity of detectors; (a) PDA10C/M InGaAs[107] and (b) PDA10A Silicon[108]

So, the first and immediate goal of this thesis work is to develop a safe, less costly, reproducible and scalable synthetic method to produce size tunable, monodisperse ultrasmall PbX NIRQDs with colloidal stability within NIR-I region. The second goal of the thesis is to achieve long term colloidal and optical stability with these ultrasmall NIR QDs in standard organic solvents and in liquid petroleum products in a period of 1 month-1 year. The third goal of the thesis is to achieve strong NIR-I emission to tag liquid petroleum products with low QD concentration, preferably with less than 100 ppm.

In an effort to achieve such goals, the following were proposed and tested:

In Chapter 2, a green synthesis to produce ultrasmall, monodisperse PbS and PbSe with strong emission in the NIR I will be discussed. As the major modification, control of particle size by using strongly binding DT during the synthesis, reduction of viscosity with a non-coordinating solvent and lower reaction temperatures are proposed. Influence of reaction variables on particle properties will be discussed in detail.

Chapter 3 focuses on the synthesis of PbS/CdS in order to improve stability with emission below 1000 nm via a novel room temperature cation exchange (RTCE) process followed by low temperature annealing was proposed to control the shell thickness and emission wavelength. Core/shell structure is suggested to increase the optical stability further. CE process was chosen for simplicity but a RTCE process was developed as a robust process to obtain a thin shell. Annealing was suggested to enhance the crystallinity and to remove defects in an effort to improve quantum yield and stability. Influence of shell growth on optical stability of QD will be discussed.

In chapter 4, use of polymeric coating was suggested to control size with improved stability. PbS and PbS/CdS QDs synthesized with a polymeric coating, poly(methacrylic acid), will be demonstrated and its influence on the size tunability, optical properties and long term stability will be discussed.

In addition, for all proposed compositions, post-synthetic ligand exchange of the weakly bound OLA with strongly binding DT is suggested to improve long-term optical stability. Optical stability means minimal spectral shift of the emission (± 10 nm) and minimal intensity loss (less than 10%). Hence, each composition was tested in chloroform and petroleum products at 100 ppm level up to a year.

Chapter 2

2 Synthesis of Strongly Luminescent, Ultrasmall PbS and PbSe Quantum Dots

2.1 Introduction

In this chapter, we aim synthesis of PbS QDs with emission maximum below 1100 nm with strong and stable luminescence. Here, we present a simple solution synthesis method to produce such particles with some key modifications adopted to standard Cademartiri's method. Hollingsworth et. al. used DT to increase solubility of elemental Se. We successfully adopted this method to elemental S.[64] Therefore, dilution of the reaction with toluene and addition of dodecanethiol (DT) to the reaction mixture reduced size with a dramatic luminescence enhancement. Post-synthetic exchange of the OLA with DT provided improved long-term stability. This methodology was easily applied to the synthesis of PbSe QDs, as well.

2.2 Experimental

2.2.1 Materials

PbCl₂ (98 %), Sulfur (99.99 %), Oleylamine (OLA) (technical grade, 70 %), 1-dodecanethiol (DT) (98 %) were purchased from Sigma-Aldrich. Selenium (99 %) was

purchased from Merck. Toluene, chloroform, ethanol was all 'for synthesis' quality and were purchased from Merck.

2.2.2 Colloidal PbS QD Synthesis

Synthesis of OLA/DT capped PbS QDs (PbS-OLA/DT) were performed under argon atmosphere to avoid oxidation. First, the sulfur precursor was prepared by dissolving 0.008 g (0.25 mmol) elemental sulfur in 2.5 mL of OLA by sonication under argon flow for an hour, followed by vacuum at RT for another hour. Lead precursor was prepared separately by dissolving 0.28 g (1 mmol) PbCl_2 in 5 mL OLA in a three-necked round-bottom flask at 110 °C under argon flow followed by vacuum at this temperature for 1 h. This colorless solution was purged with Argon again at 120 °C for 30 min, then cooled down to a desired particle growth temperature at which 0.5 mL DT was added. Color of the solution immediately turned into a clear yellow. This solution was diluted with 17.5 mL Ar purged dry toluene. Then, 2 mL of OLA-S solution (0.2 mmol of S) was injected to the PbCl_2 -DT-OLA solution. After the desired growth time, the reaction was quenched in cold water and cold ethanol was added. The solution was centrifuged at 6000 rpm and QDs were re-suspended in chloroform twice.

PbS coated with DT was prepared via ligand exchange: DT was added to chloroform suspension of PbS QD to replace the OLA at room temperature and stirred for 15 min. DT coated PbS QDs (PbS-DT) were precipitated in ethanol, removed from the supernatant by centrifugation and resuspended in chloroform. These QDs are stored in ambient conditions.

Same procedure was applied for the synthesis of PbSe QDs.

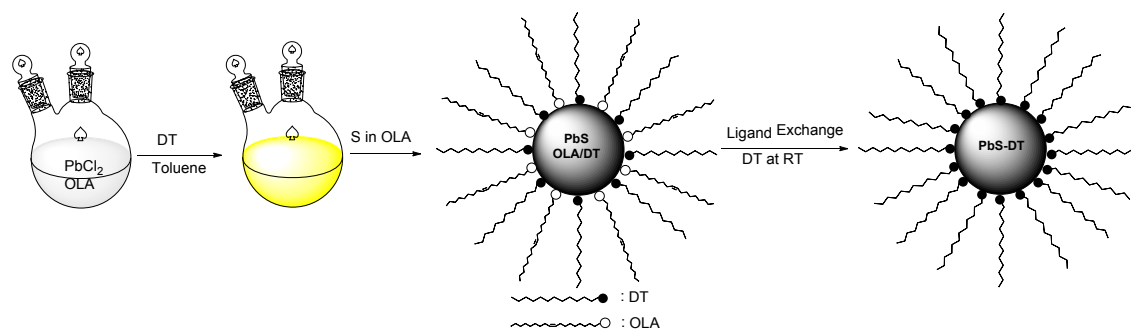


Figure 2. 1 Schematic of PbS synthesis.

2.3 Characterization Methods

Absorbance spectra were taken in the range of 400–1200 nm by a Shimadzu 3600 PC UV-Vis-NIR spectrometer. Photoluminescence spectra is a homemade system which is using a DPSS laser source working at 532 nm as an excitation source. As a monochromator (1/8 Newport Cornerstone 130) is used. PbS QDs measured with Si detector (Thorlabs PDA10A), because they are ultra-small QDs with emission below 1100 nm (Figure 1. 12). For larger particles and PbSe QDs we used InGaAs detector (Thorlabs PDA10C/M). As shown in Figure 1. 12, InGaAs detectors have fast responsivity drop between 800-1000 nm and this drop causes to shoulder in PL spectra.

Luminescence Lifetime of PbS QDs in chloroform was measured using Horiba Fluorolog equipped with TCSPC Triple Illuminator. Measurement time 360 μs was taken for 4096 channel. Components of PL decay of PbS QDs were identified to be multiexponential form of;

$$A + B1 \cdot \exp(-t/\tau_1) + B2 \cdot \exp(-t/\tau_2) \quad (\text{Eq. 1})$$

where τ_1 and τ_2 are decay components and B1 and B2 are percentage of related decay component.

Transmission electron microscope (TEM) (JEOL 2100, Japan) analysis was performed at an accelerating voltage of 200 kV. Samples were diluted with toluene and subjected to ultrasonication (10 min). A drop of this solution was placed onto ultrathin mesh copper grids and left to dry in air.

X-ray photoelectron spectroscopy (XPS) measurements were performed using Thermo Scientific K-Alpha spectrometer using an Aluminum anode (Al K α = 1468.3 eV) at electron take-off angle of 90° (between the sample surface and the axis of the analyzer lens). Spectra were recorded using Avantage 5.9 data system. The binding energy scale was calibrated by assigning the C1 s signal at 284.5 eV.

X-ray diffraction (XRD) pattern was obtained with a Bruker D8 Advance with DAVINCI design equipped with Diffractometer using a Cu K α radiation source (λ = 0.15418 nm). For measurements 0.01236 increment, 16 second integration time, 40mA, 40kV and Si holder is used.

2.4 Discussion and Results

2.4.1 Synthesis and Characterization of PbS NIRQDs

Crystalline PbS QDs produced with this modified Cademartiri's method have spherical shapes as seen in the TEM images (Figure 2. 2a). Lattice constant was calculated from the FFT image (Figure 2. 2b). From the FFT image the distance between two reflections

was used in the calculation. The reciprocal value of the distance between two reflections (L) gives spacing (d) for crystals. Also, we used this simple equation;

$$d = 2 / L \quad (\text{Eq. 2})$$

We took all distances between the center and spots to be more accurate. Calculated lattice constant 5.92 nm, is consistent with the literature (5.93 nm). XRD pattern revealed cubic crystal structure of PbS QDs (Figure 2. 2c). The XPS of Pb 4f core level indicates two types of Pb with Pb 4f 7/2-5/2 pair at 136.88- 141.78 eV and 137.78-142.68 eV which is in agreement with reported binding energies for Pb-S bond. It is possible to consider these as Pb's with two different environments such as surface versus inner core, especially in small size crystals.[83] S 2p core level also shows two different sulfurs. Sulfur with S 2p 3/2-2/1 at 161-162.8 eV belongs to Pb-S. Sulfur with 2p 3/2-2/1 at 163-164.6 eV corresponds to the S of DT.

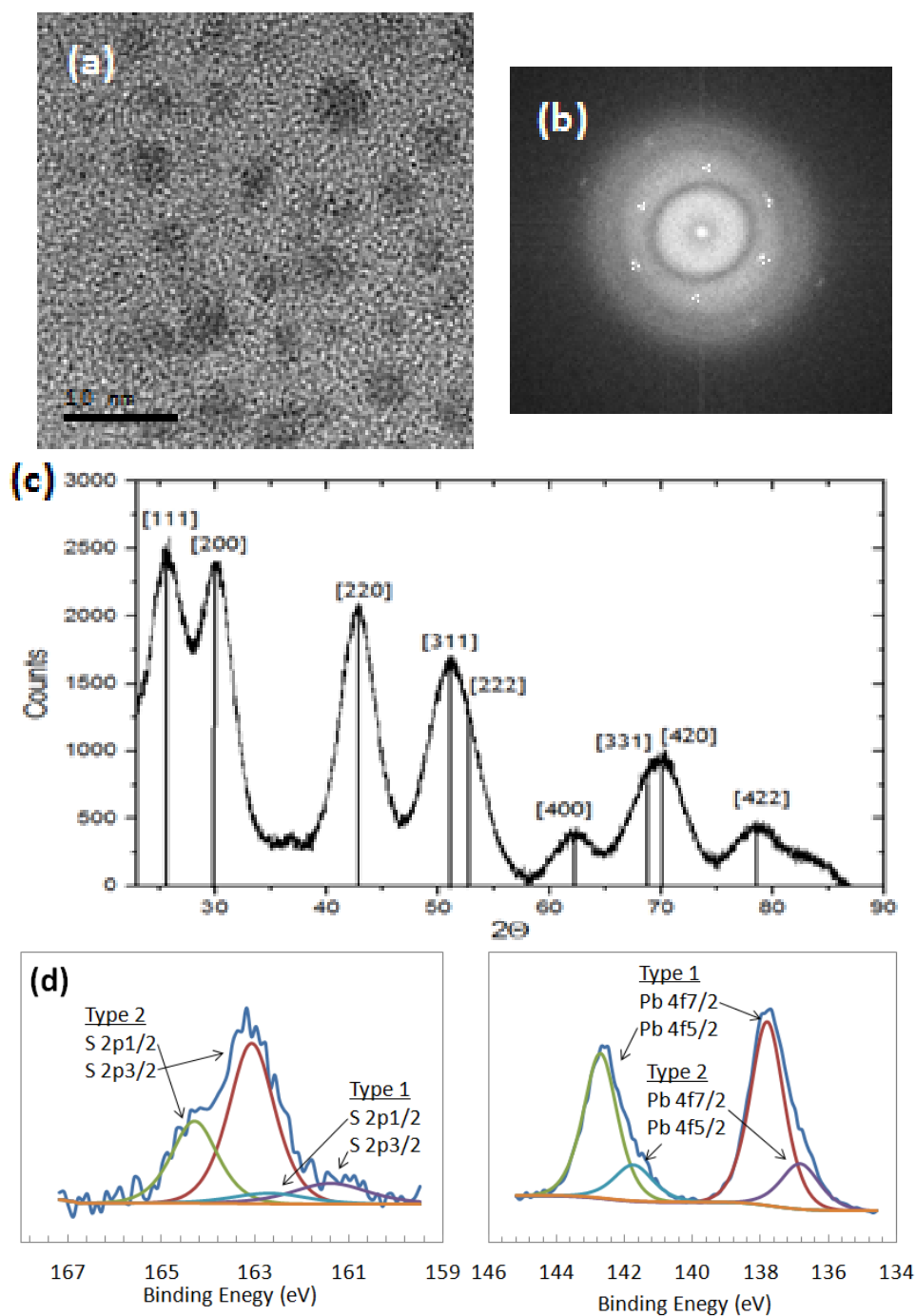


Figure 2. 2 (a) TEM image (b) FFT pattern (c) XRD of PbS-OLA/DT QDs with vertical lines indicating the positions of the peaks in rocksalt PbS structure (d) The XPS of Pb 4f and S 2p core level.

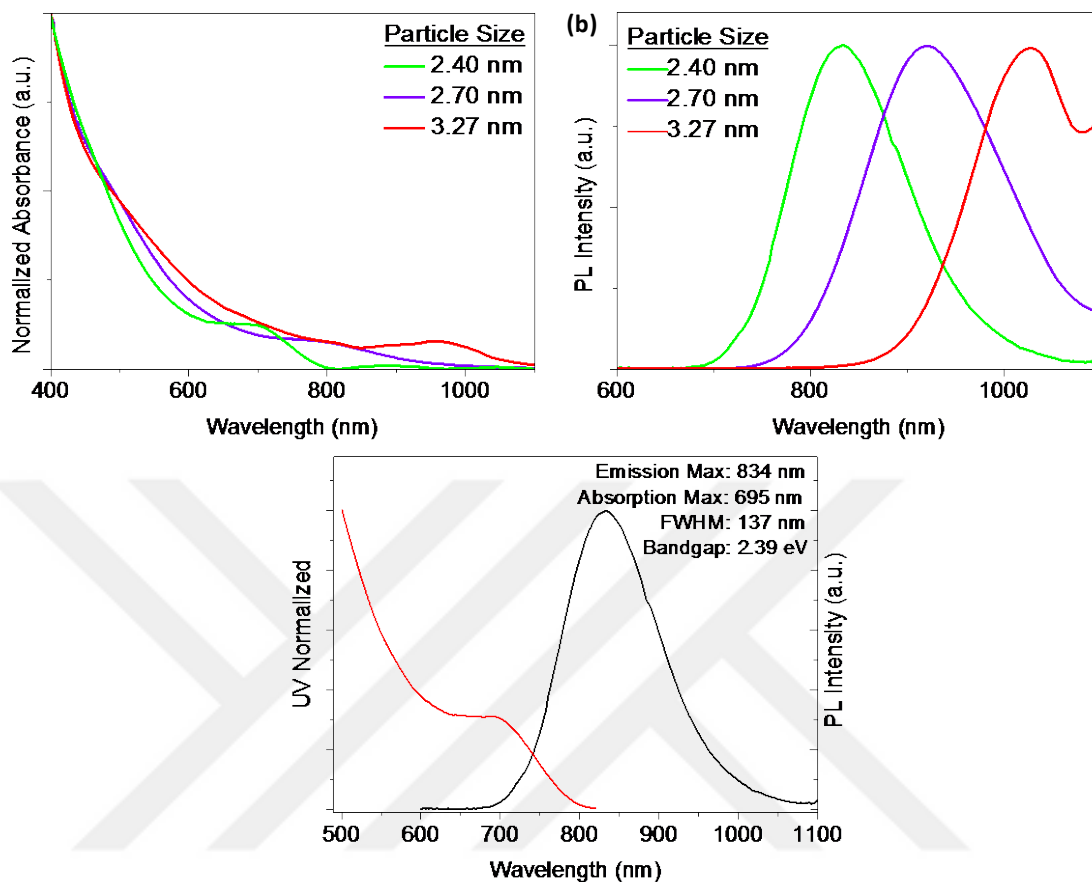


Figure 2. 3 (a) Normalized absorbance and (b) emission spectra of PbS-OLA/DT QDs synthesized with the developed method, (c) PbS-OLA/DT QDs synthesized at 65 °C.

Figure 2. 3 shows the absorbance and emission spectra of the three PbS QDs prepared in different reactions following the modifications that we have suggested. 1st absorption peaks (Figure 2. 3) are used to calculate diameters of particles according the size curve (Table 2. 1). The smallest PbS-OLA/DT synthesized with the procedure we have developed has a sharp emission centered at 834 nm and absorbance peak at 695 nm (Figure 2. 3c). Based on this, PbS as small as 2.40 nm was produced with the developed

method. This is one of the smallest PbS QD reported in the literature. Table 2. 1 shows optical properties of obtained QDs calculated by (Eq. 2), (Eq. 3) and (Eq. 4).

Table 2. 1 Optical Properties of PbS QDs				
1 st Abs. Peak ^a (nm)	Diameter ^b (nm)	E_{vb} ^c (eV)	E_{cb} ^c (eV)	Band Gap ^c (eV)
695	2.40	-5.05	-2.66	2.39
794	2.70	-5.02	-2.90	2.12
965	3.27	-4.98	-3.21	1.78

^a See Figure 2. 4 for absorbance and the emission spectra of the QDs; ^b Calculated by (Eq. 1); ^c (Eq. 2), (Eq. 3) and (Eq. 4) used to calculate E_{vb} , E_{cb} and E_0 .

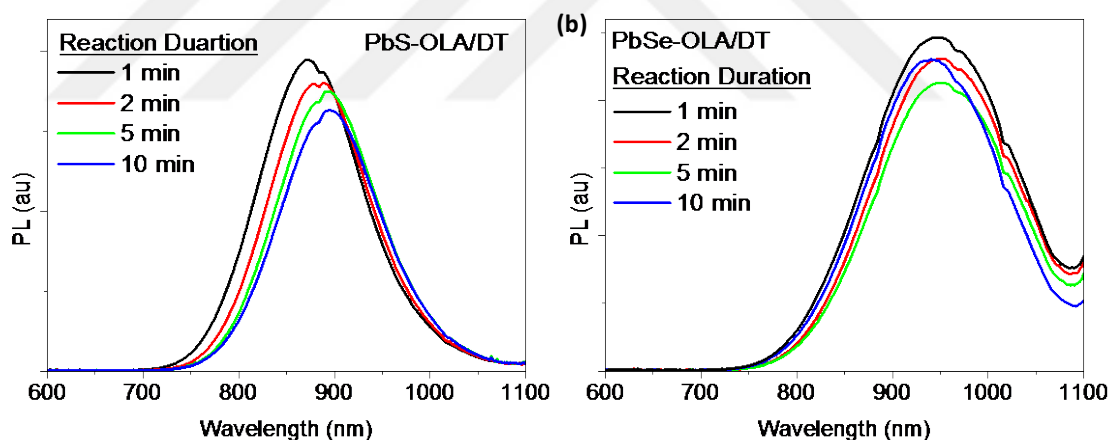


Figure 2. 4 Influence of reaction duration on PL intensity (a) PbS-OLA/DT (b) PbSe-OLA/DT

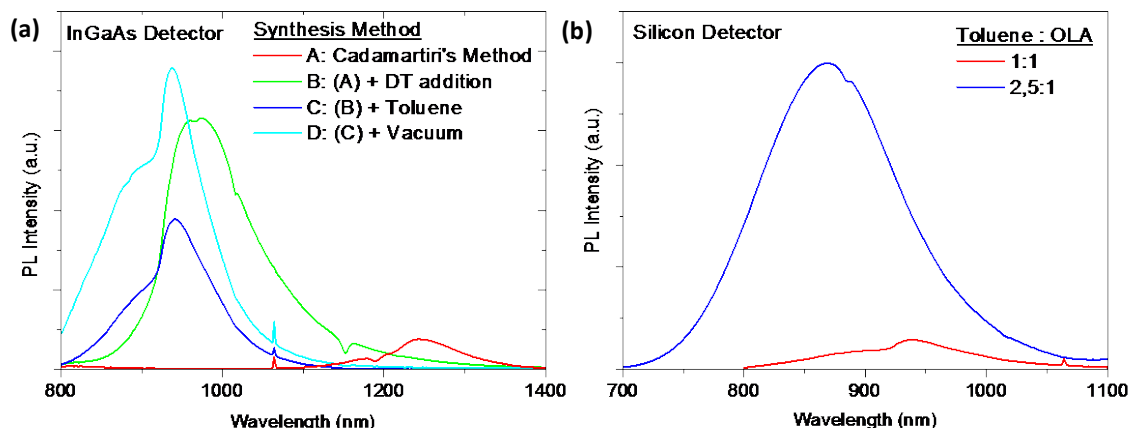


Figure 2. 5 (a) Photoluminescence spectra of PbS-OLA/DT synthesized with standard Cademartiri recipe (Curve A); with the addition of DT (Curve B); DT and dry toluene (Curve C); DT, dry toluene and after vacuum drying of reaction mixture (Curve D). Each spectrum represents a different reaction carried out at 80 °C for 2 min. All spectra were recorded with InGaAs detector and excitation wavelength of 532 nm; (b) Photoluminescence spectra of PbS-OLA/DT synthesized under identical condition with DT addition and vacuum drying but using different toluene:OLA volume ratio.

In order to reduce particle size and achieve strong luminescence and good stability, DT and toluene was added to the standard Cademartiri's method, mixture was vacuum dried and reactions were run at a relatively low temperature (80°C). Figure 2. 5a shows the PL spectrum of PbS QDs synthesized in four different recipes, investigating the influence of each modification that is mentioned here.

2.4.2 Influence of DT Addition to the Reaction Mixture

As seen in Figure 2. 5a, typical synthesis using only PbCl₂, elemental S in OLA performed at 80 °C produced PbS with poor luminescence intensity and emission

maximum around 1250 nm (Curve A). This reaction mixture is highly viscous and opaque indicating the limited solubility of the precursor. Keeping everything identical, addition of DT at the growth temperature to reaction mixture turns the color into clear yellow quickly and produces particles with emission maximum at 970 nm and three times stronger emission intensity compared to those produced with the typical method (Curve B).

Poor solubility of elemental S in OLA and high viscosity of the reaction mixture are the two major limitations in the un-modified procedure. Hence, elevated temperatures, usually above 80 °C, is needed to increase the solubility of sulfur, but this increases the crystal size as well, since the critical stable size usually increases with the temperature.[22] So, if the solubility problem can be solved, reactions can be performed at lower temperatures to produce smaller crystals. Thiolated ligands were used to reduce elemental Se in OLA.[109] We have adopted this approach to PbS synthesis using DT. We presume that DT increases the solubility of S, making it more available and hence produces more crystals and have less precursor per nuclei. These may explain the large blue shift in the emission maxima upon addition of DT to the typical procedure (Curve A versus Curve B in Figure 2. 3). Also, because DT has high affinity to PbS surface and binds more strongly than OLA,[54] its availability during the crystal growth stabilizes crystals at smaller sizes. In addition, a dramatic enhancement in the luminescence intensity was observed. This may be partially due to the smaller size of the crystals[43] or stronger binding of DT and hence, better stabilization of the surface. DT or alike are usually deposited on the PbS via ligand exchange in the literature, which is a post-

synthetic process to increase colloidal stability due to stronger binding and hence better surface passivation. But, this is usually accompanied with a loss in the emission intensity or change in the peak position. DT is usually not used directly in synthetic methods where temperature is high due to decomposition of DT and S-release, which makes the control of the crystal size difficult. However, since reactions were run at a relatively low temperature here, decomposition of DT was prevented.

2.4.3 Influence of Toluene Addition and Vacuum Drying

The typical reaction mixture in this method is very viscous, limiting mass transfer coefficient and therefore, nanocrystals tend to grow in a diffusion-controlled manner,[81] which decreases the size distribution with increasing size focusing.[110] So, dilution of reaction with equal volume of toluene to OLA provides a more manageable reaction solution and about 50 nm blueshift in emission maxima with little decrease in the emission intensity (Curve C, Figure 2. 5a). Decrease in viscosity causes faster diffusion and more nuclei formation. Increasing toluene/OLA ratio to 2.5/1 provided additional 70 nm blueshift with stronger emission intensity (Figure 2. 5b). May be this is related to larger number of smaller crystals with more effectively passivated surface at the same coating concentration. Cademartiri provides a detailed discussion on the effect of precursor concentration on FWHM, but not on the particle quality.[81]

OLA contains significant amount of water which may cause some heterogeneity in the reaction mixture and may even adsorb on the surface of the crystals. Applying vacuum at

120 °C to dry the reaction mixture enhanced the luminescence intensity substantially without changing the kinetics, hence kept the emission maxima at the same position.

When all of these modifications are applied together, small-sized PbS QDs with emission maxima at 868 nm with significantly enhanced emission intensity was achieved (Curve D, Figure 2. 5).

2.4.4 Influence of the Reaction Temperature and Stoichiometry

Size tunable emission is an important property of QDs. Reaction duration, temperature and the stoichiometry are the most effective factors used to tune the size and the luminescence wavelength of QDs.[111] In the developed synthetic method, reaction duration is not an effective variable to tune the emission wavelengths (Figure 2. 6) but temperature of reaction and the stoichiometry are.

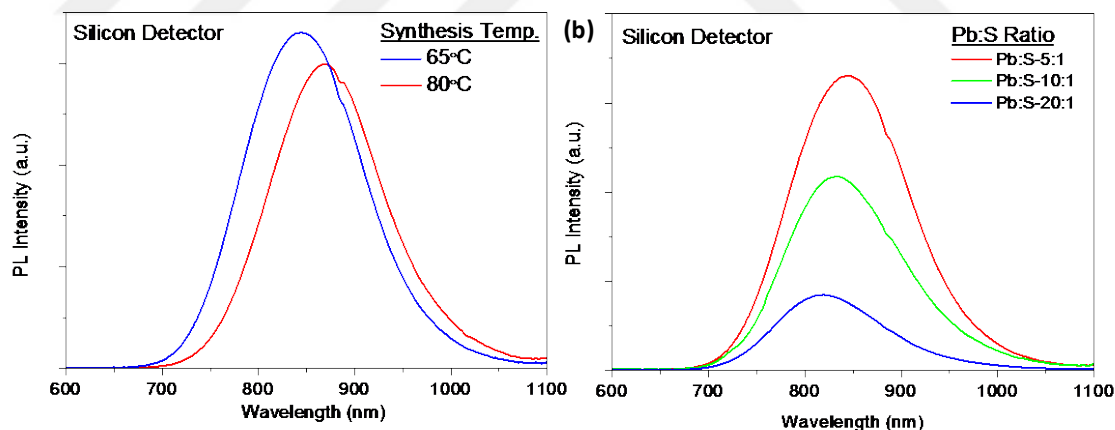


Figure 2. 6 (a) Photoluminescence spectra of PbS-OLA/DT QDs synthesized at 65 °C and 80 °C at toluene:OLA ratio of 2.5:1 (b) at different Pb:S mole ratios at 65 °C and toluene:OLA ratio of 2.5:1. Reaction time=2 min. Recorded with a silicon detector and excited at 532 nm.

Different groups have studied the growth of PbS between 40-120 °C, using various precursors and surfactants and size tunability was claimed even at room temperature.[112] In typical PbCl₂/OLA reactions, due to the limited solubility of elemental S and high viscosity of the solution, synthesis are usually performed between 80-160 °C.[43, 81, 111, 113] However, since the addition of DT and toluene to the reaction mixture increased the solubility of elemental S and reduced viscosity, we could decrease the reaction temperature to 65 °C. This decrease in temperature resulted in 30 nm blue shift in the emission peak maxima with about 15 % increase in the intensity (Figure 2. 6a). Actually, this is the lowest possible temperature for this reaction since even at 65°C, reaction mixture is again quite viscous. Slower reaction kinetics at lower temperature and possibly reduced mass transfer provided smaller particles with better surface quality (less defects) resulting in an enhanced luminescence intensity under identical conditions and reaction duration.[81]

Pb/S stoichiometry is another effective parameter to tailor crystal size.[111] Usually, reactions are formulated as Pb-rich, keeping the S as the limiting reagent. Generally, Pb:S ratios between 10:1-10:3 are used in the literature.[81, 113] Here, we have adopted the Pb:S ratio of 5:1 initially, in order to study the effects of DT and toluene additions. Then, Pb:S ratio of 20:1 and 30:1 was studied in the optimized procedure (Figure 2. 6b). Decreasing S-amount resulted in smaller, progressively blue shifted emission as expected, but with a significant decrease in the emission intensity. Surface defects and defect related non-radiative relaxations may become more effective as surface/volume ratio increases with the decreasing crystal size.[114]

2.4.5 Ligand Exchange with DT and Stability

PbS QDs were usually studied for photovoltaics and there is a large number of reports pointing out air-instability of PbS due to oxidation which is shown with a significant blue shift in the absorbance spectra.[82, 115] Usually, PL data is not shown since luminescence is not the major concern. Yet, loss of luminescence in short time period is a known drawback of PbS QDs.[22] Size dependence of oxidation stability, positive impact of strongly binding thiolated ligands in a post-synthetic procedures and effect of chloride counter ions were reported.[22, 83, 90] For example, in quantum dot sensitized solar cell fabrications, thiolated molecules such as ethanedithiol (EDT) is frequently used to enhance stability.[22, 90]

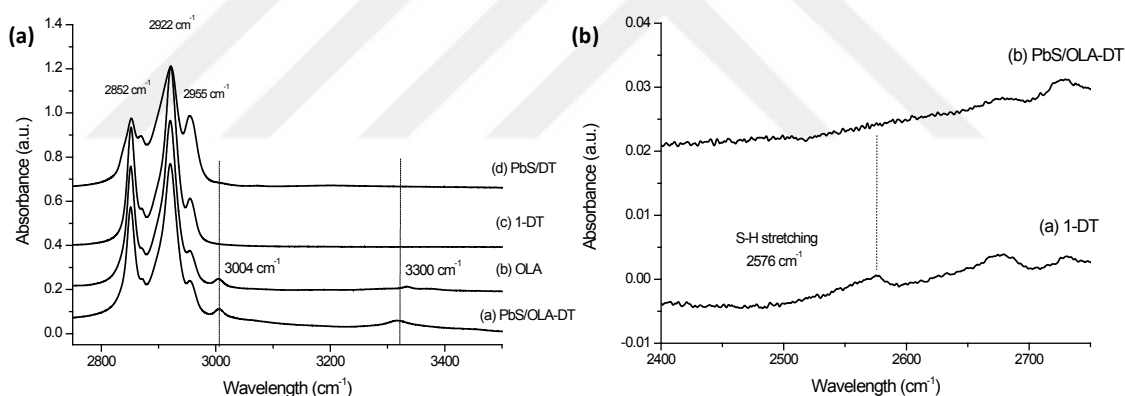


Figure 2. 7 (a) FTIR spectra of “as synthesized” PbS-OLA/DT, free OLA, free DT and PbS-DT (b) focused FTIR spectra of DT and as synthesized PbS-OLA/DT QDs.

In order to enhance the long-term stability of colloidal PbS QDs, post-synthetic exchange of OLA with strongly binding DT was performed. This process can be followed by FTIR spectra of species (Figure 2. 7). Peaks at 3004 and 3300 cm⁻¹ belong to C_{sp2}-H and N-H stretching, confirming the presence of OLA on the “as synthesized” PbS QDs.

After the ligand exchange, these two peaks disappeared, indicating complete removal of OLA. Binding of DT from the thiol is also confirmed by the absence of S-H stretching at 2576 cm^{-1} in the OLA/DT coated and the ligand exchanged PbS QDs (Figure 2. 8).

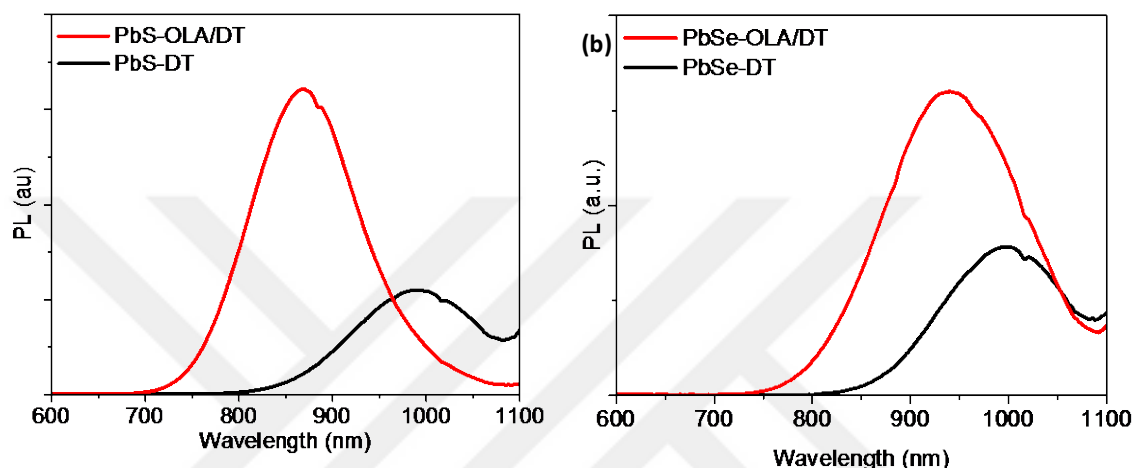


Figure 2. 8 PL intensity difference between (a) PbS-OLA/DT and PbS-DT (b) PbSe-OLA/DT and PbSe-DT

As usual, DT ligand exchange caused a red shift with some loss in the luminescence intensity based on surface perturbation (Figure 2. 8). However, both PbS-OLA/DT and PbS-DT showed excellent colloidal stability and strong luminescence over 3 months of storage at room temperature without inert atmosphere purging and protection from light. We have observed about 47 nm red shift in the emission maxima of PbS-OLA/DT in 3 months (Figure 2. 9a). Such a red shift may be due to ripening/sintering process triggered by sunlight.[115] On the other hand, only 20 nm red shift in the emission peak maxima of PbS-DT was observed after 3 months, indicating improved surface binding and stability.

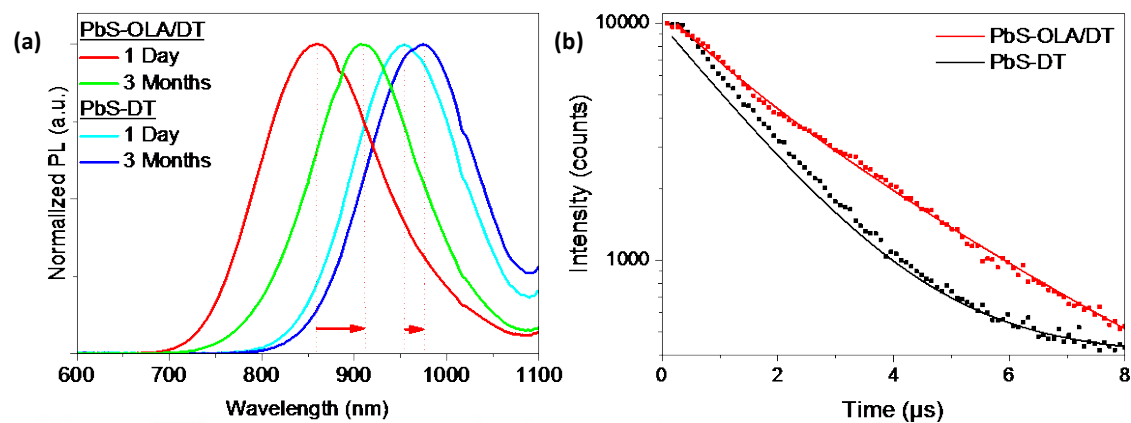


Figure 2. 9 (a) Photoluminescence spectra of PbS-OLA/DT QDs and PbS-DT QDs after synthesis (red and cyan, respectively) and after 3 months of storage (green and blue, respectively). (b) Photoluminescence lifetime of PbS-OLA/DT (red) and PbS-DT (black) with 3.27 nm diameter.

Table 2. 2 PbS QD Lifetimes							
	D (nm)	t1 (μ s)	t2 (μ s)	B1 (%)	B2 (%)	Average (μ s)	χ^2
PbS-OLA	3.27	1.07	2.67	15.97	84.03	2.414	1.081
PbS-DT		0	1.37	0	100	1.370	1.009
PbS-OLA	2.70	0.95	3.14	21.76	78.24	2.663	1.167
PbS-DT		0.32	1.93	7.52	92.48	1.809	1.109

PL lifetime of both “as made” and DT exchanged PbS QDs in two different crystal sizes were measured (Figure 2. 9b, Table 2. 2). Table 2. 2 lists the faster and slower

components of the luminescence decay and their amplitudes, which provides a better understanding of the decay mechanism. The decay curve found to be multi-exponential for PbS-OLA/DT with average lifetimes of 2.414 and 2.663 μs for 3.27 and 2.7 nm particles, respectively. These values are in agreement with the literature values.[31] A dramatic decrease in the lifetime after DT exchange was determined. The average lifetime measured as 1.370 and 1.809 μs for the 3.27 and 2.70 nm PbS-DT, respectively. So, in general, DT exchange reduced lifetimes for both sized PbS QDs. One possible source for faster average lifetime may be related to the shorter chain length of DT compared to OLA which enhances the mobility of electron and hole. Also, it is clear that, all lifetimes are decreasing (also quantum yield), with the increasing size of QD, regardless of the type of surface coating. Similar trend between size and QY was also reported by Justo *et al.*[31] In case of multi-exponential decays, the shorter (or faster) lifetime component is usually attributed to defect sites (presumably surface defects), while the longer (or slower) component is related to intrinsic recombination.[116-118] Surface dangling bonds, or electron or hole traps are considered as “defects”. These may also cause non-radiative coupling of exciton which reduces the PL intensity of QD.[119] The fast component of the larger PbS-OLA/DT (3.27 nm) vanished completely after DT ligand exchange, which may indicate removal of defect related emissions.. In case of the smaller QD, fast component was reduced significantly, but not completely diminished. This may be related to higher surface/volume ratio of the smaller crystal. Such reduction/elimination of the faster component may be interpreted as a switch to intrinsic recombination of the exciton after displacement of OLA with DT. If the changes in the luminescent lifetimes after DT

ligand exchange are evaluated along with the drop in the luminescence intensity (Figure S4) and improved long term stability (Figure 7a, red and cyan curves) we can suggest that, DT binds to surface strongly and remove/reduce surface defect. This causes long term stability, in a way, ligand exchange process changes the mechanism of the fluorescence process. Such ligand dependent changes have been reported before. [44, 51, 95, 120, 121] Wuister *et al.* suggests that when thiolated ligands are used, they may act as a hole trap if the valance band of QD is below the redox potential of the thiol (about - 5 eV), reducing the emissive coupling events.[120] Considering the calculated valance band position of our PbS QDs (Table 2. 1) and the reported redox potential of thiols, it is difficult to say that this is happing or not but, surely exists as a possibility. Yet, as expected, the long-term stability enhanced with the DT ligand exchange due to stronger surface binding.

2.5 Synthesis of PbSe QDs

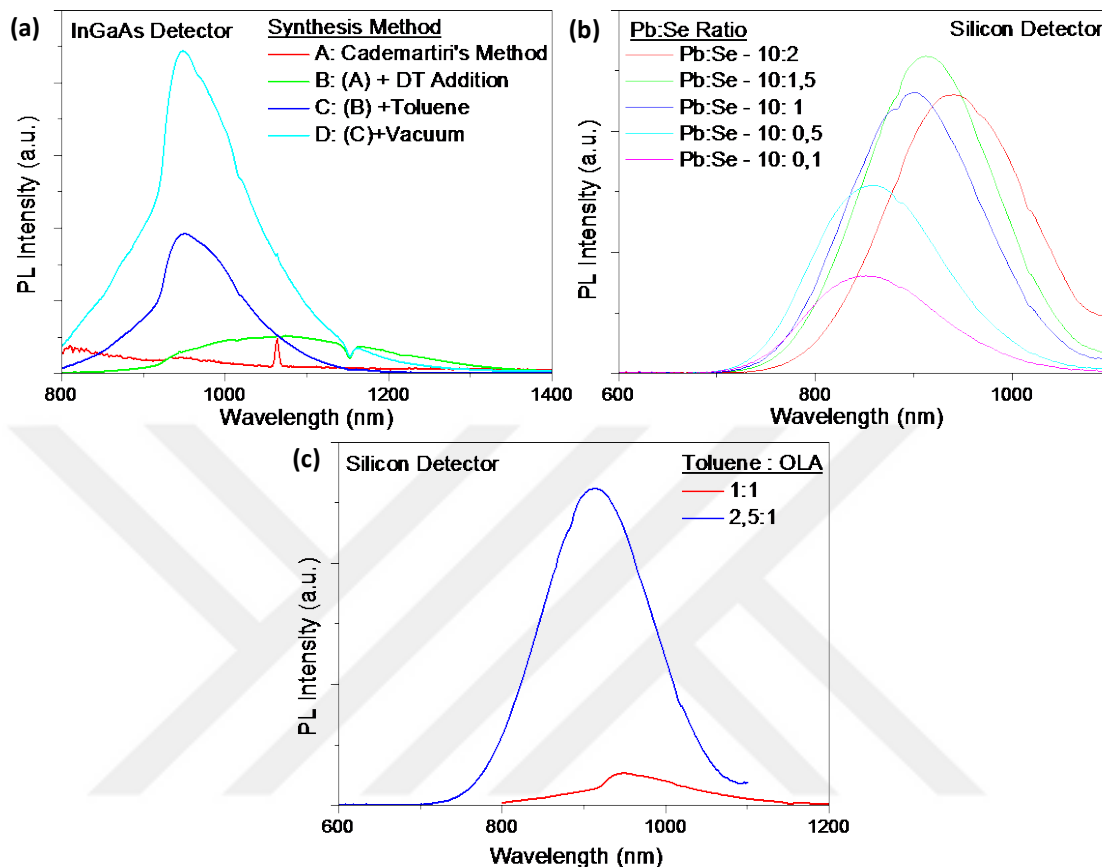


Figure 2. 10 (a) Photoluminescence spectra of PbSe-OLA/DT synthesized with standard recipe (Curve A); with the addition of DT (Curve B); DT and dry toluene (Curve C); DT, dry toluene and after vacuum drying of reaction mixture (Curve D). Each spectrum represents a different reaction carried out at 65 °C for 2 min. (b) Photoluminescence spectra of PbSe-OLA/DT synthesized under identical conditions with DT addition and vacuum drying but using different toluene:OLA volume ratio. (c) Photoluminescence spectra of PbSe-OLA/DT synthesized under identical condition with different Pb:Se mole ratio.

We successfully adopted the method to PbSe synthesis using PbCl_2 and elemental Se precursors (Figure 2. 10). Figure 2. 10a shows photoluminescence spectra of PbSe produced with the standard recipe conducted at a lower temperature, 65°C , and the impact of each modification on the emission intensity and peak position of produced PbSe QDs. No significant NIR emission was obtained from the standard recipe performed at 65°C (Curve A), whereas DT addition provided luminescent particles with broad emission peak centered at 1072 nm (Curve B). Addition of toluene in the toluene:OLA ratio of 1:1 caused 122 nm blue shift and nearly four times stronger emission intensity (Curve C). Application of vacuum drying (Curve D) again enhanced the emission intensity significantly without a major shift in peak position, similar to PbS. The shoulders seen at the shorter wavelength side of the emission peaks is again due to InGaAs detector.

For size tuning, different Pb:Se ratios were applied within the modified procedure. Increasing Pb:Se ratio, caused a blueshift in emission peak position in agreement with the observation and discussion made for PbS (Figure 2. 10b). Strongest emission was achieved at Pb:Se ratio of 10:1.5 with peak maxima at 913 nm. Yet, peak positions and intensities are relatively similar between Pb:Se ratios of 10:2 and 10:0.5, then dropped as the ratio increased (Figure 2. 10b). Probably, at this small size surface defects became quite influential. Reducing viscosity and actually overall concentration with toluene further with a toluene:OLA 2.5:1 v/v ratio, favored a dramatically enhanced intensity. In addition, this resulted in a slight blueshift and a narrower emission peak which indicates more uniform size distribution.

2.6 Conclusions

We have developed a simple, safe and economic solution synthesis method inspired from Cademartiri's to produce small particles with tunable emission below 1000 nm with crystal size as small as 2.4 nm. Typically, PbCl_2 , elemental S and OLA was used for the standard synthesis protocol at lower temperature than usual, 80 °C. Addition of DT to this recipe improved solubility of S and hence allowed lower temperature reactions and provide strong binding to PbS surface in situ. All of these factors effectively reduced the crystal size with improved luminescence intensity. Dilution of the otherwise highly viscous reaction mixture with toluene shown to be very influential in reducing the crystal size. In addition to these major modifications drying reaction mixture provided a positive impact to the quality of the particles. Increasing Pb/S ratio as well as decreasing reaction temperature provide additional small blue shift in the emission peak but 65°C is the lower limit due to viscosity of the reaction mixture in case on PbS. Use of these variables provided PbS QDs with crystal size of 2.4, 2.7 and 3.2 nm. These particles are colloiddally stable and showed only 47 nm shift in luminesce peak maxima in 3 months of storage under ambient conditions. Yet, exchange of OLA from the surface with strongly binding DT, improved stability significantly. Although, such exchange caused an initial decrease in the emission intensity and red shift in the peak position, the final PbS-DT exhibit dramatically better stability. DT ligand exchange also eliminated or reduced original defect related emissions, making the slower decay component, presumably the intrinsic coupling, the major event.

Hence, we clearly show that it is possible to produce strongly luminescent colloidal PbS QDs in small sizes in a method adopted and modified from Cademartiri. The method was easily adopted to PbSe synthesis producing QDs with emission maxima below 1000 nm, as well.



Chapter 3

3 Room Temperature Shell Growth and Low Temperature Annealing in Development of Small and Stable PbS/CdS Quantum Dots

3.1 Introduction

We are interested in small and stable PbS QDs with a strong emission below 1100 nm, which can be easily detected with a regular Si detector. Small sized PbS with strong emission below 1100 nm was achieved previously in chapter 2. In order to improve the long-term stability of such PbS QDs, we suggest a thin CdS shell formation. CdS is one of the most widely used shell material on PbS QDs to enhance optical properties and stability.

In this chapter, we applied room temperature cation exchange to grow CdS shell followed by annealing at low temperatures in the solid state and finally ligand exchange with dodecanethiol (DT) to enhance optical properties and stability of small PbS QDs (emission below to 880 nm), prepared via a modified Cademartiri method. The influence of annealing temperature and time on the luminescence properties (peak position, peak

width, emission intensity), absorbance, luminescence lifetime, crystallinity and stability of core-shell QD were investigated. Lastly, long term stability was improved further by using a ligand exchange process and coating PbS/CdS QDs with 1-dodecanethiol.

3.2 Materials and Methods

3.2.1 Materials

Lead chloride (98%), sulfur (99.99%), oleylamine (OLA) (technical grade, 70%), 1-dodecanethiol (DT) (98%), cadmium oxide (CdO) (99.5%), oleic acid (OA) (99%), 1-octadecene (ODE) (98%) were purchased from Sigma-Aldrich. Toluene, chloroform, ethanol was all 'for synthesis' quality and were purchased from Merck.

3.2.2 Colloidal PbS/CdS QD Synthesis

Synthesis of OLA/DT capped PbS QDs (PbS-OLA/DT) was described in Chapter 2. PbS/CdS core/shell QDs were synthesized by cation exchange method described by Pietryga et al.[114] As an example, 0.257 g (2 mmol) CdO, 3 mL (9.5 mmol) OA, and 12 mL ODE were heated to 250 °C under argon until whole CdO precursors had dissolved. After clear solution obtained, solution was cooled to 150 °C under Ar flow to remove moisture. The PbS core solution from above was degassed by Ar flow for ~30 min. Immediately after the temperature of the PbS solution was set to desired temperature (room temperature or 100 °C in this work), the cadmium oleate solution was added via cannula under heavy stirring. After the desired growth time, the reaction was quenched in cold water and cold ethanol was added. The solution was centrifuged at 6000 rpm and

QDs were precipitated and then re-suspended in chloroform. As can be seen in Figure 3.7, this cleaning step removes the excess OLA.

3.2.3 Annealing of PbS/CdS QDs

Precipitated core-shell QDs annealed in vacuum oven at desired temperature and duration as powder form over glass substrates.

3.2.4 PbS/CdS QD coated with DT was prepared via ligand exchange:

DT was added to chloroform suspension of PbS/CdS QD to replace the OLA at room temperature and stirred for 15 min (OLA:DT v:v-1:4). DT coated PbS/CdS QDs (PbS/CdS-DT) were precipitated in ethanol, removed from the supernatant by centrifugation and resuspended in chloroform. These QDs are stored in ambient conditions.

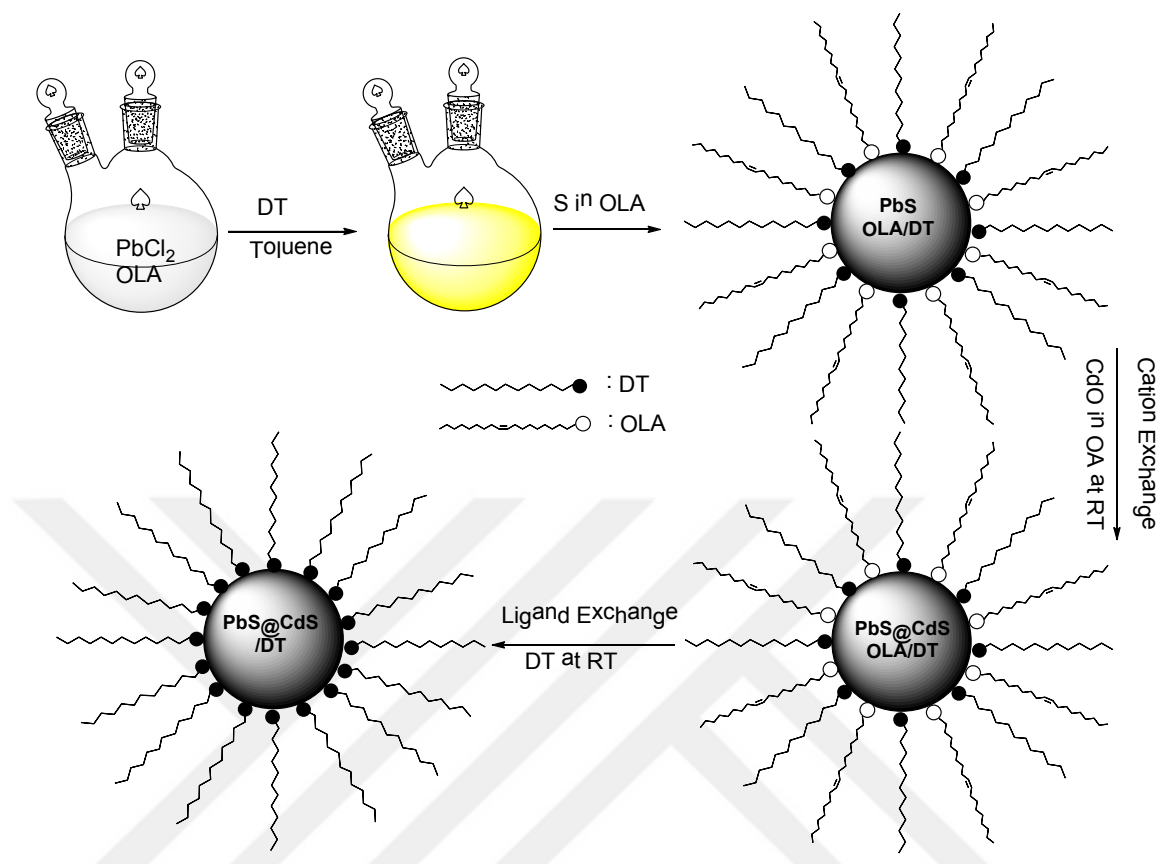


Figure 3. 1 Schematic of PbS synthesis.

3.3 Characterization Methods

Absorbance spectra were taken in the range of 400–1200 nm by a Shimadzu 3600 PC UV-Vis-NIR spectrometer. Photoluminescence spectra is a homemade system which is using a DPSS laser source working at 532 nm as an excitation source. As a monochromator ‘1/8 Newport Cornerstone 130’ monochromator (1/8 Newport Cornerstone 130) and as a silicon detector ‘Thorlabs PDF10A’ ($1.4 \times 10^{-15} \text{ W/Hz}^{1/2}$) is used.

Photoluminescence lifetime of PbS QDs in chloroform was measured using Horiba Fluorolog equipped with TCSPC Triple Illuminator. Measurement time 360 μ s was taken for 4096 channel. Formula of bi-component decay of lifetime shown in Eq. 5 (see chapter 1).

Transmission electron microscope (TEM) (JEOL 2100, Japan) analysis was performed at an accelerating voltage of 200 kV. Samples were diluted with toluene and subjected to ultrasonication (10 min). Ultrathin mesh copper grid dipped into QD solution and left to dry in air.

X-ray photoelectron spectroscopy (XPS) measurements were performed using Thermo Scientific K-Alpha spectrometer using an Aluminum anode (Al $K\alpha$ = 1468.3 eV) at electron take-off angle of 90° (between the sample surface and the axis of the analyzer lens). Spectra were recorded using Avantage 5.9 data system. The binding energy scale was calibrated by assigning the C1 s signal at 284.5 eV.

X-ray diffraction (XRD) pattern was obtained with a Bruker D8 Advance with DAVINCI design equipped with Diffractometer using a Cu $K\alpha$ radiation source (λ = 0.15418 nm). For measurements 0.01236 increment, 16 second integration time, 40mA, 40kV and Si holder is used.

FTIR spectra was taken with a Thermoscientific Nicolet iS10 instrument in the wavenumber range of 400-4000 cm^{-1} .

3.4 Results and Discussion

3.4.1 Characterization of Core-Shell QD

We have produced OLA/DT coated PbS QDs with emission maxima between 1015-880 nm via modifications done on Cademartiri method. These core QDs were subjected to cation exchange process using Cd-oleate at room temperature. Figure 3. 2a-b shows optical properties of PbS QD and PbS/CdS QD. After shell growth process, 40 nm blue shift in PL spectra and roughly 52 nm blue shift in absorbance spectra were observed. Such blue shift is expected since desorption of Pb^{2+} from surface decreases the effective crystal size of the PbS. These dissolved surface ions were replaced with Cd^{2+} as can be confirmed by the size average of nanoparticles detected by TEM. This is confirmed by many studies. [122, 123] Hens et. al., calculated the size from ICP-OES and showed that it correlates well with the size calculated from the absorbance data.[31] We calculated sizes of our QDs from an empirical sizing curve which is developed by Cademartiri et al.[35] Based on this, PbS QD in Figure 3. 2a has a diameter of 2.70 nm. After shell growth process, according to size curve our core QD diameter is 2.55 nm. So, with cation exchange we obtained very thin shell (roughly ~15 nm), a few monolayers.

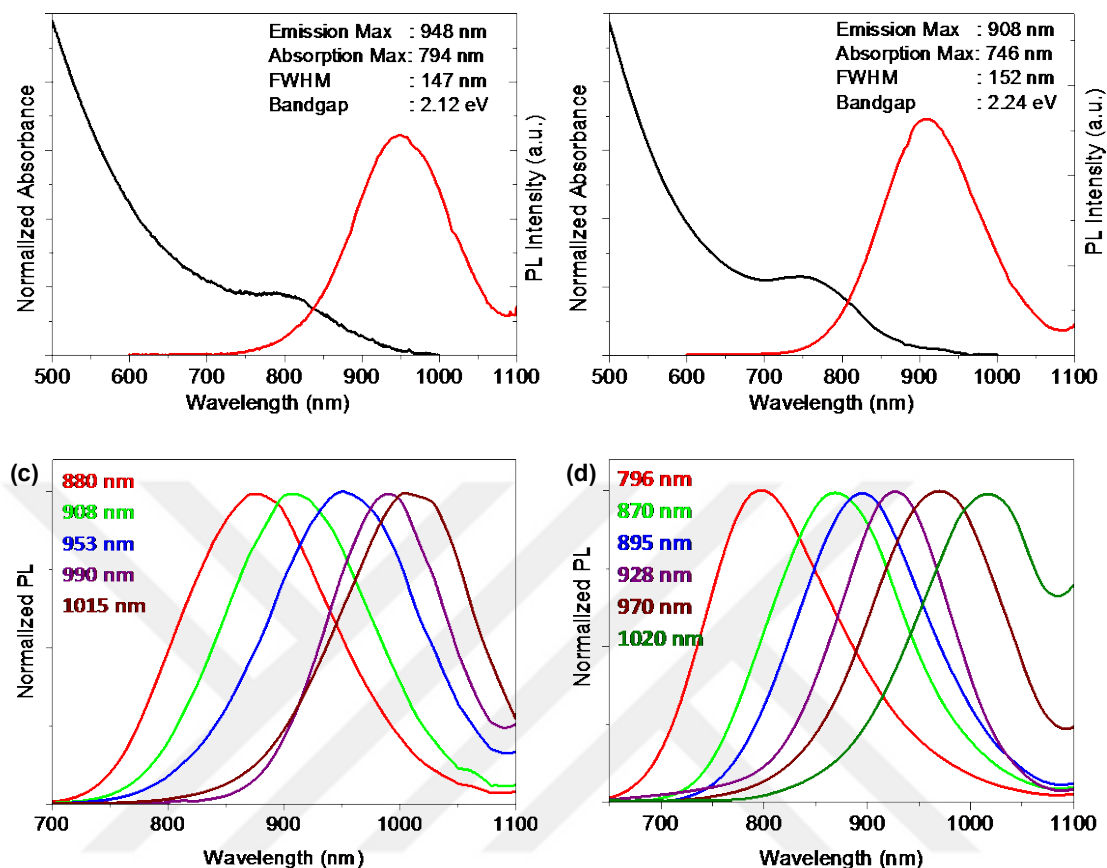


Figure 3. 2 Optical properties of (a) PbS, (b) PbS/CdS QDs (see appendix A for calculation of bandgap), different sized (c) PbS, (d) PbS/CdS QDs

Another advantage of growing a shell on the core is the possibility of further tuning of the emission wavelength as the core size decrease. Figure 3. 2c shows different PbS QD with emission between 880-1015 nm produced with different reaction parameters (described in chapter 2). Due to fast reaction kinetics, it is difficult to obtain small-sized PbS QDs by using lead chloride as a precursor. By shell growth process we enable to decrease emission below to 796 nm and provide better coverage at the sensitive detection range of cheap silicon detectors.

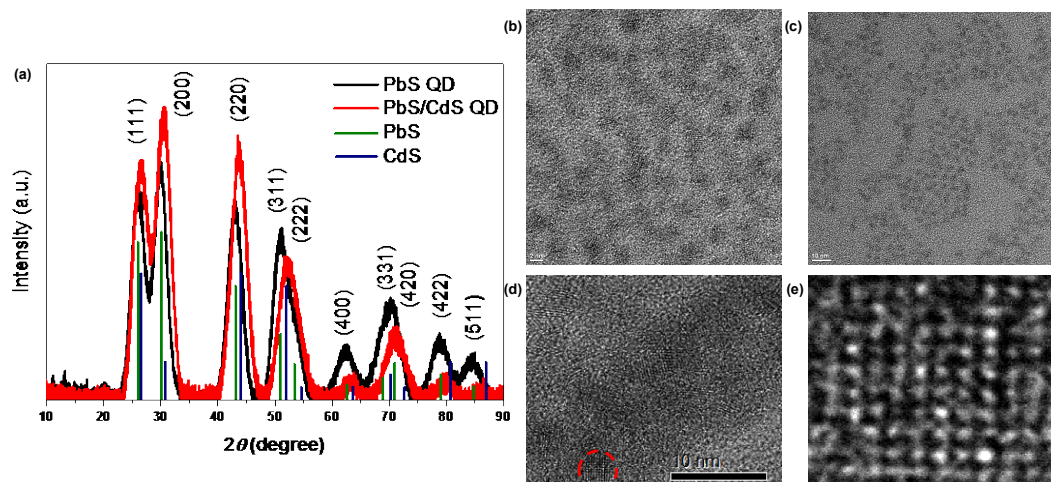


Figure 3. 3 (a) XRD of PbS and PbS/CdS QDs (syntheses at 100 °C) with vertical lines indicating the peak positions of PbS and CdS crystals, TEM images of (b) PbS QD, (c) PbS/CdS QD, (d) HR-TEM image of PbS/CdS QD, (e) magnified area indicated with a red circle in (d).

XRD pattern of PbS/CdS QDs compared with that of PbS and CdS, which are cubic, indicates no CdS formation but a slight shift of PbS peaks to larger angles since CdS has smaller lattice constant than PbS crystal, confirming core/shell structure formation (Figure 3. 3a).[62]

TEM image reveals monodisperse spherical PbS and PbS/CdS QDs (Figure 3. 3b-c). A d-spacing of 0.290 nm was measured from the crystal in red dotted circle area in Figure 3. 3d, which is similar to literature value of PbS QDs.[124] Since CdS shell is a few layers thick, we were unable to observe CdS shell with the TEM. Yet, EDX shows co-existence of Pb and Cd with higher concentration of Pb (Figure 3. 4).

Cation exchange process is mostly applied at elevated temperatures, because it is diffusion controlled process. Hens *et. al.*, reported that vacant positions at QD surface plays a key role to exchange process. They reported PbS QDs, which were synthesized from lead chloride precursor, have empty surface sites, which enables to grow a thin shell at room temperature.[76]

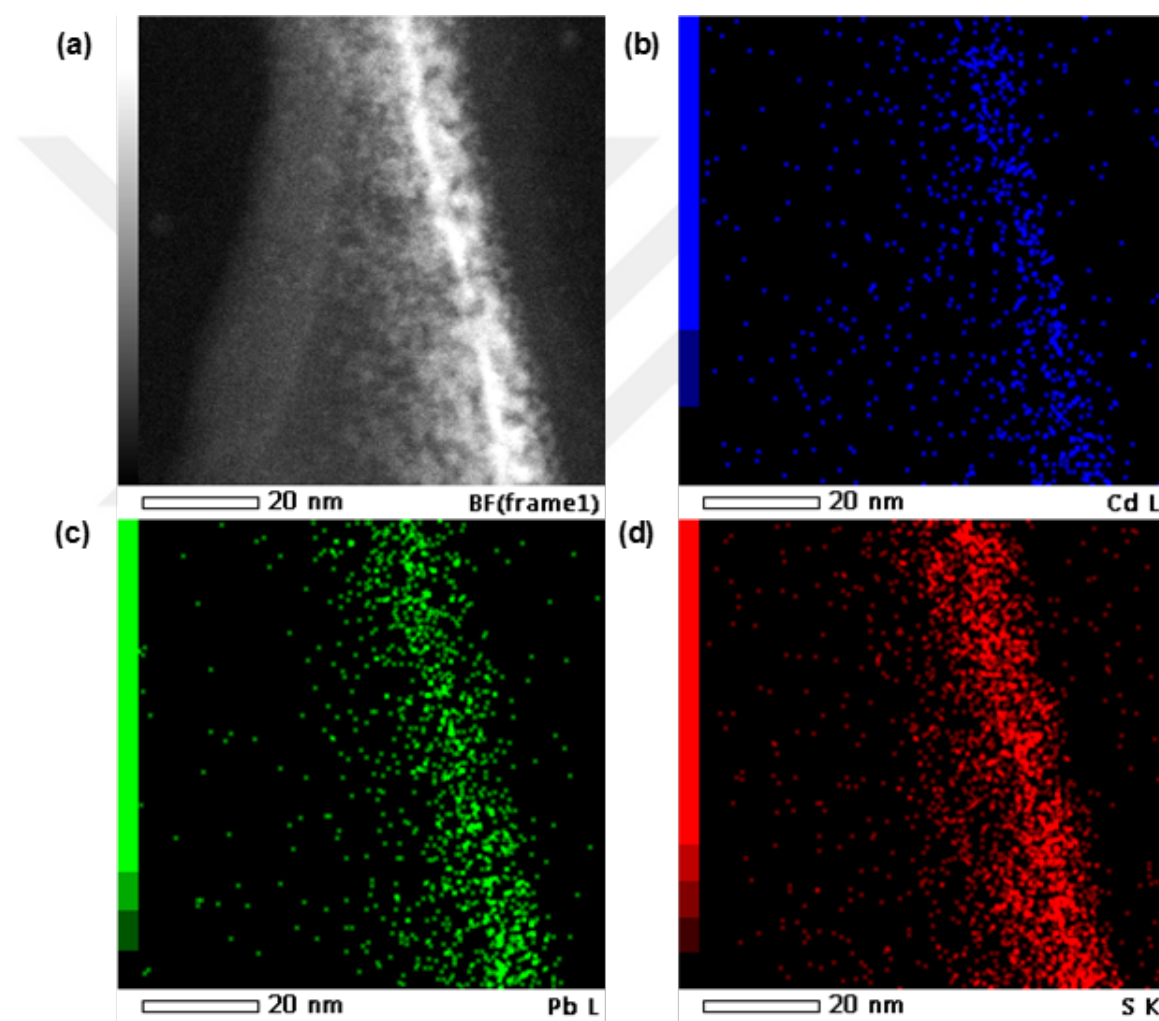


Figure 3. 4. (a) TEM image for EDX analyses, (b) Cd, (c) Pb, (d) S elements

3.4.2 Influence of Shell Growth Temperature on Optical Properties

To investigate the influence of cation exchange temperature on the properties of core-shell QDs, procedure was performed both at traditional 100 °C and at room temperature using the same PbS cores. In first few minutes, a dramatic increase (ca 5.4-fold) in the emission intensity was detected in both cases with about a 105 nm blue shift which corresponds roughly to a 0.3 nm shell thickness (Figure 3. 5a-b) (see appendix A for size calculation). Size of the PbS core shrink as Pb^{2+} are displaced by Cd^{2+} , resulting in blue shift in the emission and absorption spectra. Formation of such a thin CdS shell seems to successfully passivate surface defects and reduce non-radiative events, causing such a dramatic enhancement of emission intensity. But, at 100 °C, cation exchange continued with time, as indicated by a further blue shift of the emission peak accompanied by a significant decrease in its intensity. The major change in the emission peak was completed in 1 h. At this time point, the emission intensity fell below the intensity of the PbS core with about 200nm blue shift, which corresponds roughly 0.7 nm shell thickness. Our result is perfectly correlates with the findings of Zhao et. al., which states QY decrease after 0.7 nm shell thickness.[122] . Many reports indicate that a thick shell causes a drop in the emission intensity due to defects formed through the shell layer or growing lattice mismatch between PbS and CdS crystals (although there is a small lattice mismatch).[122, 125] This is fully supported with our data when cation exchange was performed at 100 °C. Also, broadening in the emission peak with increasing reaction time, indicates increasing polydispersity may be due to particle to particle difference in the rate of cation exchange. However, at room temperature, shell growth process was

found to be independent from the reaction time. After the initial blue shift and enhancement of the emission intensity observed in the first 5 minutes, no further shift in the peak position or change in the intensity was detected in 2h. At room temperature, only weakly bound surface Pb^{2+} ions were displaced with Cd^{2+} ions, and further dissolution Pb^{2+} from the core did not take place. Weller et. al. suggests that ca 30% conversion takes place within the first minute of the CE due to surface reactions.[126] Van Huis et. al. also, indicates that the first two layers go under CE quite fast but the exchange rate of the fourth layer is nearly zero, based on classical molecular dynamics simulations performed on 4.7 nm PbSe core.[74] Both of these reports supports our observations for the CE at room temperature. After the initial one or two layers, further migration of Cd^{+2} in and Pb^{+2} out is prevented at room temperature.

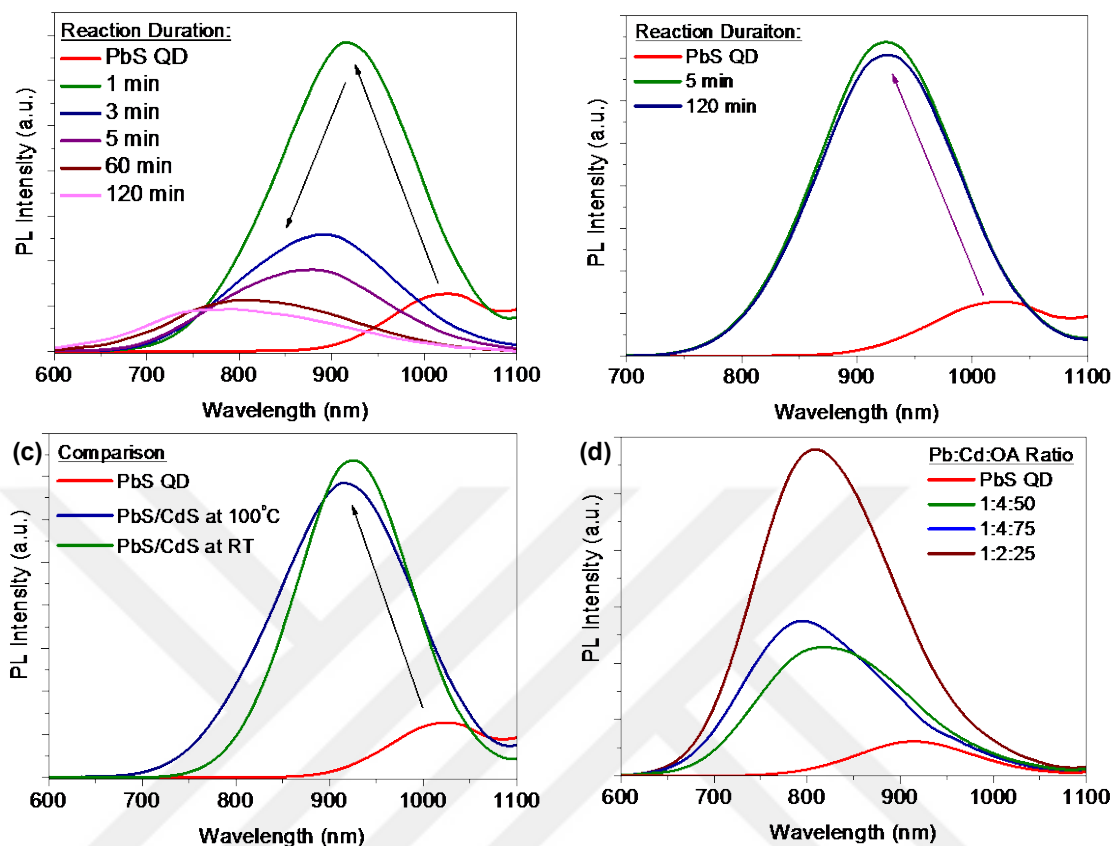


Figure 3. 5 PL spectra of shell growth process performed at (a) 100 °C, (b) RT, (c) PL spectra of PbS/CdS synthesized at RT and 100 °C, (d) PL spectra of the PbS core and PbS/CdS QDs prepared at different Pb:Cd:OA ratios

Hens et. al. have also attempted PbS/CdS synthesis via cation exchange at 20 °C yet, using 5 nm PbS-OA prepared from PbS-OLA via ligand exchange, they have observed only 0.1-0.16 nm thick shell.[76] Here, we do observed a much more effective shell formation. Considering the PbS/CdS structure, the thermodynamics is not very favorable, therefore high exchange temperatures are usually applied.[73] But, size of the crystal and ligand is important. In our case, ultrasmall PbS core and weakly bound OLA are probably

positively affecting the CE process at room temperature.[74, 76] Pb^{2+} is a borderline acid compared to soft Cd^{2+} . Oleate is a harder base than OLA and sulfide. It is possible to think that preferential ligation of dissolved Pb^{2+} with OA and Cd^{2+} with sulfide and OLA, may facilitate the reaction in the desired direction. Room temperature cation exchange (TRCE) process was performed on two different PbS cores with emission maxima at 1015 and 912 nm (3.16 and 2.65 nm), producing PbS/CdS QDs with ca 5.8 and 9.0-fold increase in the emission intensity and about 100 nm blue shift in the peak position, result in PbS/CdS QDs with emission maxima at 924 and 807 nm, respectively. More dramatic enhancement in the smaller particle emphasized the importance of crystal size, especially in such a small size regime where more of the ions are on the surface (Figure 3. 6).

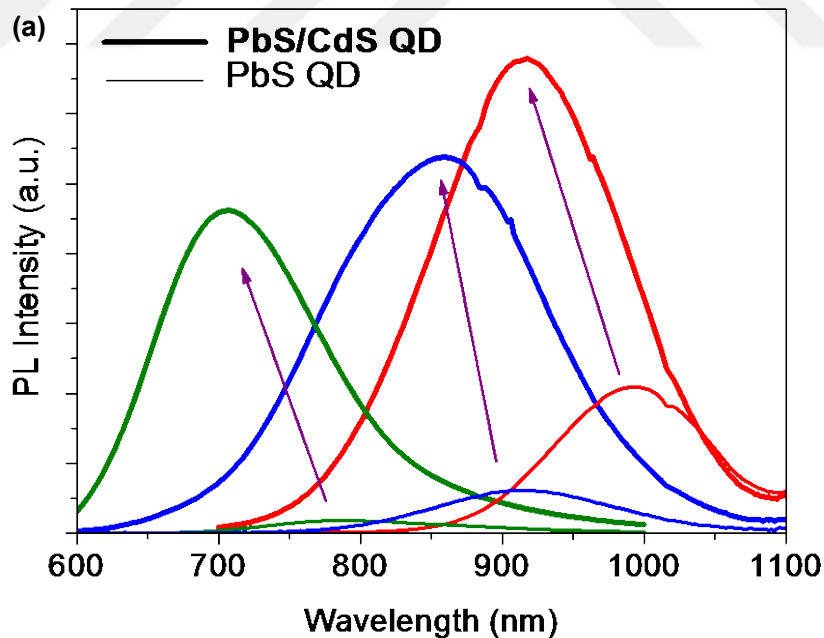


Figure 3. 6 PL spectra shows different influence of shell growth process on the PL intensity of different sized PbS QD

Mechanism of CE process is under debate. Cation and vacancy diffusion as well as kick-off mechanism were suggested yet, in case of PbS/CdS the excepted mechanism is cation and vacancy exchange which is supported by our observations.

Room temperature process also, showed a narrower emission peak, indicating slightly better size distribution (Figure 3. 5c). This observation has two significant implications: 1) Tuning emission wavelength with timing the cation exchange process at room temperature is not possible; 2) Cation exchange at room temperature is time independent, so it is very simple to get strongly luminescent PbS/CdS at ca 100 nm shorter wavelengths.

As we discuss previously shell growth process can enable to further size tuning via core size change during cation exchange. Diffusion, adsorption and desorption of ions is temperature-driven processes. Also, temperature and reaction duration are parameters of cation exchange process. Another parameter is the ratio of Pb:Cd:OA to tune optical properties of core-shell QD. Figure 3. 5d shows the effect of different Pb:Cd:OA on emission wavelength and intensity of QDs. It is clear that, excess amount Cd, didn't required at room temperature to shell growth, because it is already having a limit at room temperature.[76] We observe that Pb:Cd:OA didn't changed significantly wavelength of emission of core QD, but changed intensity. The ratio of 1:2:25 resulted best optical properties in terms of emission intensity.

3.4.3 Influence of Heat Treatment on Core-Shell Structure

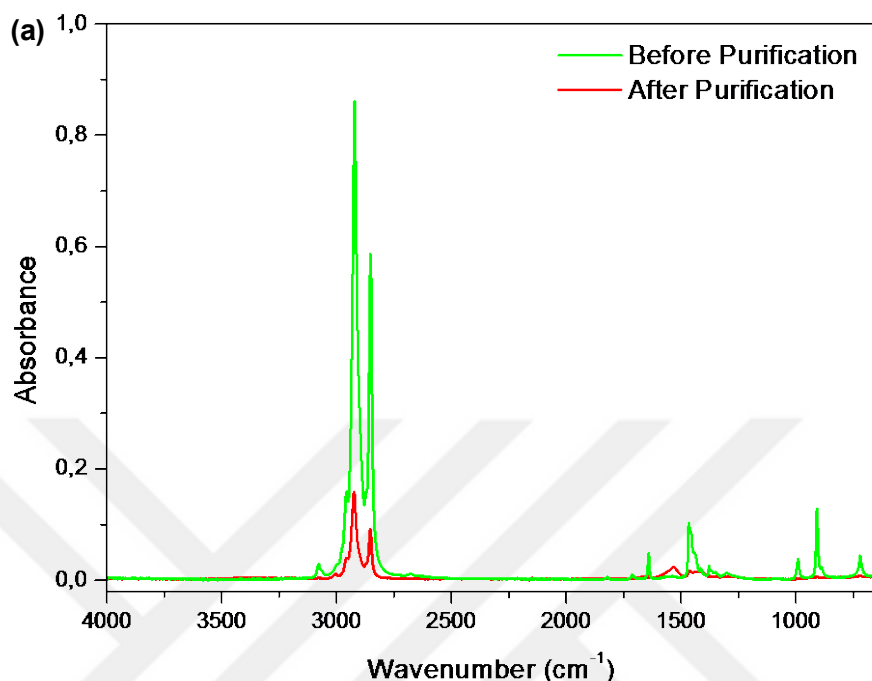


Figure 3. 7 FTIR spectra of PbS/CdS QD before and after purification

Although a thin layer of CdS shell obtained at RT was enough to enhance emission intensity with a controlled shift to shorter wavelengths, XPS data (Figure 3. 12, Figure 3. 13, Figure 3. 14) revealed poor crystallinity, which can reduce stability overtime. Heat treatment process generally applied after SILAR process to reduce interfacial defects between PbS and CdS layers.[70, 87] For the colloidal QDs, heat treatment is not preferred due to possibility of Ostwald ripening, which generally decreases optical properties of QD.[64, 75] Zhao *et. al.*, reported shell formation provides better thermal stability to QD.[75] Due to higher thermal stability of core-shell QDs, heat treatment was applied to increase crystallinity and stability to purified core-shell QDs.[72] We have

extensively washed PbS/CdS QDs before annealing, to remove all Cd^{2+} from the material to prevent shell thickening (Figure 3. 7). If annealing is performed in solution a large red shift was observed with almost completely diminished emission. This indicates Ostwald ripening during solution annealing which is a known phenomenon for PbS QD[22, 43, 115], even during storage.[59, 127] The ripening of core/shell particles are interesting and the mechanism is not clear yet. More interestingly, if PbS/CdS QDs are annealed in the powder form in vacuum oven, again a red shift in absorbance and luminescence spectra were observed, but without the loss of emission. This is indicating faster kinetics in the solution phase and combination of different reactions. Probably reaction in solution-state is faster due to faster diffusion rate and homogenous medium of solvent.

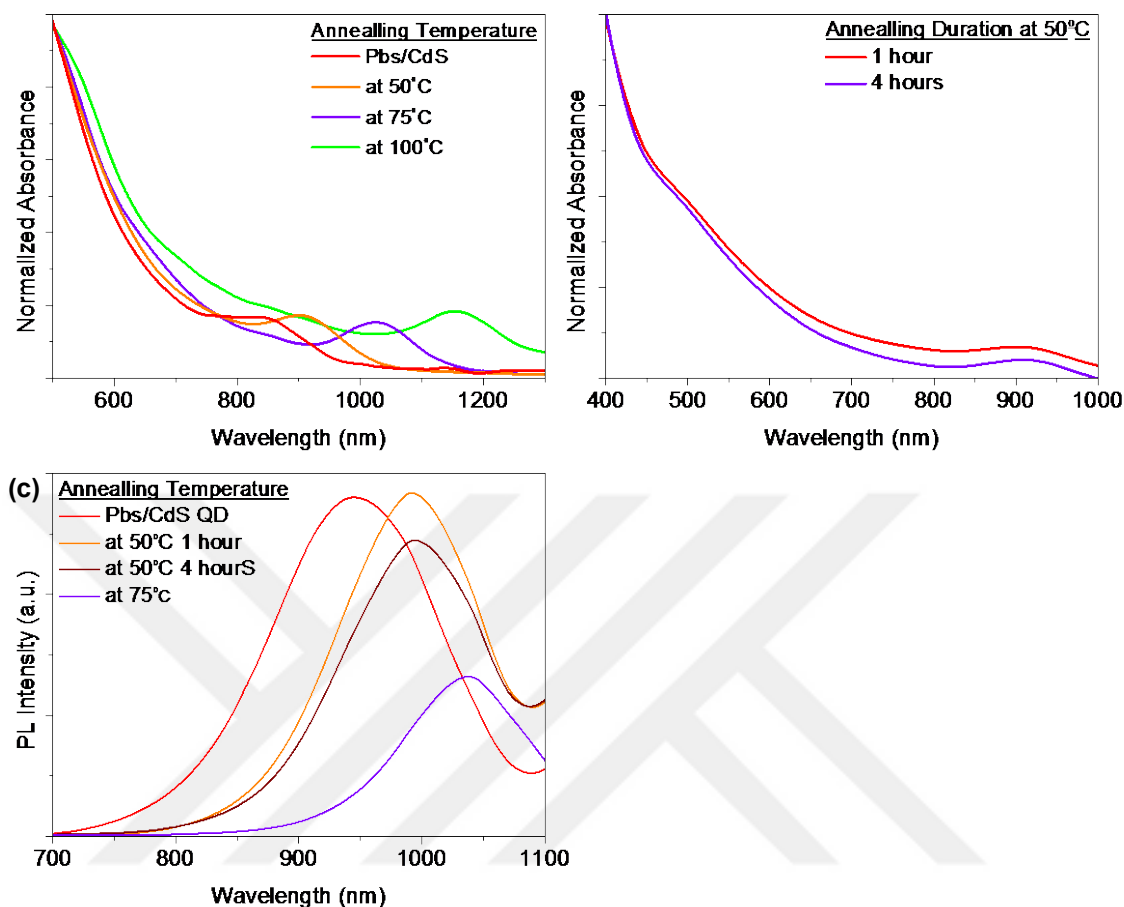


Figure 3. 8 Absorbance spectra of PbS/CdS QDs annealed (a) at different temperatures, (b) for different durations, (c) PL spectra of PbS/CdS QDs annealed at different temperatures

Absorbance onset of the PbS/CdS QDs shift to longer wavelengths with the increasing annealing temperature (Figure 3. 8) as follows: 65, 187 and 316 nm red shift upon annealing at 50, 75 and 100 °C, respectively, with no loss in absorption value. According to sizing curve of Cademartiri et. al.[35], annealing at 100 °C causes particles to grow from 2.82 nm to 3.99 nm . Because, this size difference is quite small, we couldn't observe

such enlargement in TEM images. Interestingly, effect is independent of time after 1h annealing at low temperature (Figure 3. 8b).

Luminescence peak maxima showed a red shift with annealing temperature as well (Figure 3. 8c). A 49 and 95 nm red shift from the as-made PbS/CdS emission maxima was observed at 50 and 75 °C, respectively. Since annealing at 100 °C caused a dramatic growth, the emission peak shift outside of the detection limit of Si detector. Decreasing band gap and coalescence of particles during annealing of QD-films have been reported before[128].

Annealing at 50 °C for one hour didn't change the PL emission intensity of as-made PbS/CdS QD, but FWHM became narrower, which indicates lower size distribution. Annealing temperatures above than 50 °C, PL intensity is decreasing with increasing annealing temperatures unlike the absorption. We assume possible two explanations to PL intensity loss, (i) according to PL and UV spectra, core QD become bigger and for PbS QD size increase causes QY reduce due to reduce in confinement regime.[31, 43] (ii) Annealing temperature interfere organic surface ligands, which causes QY reduce. For both absorption and PL, there is little loss observed between 1-4 hours annealing for 50 °C.

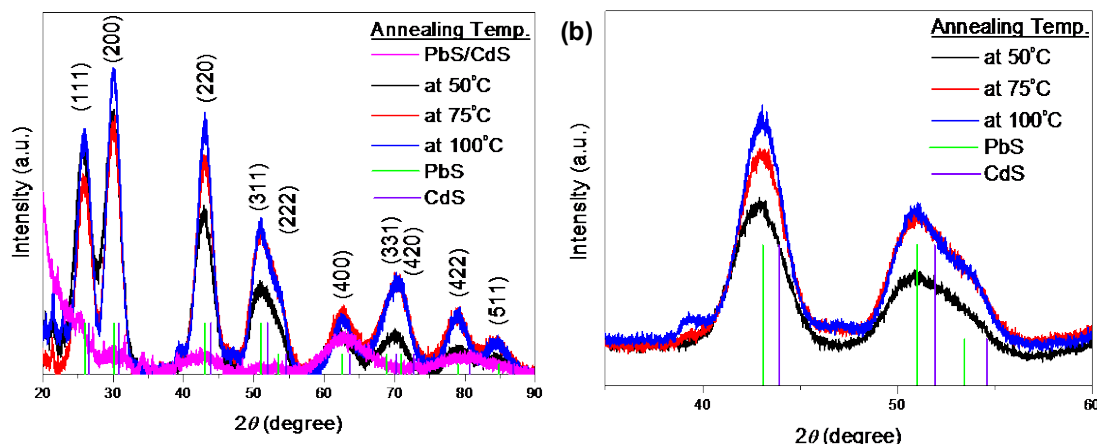


Figure 3. 9 (a) XRD patterns of PbS/CdS QD and annealed PbS/CdS QDs at different temperatures, (b) Enlarged area of XRD pattern shows two peaks

Unlike the CE process at 100 °C (Figure 3. 3), RT CE produced poor crystallinity (pink curve in Figure 3. 9) based on the XRD patterns of the QDs. High temperature process not only increases the diffusion of ions in and out but also within the crystal, providing better crystal structure. Yet, crystallinity was improved by annealing after RT CE process as seen in Figure 3. 9. Annealing did not shift the peak positions, so no compositional change is expected. Major enhancement of the peak intensities observed at 50 and 75 °C. Highest crystallinity obtained at 100 °C. Probably, RT CE was able to grow a couple of CdS layers on PbS, but not complete crystallization, which was achieved by annealing as a post-synthetic process. After annealing at 75 and 100 °C, two new peaks at 2θ at 39.2° and 46.9° were emerged. These peaks correlate well with elemental S, which may form due to decomposition of surface ligand DT coming from the modified Cademartiri method that we have developed (chapter 2), which is more significant after annealing at

100 °C. Decomposition of ligands introduce surface trap sites, which may explain some loss of intensity at high annealing temperatures.

3.4.4 Stability of Core-Shell QDs

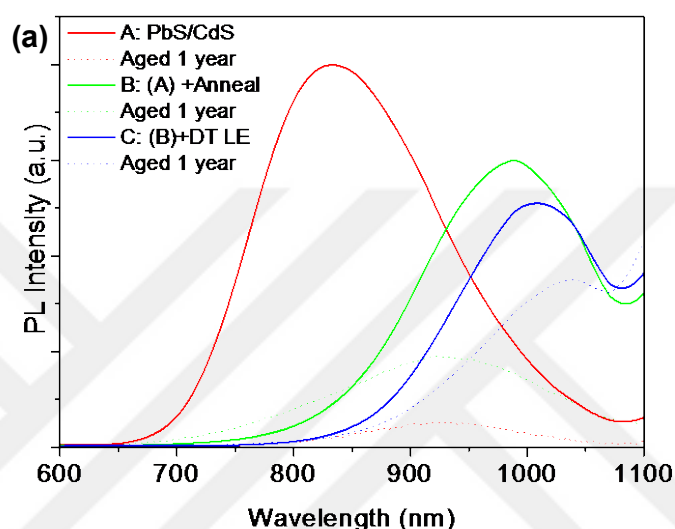


Figure 3. 10 Photoluminescence spectra of QDs shortly after synthesis (solid lines) and 1 year after (dotted lines) the initial measurement. Unannealed PbS/CdS (Curve A); annealed at 100 °C (Curve B); annealed at 100 °C and DT ligand exchanged (Curve C).

Long-term colloidal stability of all particles is excellent over years, already. When optical stability is concerned, we have seen 102 nm red shift in the position and 93% decrease in the emission intensity (Figure 3. 10) of the as-made PbS/CdS. If annealed at 100 °C, 66 nm blue shift and 68% decrease in the emission intensity was observed, indicating improved optical stability upon annealing. Red shift of the emission peak in time coupled with low crystallinity of the as-made PbS/CdS suggests possibility of slow

dissolution of the smaller particles and adding up to larger ones. On the other hand, annealing enhanced the crystallinity, but there is indication for DT loss from the surface. Actually, if strongly bound DT can be lost, probably OLA can do the same as well. Such can cause surface defects, and in the long-term, surface oxidation and or loss of surface ions as well, which would cause a blue shift in the emission peak with a loss in the intensity. Yet, such loss is not as dramatic as the as-made PbS/CdS, since the crystalline shell is more stable.[129] To improve the stability further, weakly bound OLA was displaced with DT on the surface of PbS/CdS annealed QDs. This may be due to reduced inter-QD spacing or closer packing of QDs due to shortening of surface ligands as well as new intra-band defects formed during ligand exchange.[70] Yet, annealed PbS/CdS QDs with DT ligand exchanged showed a minimal change in their properties: 30 nm red shift and only 31% losing the emission intensity after 1 year store in chloroform. This observation suggests that Ostwald ripening and oxidation is mostly eliminated after the full process consisting of RT CE to form a thin CdS shell, annealing at low temperatures followed by DT ligand exchange.

Lifetime spectroscopy is a useful technique to understand the mechanism of fluorescence by comparing exciton lifetimes. Generally, a biexponential decay is observed with QDs related to existence of both radiative and non-radiative events. Fast component (t_1) arise from defect states, which are acting as hole and electron traps, and causes non-radiative decay, which reduces QY of QDs. Slow component (t_2) represents radiative decay and means slower (longer) relaxation (hole and electron recombination). Hens et. al., reported that with the increasing size of PbS QDs, lifetime and QY

decreases[31], probably due to weakening of confinement regime. Comparison of amplitudes of fast (B1) and slow (B2) components can provide information about the change in mechanism of fluorescence after processes such as shell growth, annealing and ligand exchange.

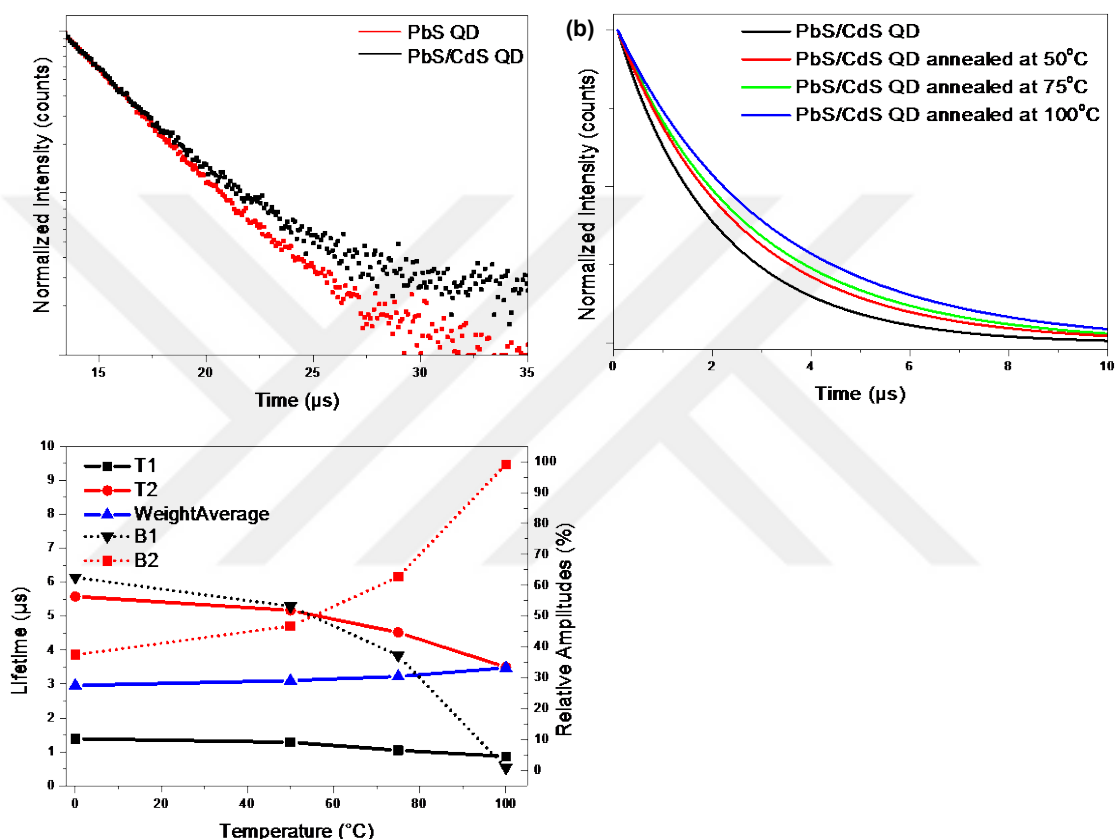


Figure 3. 11 (a) Lifetime decays of PbS and PbS/CdS QDs, (b) Lifetime decays of annealed PbS/CdS QDs, (c) Lifetime decays and relative amplitude comparison of annealed PbS/CdS QDs with different annealing temperatures.

Table 3. 1 Influence of Shell

	t1 (μ s)	B1 (%)	t2 (μ s)	B2 (%)	Weight Average (μ s)	χ^2
PbS	2,63	65,55	3,74	34,45	3,01	1,02
PbS/CdS	1,54	62,54	5,58	37,46	3,06	1,05

As reported in many studies, shell growth process increases PL lifetime by reducing non-radiative decays.[75] Table 3. 1 and Figure 3. 11 compares lifetimes of core and core-shell QDs. Increased lifetime (3,01 μ s for PbS QD and 3.06 μ s for PbS/CdS) confirms effective passivation of shell. As discussed before in type-1 core-shell QD, shell has larger bandgap than core and by that way shell confines exciton in core.[114] Also it is clear that shell growth should change fluorescence mechanism. According Table 3. 1 confirms shell growth reduces non-radiative decay lifetime, while increases radiative decay lifetime.

Table 3. 2 Influence of Annealing Temperature

	t1 (μ s)	B1 (%)	t2 (μ s)	B2 (%)	Weight Average (μ s)	χ^2
PbS/CdS	1,54	62,54	5,58	37,46	3,06	1,05
50°C	1,29	53,2	5,17	46,8	3,11	1,01
75°C	1,05	37,29	4,52	62,71	3,22	1,13
100°C	0,87	0,88	3,5	99,12	3,48	1,15

Table 3. 2 and Figure 3. 11b-c shows the changes in the luminescence mechanism based on the annealing temperature related changes in the slow and fast decay components of annealed PbS/CdS. Average lifetimes are 3.06 μ s, 3.11 μ s, 3.22 μ s, 3.48 μ s for PbS/CdS QD annealed at 50, 75 and 100 °C, respectively. Interestingly, while both lifetime

components are getting faster with increasing annealing temperatures, average lifetime is increasing due to increased amplitude of slower component. As the size of the PbS increases, average lifetime usually decreases[31]. This may suggest that an increase in the overall size is not the underlying cause of such observation. TEM analysis of annealed samples did not reveal any significant coalescence, and such small increase in size was not detectable from our images. So, shift of the emission peaks to longer wavelengths with slower average decay time is probably related to the quality of surface and interface, and the degree of crystallinity. Increasing annealing temperature dramatically improved crystallinity as discussed above, which probably cause an ordered structure and a better energy wall around the PbS core.

Table 3. 3 Influence of Ligand Exchange to Annealed Core-Shell QD

	t1 (μ s)	B1 (%)	t2 (μ s)	B2 (%)	Weight Average (μ s)	χ^2
PbS/CdS	1,29	53,2	5,17	46,8	3,10	1,01
PbS/CdS-DT	1,85	37,89	2,95	62,11	2,54	1,03

Exchange of OLA with DT after annealing at 50 °C reduced lifetime further from 3.10 μ s to 2.54 μ s (Table 3. 3). Again, both events seem to be faster but the reduced amplitude of the faster component coupled with an increase in the amplitude of slower component. Many reports indicates shorter ligands cause shorter exciton lifetime due to smaller inter-QD spacing which increases hole and electron mobility.[70, 130, 131] DT passivates QD surface better due to stronger binding to surface Cd atoms. Many reports relate ligand exchange with formation of new surface defects due to PL intensity loss during the

exchange process.[70, 129, 132] Besides, DT ligands may act as a hole trap if the valence band of QD is below the redox potential of the thiol (about -5 eV), reducing the emissive coupling events.[120] We observed PL intensity loss after ligand exchange, as well, but not sure about the reason, since actually emission should be originating from the confined core, but DT exchange was done on the surface of the shell. Yet, defect related emissions as discussed in Chapter 2 may take place here, as well

3.4.5 XPS Analyses

Binding energies determined by XPS, reveals different states or environments of Pb, S and Cd atoms (Table 3. 4). In PbS there are two types of Pb with different binding energies: Pb4f 7/2-5/2 pair at 136.88- 141.78 eV and 137.78-142.68 eV. We suggest that these correspond to surface versus inner core Pb's, respectively. These values are in agreement with the literature, but Ma et. al., suggests that the Pb with the lower binding energy represent uncoordinated Pb.[98] There are two different sulfurs, as well: S 2p 3/2-2/1 at 161-162.8 eV belongs to Pb-S, 2p 3/2-2/1 at 163-164.6 eV corresponds to the S of DT.

Table 3. 4 Binding energy of Pb, Cd and S core level						
Sample	Pb 4f 7/2-5/2		S 2p 3/2-2/1			Cd 3d 5/2-3/2
PbS	136.88-141.78	137.78-142.68	161-162.8	163-164.6		
PbS/CdS		138.28-143.18	162.9-164.4	166.1-167.3	168.4-169.8	404.78-411.58
annealed at 50°C		138.38-143.28	160.7-161.8	162.9-164	167.6-168.9	405.08-411.78
annealed at 50°C + DTLE	137.28-142.18	138.18-143.08	160.78-161.98	162.78-163.88	165.48-166.88	404.78

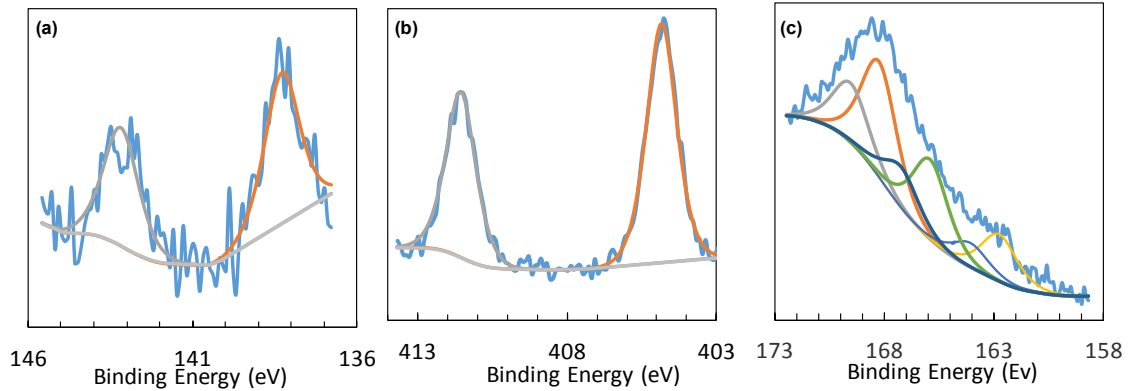


Figure 3. 12 XPS characterizations of elements in PbS/CdS QD (a) Pb, (b) S, (c) Cd.

Figure 3. 12 shows XPS spectra of as-made PbS/CdS QDs, indicating the presence of Pb 4f 7/2-5/2 pair at 138.28 – 143.18 eV and Cd 3d 5/2-3/2 pair at 404.78 – 411.58 eV. These values correlate well with Pb-S and Cd-S bonds. The disappearance of the Pb peak attributed to the surface atoms along with the appearance of Cd signal confirm the CdS shell formation. Hence, in PbS/CdS. XPS reveals three types of S: S 2p 3/2-2/1 at 162.9 – 164.4 eV may be Cd-S, S at 166.1-167.3 eV may correspond to the S of DT and S at 168.4 – 169.8 eV corresponds to oxidized sulfur such as –SO and –SO₄. Yet, there is no peak for PbSO₄. [82] Actually, the core Pb and S peaks are slightly at higher binding energies which may be due to the reduced crystal size of the PbS core during the cation exchange.

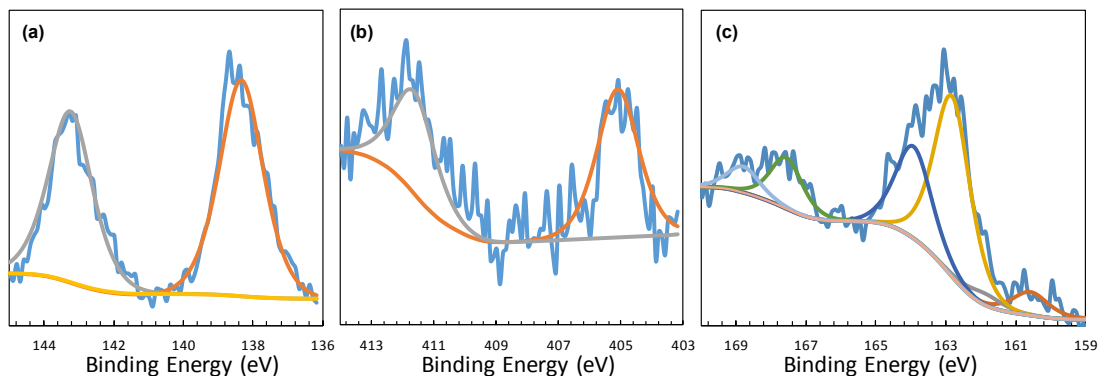


Figure 3. 13 XPS characterizations of elements in PbS/CdS QD annealed at 50 °C (a) Cd, (b) Pb, (c) S.

Figure 3. 13 shows XPS spectra of core-shell QDs annealed at 50 °C. Binding energies of Pb with 4f 7/2-5/2 pair at 138.38- 143.28 eV and binding energies of Cd with 3d 5/2-3/2 pair at 405.08 - 411.78 eV is perfectly matching with binding energies of PbS/CdS before annealing, which confirms no or little oxide formation during annealing. There are again three different S atoms: First two with the binding energies of S 2p 3/2-2/1 at 160.7 – 161.8 eV belongs to Cd-S, S at 162.9-164 eV corresponds to the S of DT. Annealing, decreased binding energies of these two types of S back to the PbS-core values. This may be related to better crystallization of the material during annealing. Yet, there seems to be an oxidized S at BE of 167.6 – 168.9 eV again. This may correspond to oxidized DT. Actually, based on the XRD data, S 2p peak for elemental S was expected based on XRD data, yet if there is a small amount of elemental S, it should be under the existing peaks.

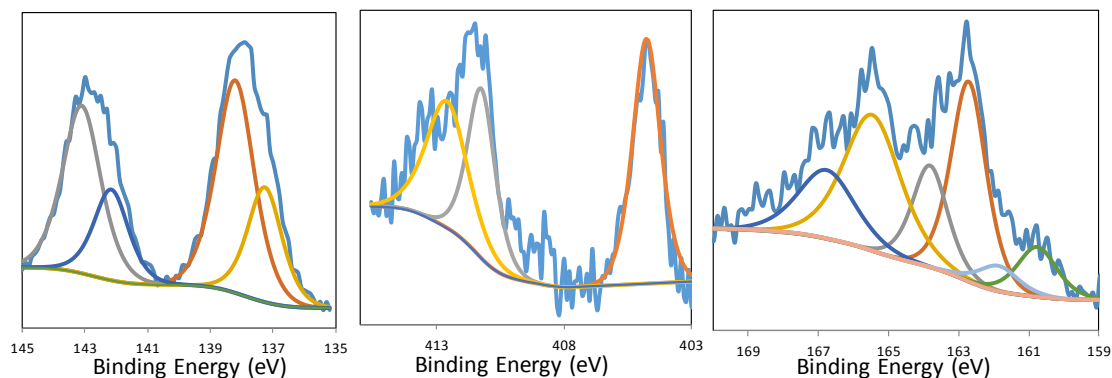


Figure 3. 14 XPS characterizations of elements in PbS/CdS-DT QD annealed at 50 °C (a) Cd, (b) Pb, (c) S after ligand exchange process.

Figure 3. 14 shows the XPS spectra of PbS/CdS-DT QD annealed at 50 °C annealed and subjected to DT ligand exchange. Interestingly, we observed two types of Pb with 4f 7/2-5/2 pair at 137.28 – 142.18 eV and 138.18 – 143.08 eV, emerged again. These binding energies are similar with core QD binding energies reported for PbS. Actually, no change in the PbS core was expected after ligand exchange since it is a surface event. We can identify only 5/2 binding energy for Cd 3d at 404.78 eV because of overlap of 3d Pb binding energy. The only difference in the S 2p spectra is the oxidized S at lower binding energy, 165.48 – 166.88 eV corresponds sulfonates (Table 3. 4).

3.5 Conclusion

PbS/CdS core shell QDs were developed from ultrasmall PbS with a very thin CdS shell via room temperature cation exchange process using Cd-oleate. Process is self-limiting and time independent at room temperature which is very practical, compared to CE at 100 °C. Shell growth at RT provide effective passivation of the surface and

confinement of the exciton within the core, causing 5.8-9 fold increase in the emission intensity with roughly 100 nm blue shift in the emission maxima. So, it is possible to obtain a series of QDs with tuned emission wavelength by starting from a series of PbS cores with well separated emission peaks. RT process provided a slower average decay with stronger contribution of the core exciton coupling. Although control of the process was more difficult at 100 °C, CE at high temperature provides better crystallinity and stability. Hence, PbS/CdS QDs formed by RT CE process, were subjected to annealing between 50-100 °C, to improve crystallinity. A dramatic enhancement in crystallinity was accompanied with red shift in absorbance and luminescence peaks, which may indicate some coalescence of particles. Annealing at 100 °C caused a large drop in the bandgap, so emission of the QD was not detected within the limits of Si detector. Also, annealing at high temperature may cause some decomposition of surface DT coming from the synthesis of ultrasmall PbS. Shell growth slowed down the average exciton lifetime compared to PbS core with faster decay of both slow and fast components. Annealing reduced the average lifetime further, yet also reversed the mechanism from more defect related to exciton coupling with increasing annealing time. Overall, we have concluded that RT CE process coupled with 1h annealing at 50 °C, provides a thin crystalline CdS shell around PbS causing luminescence intensity increase with overall ca 50 nm blue shift in the peak position. Although such core/shell QDs are much more stable than PbS core, DT ligand exchange provided further stability up to a year.

Overall, this is the first time a PbS/CdS structure with emission below 900 nm was synthesized from ultrasmall sized PbS QDs.[133] Emission tunability, control of shell

thickness and quality was demonstrated in a very simple and economic RT CE followed by low temperature annealing processes which is high applicable to industrial scale.



Chapter 4

4 Synthesis of Polymethacrylic Acid Coated Colloidal PbS and PbS/CdS Quantum Dots and Their Stability in Petroleum Products

4.1 Introduction

In previous chapters, a new method for the synthesis of highly luminescent small-sized PbS QD with emission below to 880 nm, via a modified Cademartiri's method using non-toxic, non-oxidative, abundant and cheap precursors, has been reported (Chapter 2). These PbS QDs have a mixed oleylamine (OLA) and dodecanethiol (DT) coating and are more stable than the ones reported in the literature due to smaller crystal size and better passivation of surface with the addition of DT added to the reaction. However, to improve the stability further, all surface was passivated by DT, via post-synthetic ligand exchange of OLA with DT. PbS-DT shows better stability overtime, but cannot resist to a slow Ostwald repining over time. In order to prevent such events which can shift the peak position and reduce emission intensity, a CdS shell was grown on PbS core via room temperature cation exchange (Chapter 3). PbS/CdS QDs, have better emission intensity compared to the core PbS. Besides, PbS/CdS formed via this method resulted in a predictable blue shift in the absorbance, hence emerged as an additional tool to tune

emission wavelength of larger PbS QDs. Indeed, room temperature cation exchanged allowed synthesis of PbS/CdS with emission maxima below 800 nm, which is lowest emission wavelength for PbS/CdS QD prepared via such method. These PbS/CdS QDs have excellent colloidal stability over years and kept emission peak position and strength within months but still a considerable red shift and some loss of emission intensity over a year. What is desired for optical tagging of valuable liquids, including liquid petroleum products, a long-term stability is needed. This includes colloidal stability and non-significant shift in the emission wavelength and intensity.

Our group has previously shown that, coating QDs with polymeric coatings improve colloidal stability dramatically yet, since repeat units repel each other, it leaves uncoordinated sites on the crystal surface acting as defects, hence provide a weak luminescence.[134] Combination of polymers with a small thiolated molecules overcomes this problem. Small molecules diffuse to the crystal surface and pacify the uncoordinated sites. Polyacrylic acid (PAA)/thioglycolic acid (TGA) mixture used to coat CdS QDs, actually provided QDs as strongly luminescent as TGA coated CdS, yet with excellent colloidal stability over years.[134] In this chapter, a similar approach will be discussed in an afford to synthesize colloiddally and optically stable PbS and PbS/CdS QDs in hydrocarbon liquids as well as liquid petroleum products.

Synthesis and properties of PbS and PbS/CdS QDs, with poly(methacrylic acid) (PMAA) in its coating will be discussed. Here, since the targeted carrier solvents or liquids are hydrophobic, poly(methacrylic acid) (PMAA) is suggested as the polymeric part of the coating. Carboxylic acid units of PMAA would adsorb on the crystal surface

and methyl units would provide some favorable hydrophobic interactions with the solvent and some steric stabilization. So, in the synthetic method developed for the subject matter of this thesis and detailed in Chapter 2, PMAA was used as a coating material in addition to OLA and DT, to produce PbS coated with PMAA/DT/OLA mixture. Later, the room temperature cation exchange method explained in chapter 3 was applied to these particles for PbS/CdS QDs with polymeric coating. Influence of the polymer molecular weight and amount on particles properties as well as the impact of polymeric component in the coating on the stability of these QDs will be discussed within this chapter.

4.2 Experimental Section

4.2.1 Materials

Lead chloride (98%), sulfur (99.99%), oleylamine (OLA) (technical grade, 70%), 1-dodecanethiol (DT) (98%), cadmium oxide (CdO) (99.5%), oleic acid (OA) (99%), 1-octadecene (ODE) (98%) were purchased from Sigma-Aldrich. Toluene, chloroform, ethanol were all 'for synthesis' quality and were purchased from Merck. Two types of PMAA was used: (1) $M_n = 131500$ g/mol, synthesized in our group via free radical polymerization of methacrylic acid and treated with NaOH to generate poly(methacrylic acid sodium salt); (2) $M_n = 5000$ g/mol was purchased from Sigma-Aldrich.

4.2.2 Colloidal PbS- OLA/PMAA QD Synthesis

Synthesis of OLA/PMAA coated PbS QDs (PbS-OLA/PMAA) was performed under argon atmosphere to avoid oxidation. First, the sulfur precursor was prepared by dissolving 0.008 g (0.25 mmol) elemental sulfur in 2.5 mL of OLA by sonication under

argon flow for an hour, followed by vacuum at RT for another hour. Lead precursor was prepared separately by dissolving 0.28 g (1 mmol) PbCl₂ and desired amount of PMAA in 5 mL OLA in a three-necked round-bottom flask at 110 °C under argon flow followed by vacuum at this temperature for 1 h. This colorless solution was purged with Argon again at 120 °C for 30 min, then cooled down to a desired particle growth temperature at which desired amount of DT was added. Color of the solution immediately turned into a clear yellow. This solution was diluted with 17.5 mL Ar purged dry toluene. Then, 2 mL of OLA-S solution (0.2 mmol of S) was injected to the PbCl₂-PMAA-DT-OLA solution. After the desired growth time, the reaction was quenched in cold water and cold ethanol was added. The solution was centrifuged at 6000 rpm and precipitated QDs were re-suspended in chloroform, twice.

4.2.3 Colloidal PbS/CdS-OLA/PMAA QD Synthesis

PbS/CdS core/shell QDs were synthesized by the cation exchange method. As an example, Cd-oleate was prepared as described by Pietryga et al.[114]: 0.257 g (2 mmol) CdO, 3 mL (9.5 mmol) OA, and 12 mL ODE were heated to 250 °C under argon until whole CdO precursors had dissolved. After clear solution obtained, solution was cooled to 150 °C under Ar flow to remove moisture. The PbS core solution from above (section 4.2.2.) was degassed by Ar flow for ~30 min. Immediately after the temperature of the PbS solution was set to desired temperature (room temperature or 100 °C in this work), the cadmium oleate solution was added via cannula under vigorous stirring. After the desired growth time, the reaction was quenched in cold water and cold ethanol was added.

The solution was centrifuged at 6000 rpm to precipitate QDs and then re-suspended in chloroform.

4.2.4 DT ligand exchange

DT was added to chloroform suspension of PbS/CdS QDs and stirred for 15 min to replace the OLA of the coating at room temperature (OLA:DT v:v-1:4). Resulting PbS/CdS QDs (PbS/CdS-PMAA/DT) were precipitated in ethanol, removed from the supernatant by centrifugation and resuspended in chloroform. These QDs were stored in ambient conditions.

4.2.5 Annealing of PbS/CdS-OLA/PMAA QDs

Precipitated core-shell QDs annealed in vacuum oven at desired temperature and duration in solid powder form over glass substrates.

4.3 Characterization Methods

Absorbance spectra were taken in the range of 400–1200 nm by a Shimadzu 3600 PC UV-Vis-NIR spectrometer. Photoluminescence spectra were recorded by a homemade system consisting of a DPSS laser source working at 532 nm, a monochromator (1/8 Newport Cornerstone 130) and a silicon detector (Thorlabs PDF10A, 1.4×10^{-15} W/Hz^{1/2}). Long-pass filter is used that had a transmission of 90% from 550 to 1100 nm.

4.4 Result and Discussion

4.4.1 Influence of PMAA coating on Emission of PbS-OLA QD

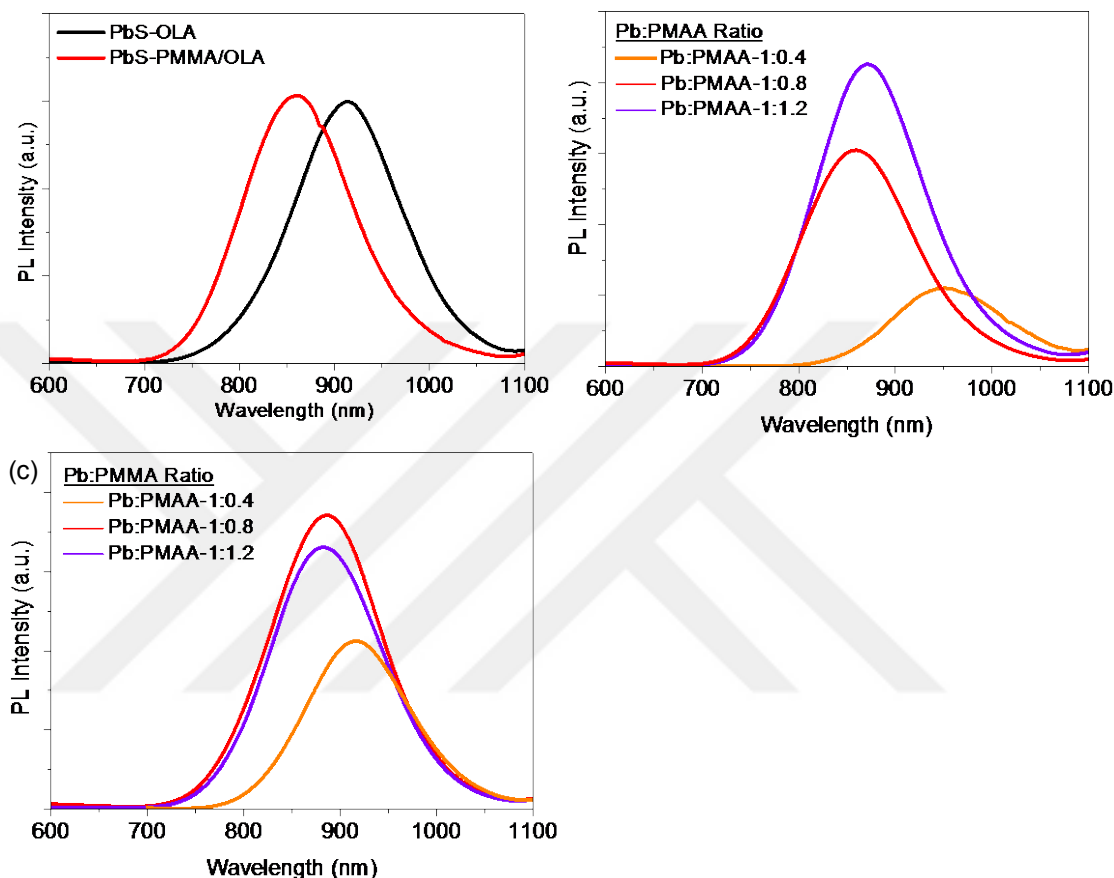


Figure 4. 1 (a) Photoluminescence spectra of PbS produced with and without PMAA as a coating component in the method detailed in Chapter 2. Pb:S:OLA=1:0.2:15, reaction temp=80 °C. Photoluminescence spectra of different PbS synthesized at different Pb:PMAA ratios under identical conditions and allowed to grow (b) 1 min. and (c) 10 min. Mn PMAA=131500 g/mol λ_{exc} = 532 nm.

To understand influence of PMAA on the optical properties of PbS QD, PbS QDs were prepared with and without PMAA under same conditions (in terms of reaction duration, temperature, stoichiometry (Pb:S:OLA:DT ratio)) following the method described in Chapter 2. For simplicity in naming different QDs, although the synthesis produce a coating comprised of OLA, DT with or without PMAA, QDs with mixed coating of DT and OLA will be mentioned as only OLA, and QDs with mixed coating of DT-OLA-PMAA will be mentioned as PMAA/OLA. Interestingly, there is no critical change in the emission intensity of PbS with either coating when they were synthesized at 80 °C for 1 min and if PbS-PMAA/OLA was prepared with Pb:PMAA ratio of 1:0.4 (mol:mol) (Figure 4. 1). However, PbS-OLA had an emission maxima at 913 nm, but PbS-PMAA/OLA had emission maxima at 859 nm, indicating a 54 nm blue shift. This shift equals to roughly ~0.15 nm size difference according to (Eq. 1. 5). Organic fatty acids (ligands), such as oleic acid, reduce particle growth by reduced mass-transfer. Usually, as the amount of the ligand increases, the particle size decrease. Heavier ligands, such as polymers, would have smaller diffusion rate, hence limiting growth further. Besides, PMAA complexes Pb^{+2} ions in solution, so each polymer chain may be also considered as a nanoreactor. As the amount of PMAA increased, there will be less Pb^{+2} ions per polymer chain. If these PMAA/ Pb^{+2} complexes are considered like nucleation sites, smaller particles will be produced at smaller Pb:PMAA ratio. Figure 4. 1b-c shows the difference in luminescence of QDs, produced in 1 and 10 min reactions, respectively, using different Pb:PMAA ratios. With the increasing amount of PMAA in the coating composition keeping the Pb concentration constant, produced PbS QDs emit at shorter

wavelengths. However, the difference between Pb:PMAA ratios of 1:0.8 and 1:1.2 is very low but their peak position and emission intensity is significantly different than Pb:PMAA-1:0.4 ratio. Difference between the former two is 12 nm but with the latter is 5 nm. This indicates that, emission/size tuning with PMAA amount beyond Pb:PMAA ratio of 1:0.8 is not possible. When the emission intensities of these QDs were compared, significant enhancement with decreasing Pb:PMAA ratio was obvious. Emission intensity increased roughly 3-fold and 4-fold, respectively, at the Pb:PMAA ratio of 1:0.8 and 1:1.2, relative to the emission of PbS QDs produced at Pb:PMAA-1:0.4 ratio, in 1-min reaction (Figure 4. 1b). QDs let grow for 10 min. under same conditions, showed the same trend with less difference between the two small Pb:PMAA ratios (Figure 4.1c). This indicates that, there is an optimum Pb:PMAA ratio that provides the best possible surface passivation-size control. More –COOH along with smaller crystal size may bring about a better surface passivation.

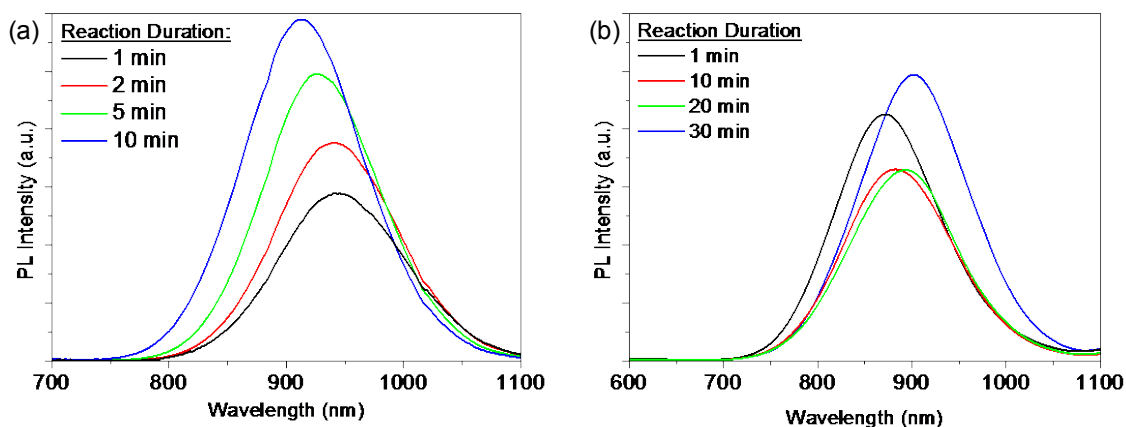


Figure 4. 2 Photoluminescence spectra of PbS-PMAA/OLA QDs produced with different Pb:PMAA ratios (a) 1:0.4, (b) 1:1.2, collected at different time points of crystal growth.

Particle growth mechanism explained with Ostwald ripening for PbS QDs in many studies.[43, 75, 81, 86] In short, smaller particles dissolve and join to bigger particles as reaction continues to reduce their surface energy. As a result of Ostwald ripening, redshift will occur in the emission wavelength. Few studies reported blue shift during reactions which is a result of digestive ripening.[135-139] Digestive ripening has been mostly reported for metallic particles[136] and there are at least one report on ZnO[135] and CdX/ZnS.[137] Although not clearly understood, it is driven by strong ligand-metal interaction, breaking apart the particles and producing smaller ones so that more ligand can be bound on the surface.[138] This usually happens when small particles attain a high surface charge which prevents coalescence or agglomeration.[135, 139] Figure 4.2a shows a blue shift in the emission peak of PbS prepared at Pb:PMAA ratios of 1:0.4 with an increasing intensity within the 30 min growth period. Considering that PMAA has –COOH groups and it is impossible to have all of these groups on the crystal surface, PbS QDs with PMAA in coating would have some negative charge on the surface. It may be possible that strong interaction of Pb with –COOH would also enhance dissolution of surface Pb ions, and hence achieve a thermodynamically feasible state to enhance digestive ripening.[135] Increasing emission intensity may be due to the removal of defects originating from ad-atoms during the digestive ripening. However, at lower ratios of Pb:PMAA (1:1.2), such effect has been lost. This may be due to better surface stabilization resulting in Ostwald ripening (Figure 4. 2b).

4.4.2 Influence of DT addition to synthesis of PbS-PMAA/OLA QD

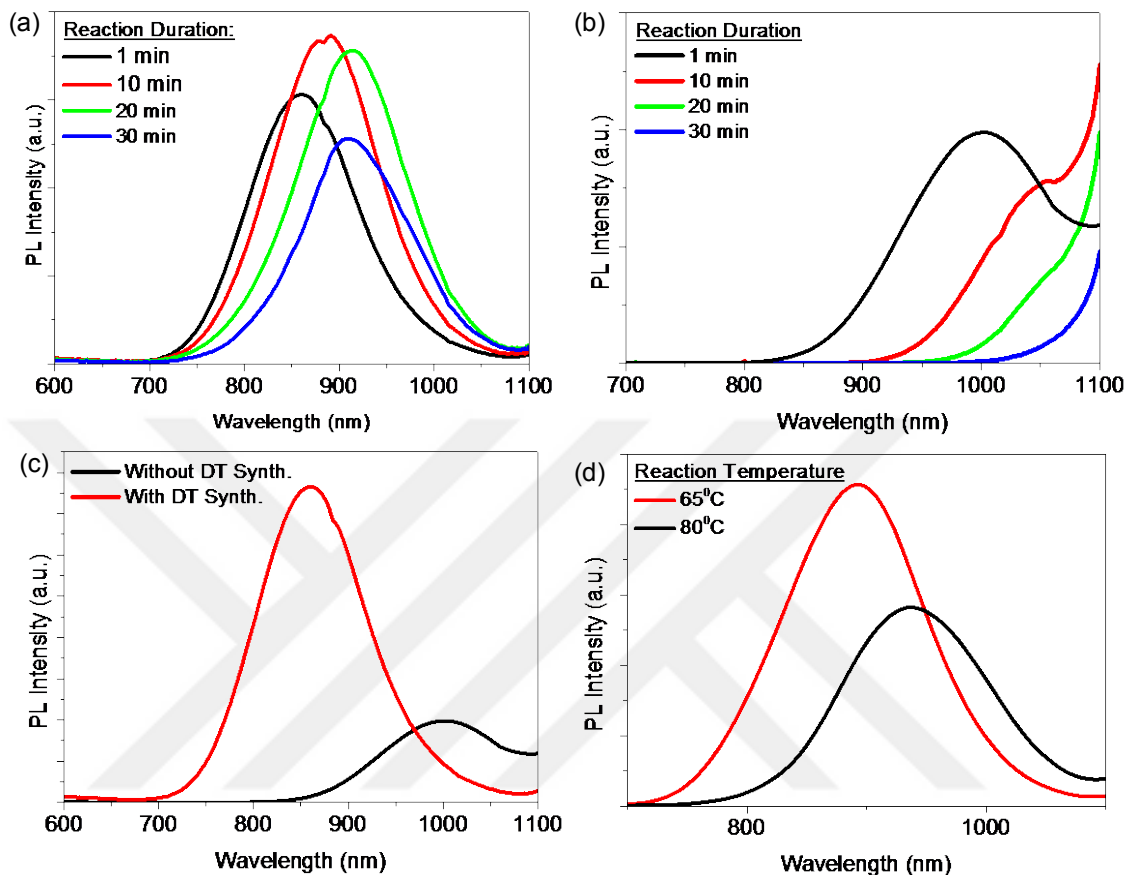


Figure 4. 3 Photoluminescence spectra of PbS-PMAA/OLA QDs synthesized with the method detailed in Chapter 2 (a) with 1 mL DT and (b) without DT in 30 min. synthesis, (c) in 1 min. synthesis comparison, (d) with 0.5 mL DT at different temperatures.

In chapter 2, benefits of DT addition during the synthesis of PbS was explained lengthy. DT binds to surface via Pb-S bonds and provide surface passivation, hence dramatically enhances the emission intensity. Also by increasing the solubility of elemental S, reduces the necessary reaction temperature, hence allows production of small PbS crystals. In order to understand the necessity of DT in PMAA containing reactions, PS-PMAA/OLA

has been synthesized with and without DT addition. Figure 4. 3 shows the difference of PbS produced with the Pb:S:OLA:PMAA-1:0.2:15:0.8 ratio at 80 °C with 1 mL DT and without DT. Figure 4. 3a-b shows that all particles with DT sampled within the 30 min period have a luminescence maxima between 850-950 nm, but those produced without DT were larger crystals with emission maxima mostly above 1100 nm after the first minute sample. These indicate that, despite of the PMAA, there is still a critical need to DT in the synthesis to produce ultra-small PbS with emission maxima below 1000 nm. Also, PbS without DT grows faster, which is due to less strong surface binding of -COOH and OLA with respect to thiol. Figure 4. 3c also clearly shows that, in case of PMAA/OLA coating, DT is not only needed to reduce the size but also to improve the emission intensity. Without DT addition PbS-PMAA/OLA produced under such conditions have an emission maxima at 1002 nm. But, DT addition caused a 152 nm blue shift with roughly 3.5 times stronger emission intensity. Also, presence of DT improves the solubility of S, hence the reaction temperature could be reduced to 65 °C (below this temperature reaction became gel-like viscous, which prevent homogenous reaction) to reduce the size further. QDs with emission maxima at 894 nm and 936 nm were obtained at 65 and 80 °C, respectively (Figure 4.3d). Figure 4. 4 shows the effect of different amounts of DT addition to PbS-OLA/PMAA QD synthesis. Going from 0.5 mL to 1 mL DT, a slight blue shift along with a 100% enhancement in the intensity of emission peak was observed but any further increase in the DT amount caused a slight red shift with decreasing intensity. 1.0 ml of DT addition came out as the optimum amount for best outcome.

Data provided in section 4.4.1, indicated that PMAA addition to PbS QD synthesis provides better surface passivation and reduce crystal size. Data provided here indicates that presence of DT is absolutely a must to have ultrasmall size and strong emission. So, combination of the two is the best approach to achieve strongly luminescent ultrasmall and colloiddally stable PbS QDs.

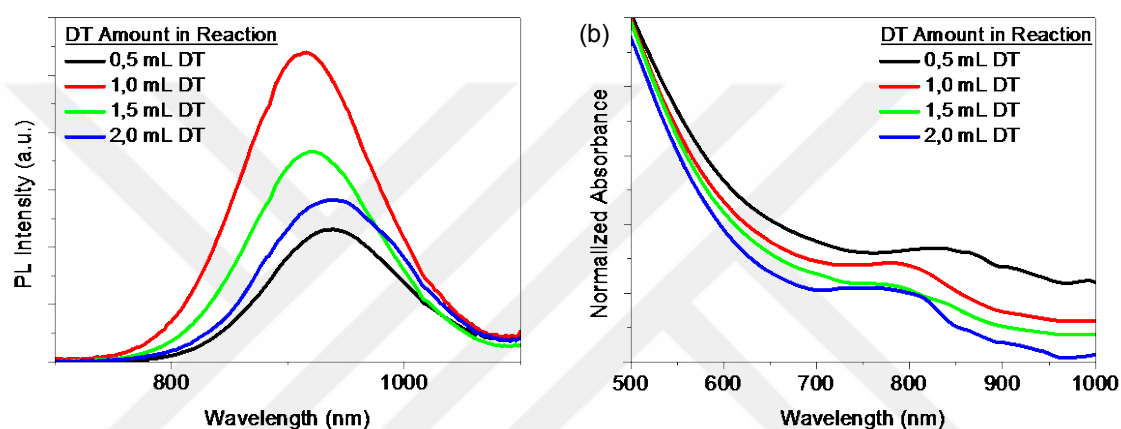


Figure 4. 4 (a) Photoluminescence and (b) absorbance spectra of PbS prepared with PMAA-DT-OLA at different DT amounts at 65 °C.

4.4.3 Influence of PMAA Molecule Weight on the Luminescent Properties of PbS QDs

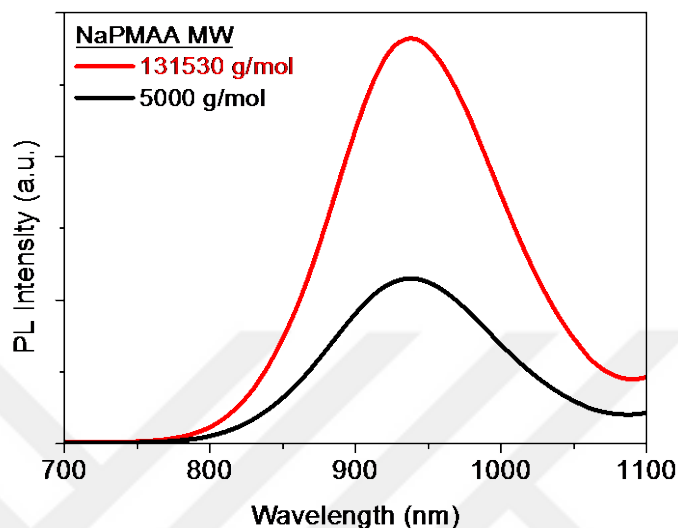


Figure 4. 5 Photoluminescence spectra of PL comparison of PbS-PMAA/OLA QDs prepared with PMAA of molecular weights.

PMAA was nucleation sites to grow nanocrystals and increased amount of PMAA provides smaller nanocrystals due to less precursor for each polymer chain. More interesting, longer polymer chain means increased number of repetitive carboxylic acid groups, these passivate QD surface. So, we tried to change molecular weight to understand effect of polymer on passivation of QD. We have two different molecular weight for PMAA polymer, also we compare small chain with longer chain. We used same mole ratio of Pb:S:OLA:PMAA, which is 1:0.2:15:0.8, for both reactions. This means, when higher molecular weight polymer was used, more -COOH was introduced. As a result, significant difference in the emission peak position between the two QDs, but 2.5 times stronger emission intensity was observed with high molecular weight polymer

(Figure 4. 5). This observation may have couple of indications: (1) at this Pb:PMAA ratio, crystal size is not affected further by the PMAA chain length; (2) increased amount of carboxylic acid units provide better surface passivation, due to freedom of mobility at distant ends of the polymer chain. Hence, it seems like molecular weight of the polymer at this amount didn't play a role on the crystal size, but played a significant role on surface passivation.

4.4.4 Synthesis of PbS/CdS QDs from PbS-PMAA/OLA

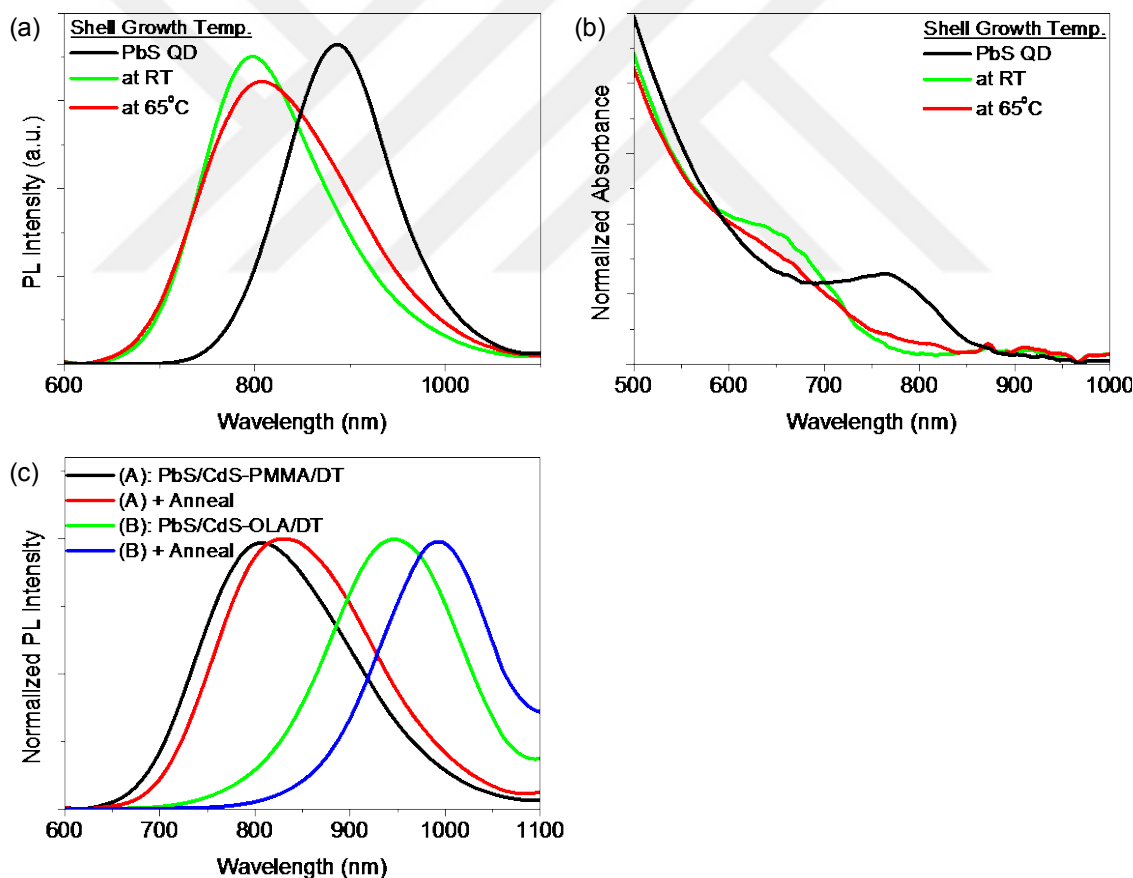


Figure 4. 6 (a) Photoluminescence, (b) Absorbance spectra of PbS/CdS-PMAA/OLA QDs prepared via cation exchange at RT and 65°C at identical stoichiometry and time,

(c) Comparison of the emission peak before and after thermal annealing of PbS-PMAA/OLA (Curve A) and PbS/CdS-OLA/DT (Curve B) for one hour.

In chapter 2, CdS shell growth on PbS cores via room temperature cation exchange process (RTCE) was shown as a successful method to improve stability and luminescence efficiency of PbS and discussed in length.

Here, CE was applied to PbS QDs with PMAA in its coating mixture and its influence of the optical and colloidal studies were investigated. In this case both RT and 65 °C was applied for cation exchange step. As seen in the PL and absorbance spectra of the particles in Figure 4. 6a-b a blue shift in the same magnitude at both temperatures were observed, confirming the shell formation. In case of PbS with no PMAA in the coating, about 100 nm blue shift was observed with RTCE, but it was increasing with time at higher temperatures. When PbS QDs with PMAA in the coating composition was used, such sensitivity to temperature seems to be reduced significantly and 80 nm blue shift was observed. Similarly, with the results reported in Chapter 2, shell growth provided narrower FWHM, this time at RT process. At higher temperature, dispersity increased slightly. Different from the PbS-OLA/DT, interestingly, shell growth process did not increase the emission intensity of PbS-PMAA/OLA. This result supports the previous suggestion about better surface passivation and stabilization by deposition of PMAA as a part of the coating. Since the surface quality of PbS-PMAA/OLA is relatively good, shell growth process does not provide additional passivation or removal of major surface defects. This is actually in agreement with thinner shell of CdS indicated by smaller blue

shift in the absorbance and emission peak. As a result, PbS/CdS-PMAA/OLA QDs emitting strongly at 790 nm was achieved. This is smallest particle (2.28 nm) reported in literature obtained via Cademartiri's synthesis route (reported smallest particle has first excitonic peak at 950 nm (3.70 nm particle size)[133]).

To increase the crystallinity of core-shell QDs, annealing at 100 °C was performed. Annealing resulted in a red shift in the emission peak of the polymer coated particles similar to those with no polymer in the coating. Yet, the previous one had 24 nm but the later had 50 nm red shift, indicating better stability via PMAA (Figure 4. 6c).

4.4.5 DT Ligand Exchange

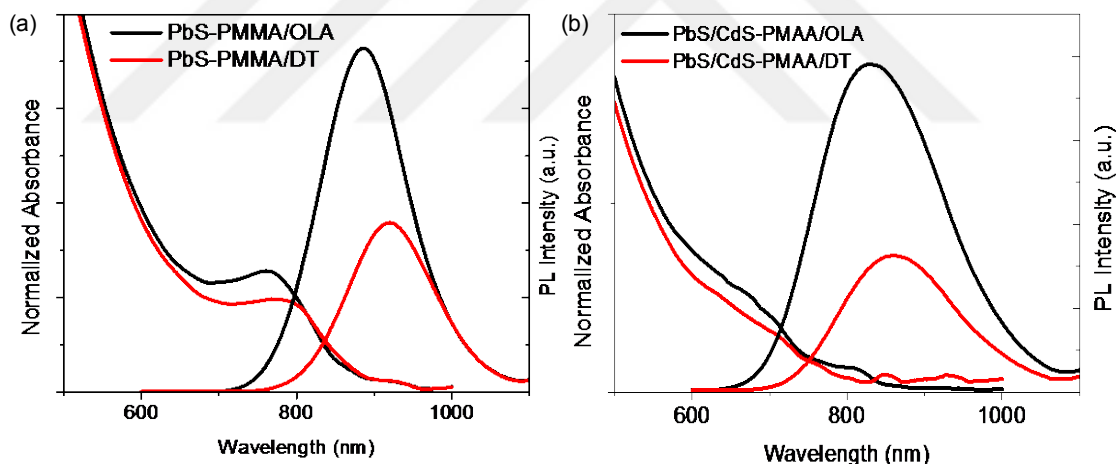


Figure 4. 7 PL and absorbance spectra of (a) PbS-PMAA/OLA, (b) PbS/CdS-PMAA/OLA before and after exchange of OLA with DT in a post—synthetic process.

PMAA chains, make bonds with repetitive carboxylic units with QD surface. We assume long chains of polymer could not form bonding with every carboxylic unit due to the constraints of the chain. This leaves some surface Pb and Cd atoms unpassivated, if

the polymer is the only coating material. OLA and DT ligands are relatively small (18 and 12 hydrocarbon units respectively), so can easily diffuse to the uncoordinated sites hence provide better coverage.

In previous chapters, positive influence of DT ligand exchange process discussed in terms of better stability against photodegradation/photooxidation during long-term storage. Same strategy was evaluated for PbS and PbS/CdS coated with PMAA-DT-OLA mixture as suggested by the methods developed within this thesis work. Exchange of heavy PMAA chain which probably adsorbed to the crystal surface from multiple sites is not expected, but exchange of relatively loosely bonded OLA ligands (as shown previous chapters) is expected. DT ligand exchange usually results in a significant red shift in both emission and absorbance spectra of QDs. For an example, a 95 nm and 22 nm shift to longer wavelengths were recorded in the emission peak of PbS-OLA and PbS/CdS-OLA QDs (see previous chapters). Interestingly, such shift is much less when particles contain PMAA in the coating, resulting in only 37 nm and 20 nm red shift for PbS and PbS/CdS QDs, respectively (Figure 4. 7). This may indicate less OLA in the polymer containing coating, limited diffusion of DT to surface and already strong surface stabilization. Yet, DT exchange still resulted in reduction in the emission intensity as usual.

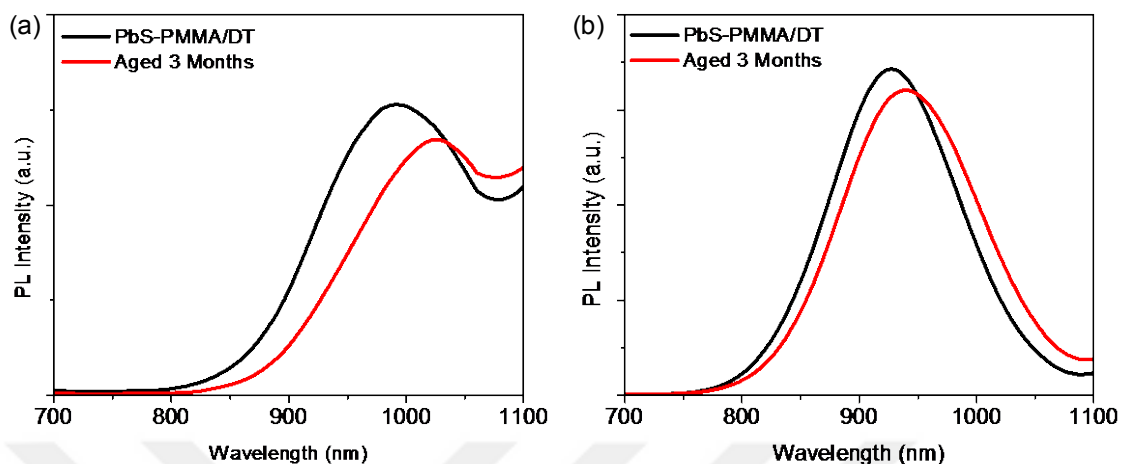


Figure 4. 8. Stability of the emission peak of DT ligand exchanges PbS-PMMA/OLA produced at Pb:PMAA ratio of (a) 1:0.4, (b) 1:0.8 in 3 months period (in CHCl_3).

On the other hand, after DT exchange, particles retained their emission strength and position as well as colloidal stability over 3 months period within acceptable range (Figure 4.8). Previously, data showed that as more $-\text{COOH}$ is introduced, better surface coverage, less aggregation and hence stronger emission was obtained. Here, when stability of DT exchanged PbS-PMMA/OLA prepared at Pb:PMAA ratio of 1:0.4 and 1:0.8 was compared, 38 nm and 11 nm red shift in 3 months, respectively, were recorded. Loss of emission intensity by 11.8% and 6.4% for Pb:PMAA ratios 1:0.4 and 1:0.8, respectively, was also detected. These prove better quality particles obtained at higher amounts of PMAA, which enhances not only the emission intensity but stability over time.

4.4.6 Stability in Petroleum Products

DT ligand exchanged PbS and PbS/CdS QDs are colloiddally stable up to years and showed enhanced optical stability in chloroform. Optical stability means minimum change in both emission wavelength and emission intensity. Stability of these QDs in 3 types of petroleum products. These QDs were added into these liquids at 100 ppm level to check the stability. This is very challenging because dilute solution of QDs undergo fast degradation due to desorption of ligands from the surface. All of the petroleum products under the investigation in this thesis work, have strong emission under 700 nm and contain chemically active additives to improve efficiency of petroleum products. These additives and harsh usage conditions of requires highly stable QDs. Type 1 petroleum product has expiration date of 1 year, so QDs that will be used that product needs at least 1 year stability. Type 2 and type 3 petroleum products have a shelf life of 1 month, so stability of QD for 1 month is enough but longer is preferable. Four different QDs were tested in these petroleum products;

- (a) PbS-DT, which is PbS produced in OLA/DT mixture and subjected to post synthetic ligand exchange (see chapter 2),
- (b) PbS/CdS-OLA, which is obtaining by CE from PbS-OLA/DT. After CE, annealing was applied to particles and they subjected to post synthetic ligand exchange (PbS/CdS-DT) (see chapter 3),
- (c) PbS-OLA/PMAA, which is produced in OLA/DT/PMAA mixture. Particles were subjected to post synthetic ligand exchange (PbS-PMAA/DT),

(d) PbS/CdS-OLA/PMAA, which is obtaining by CE from PbS-OLA/PMAA.

After CE, annealing was applied to particles and they subjected to post synthetic ligand exchange (PbS/CdS-PMAA/DT). All QDs stored in ambient conditions to create similar conditions to industrial usage.

Stability in chloroform: Long-term colloidal stability of all particles is excellent over years in chloroform, which is quite an improvement compared to particles found in the literature.

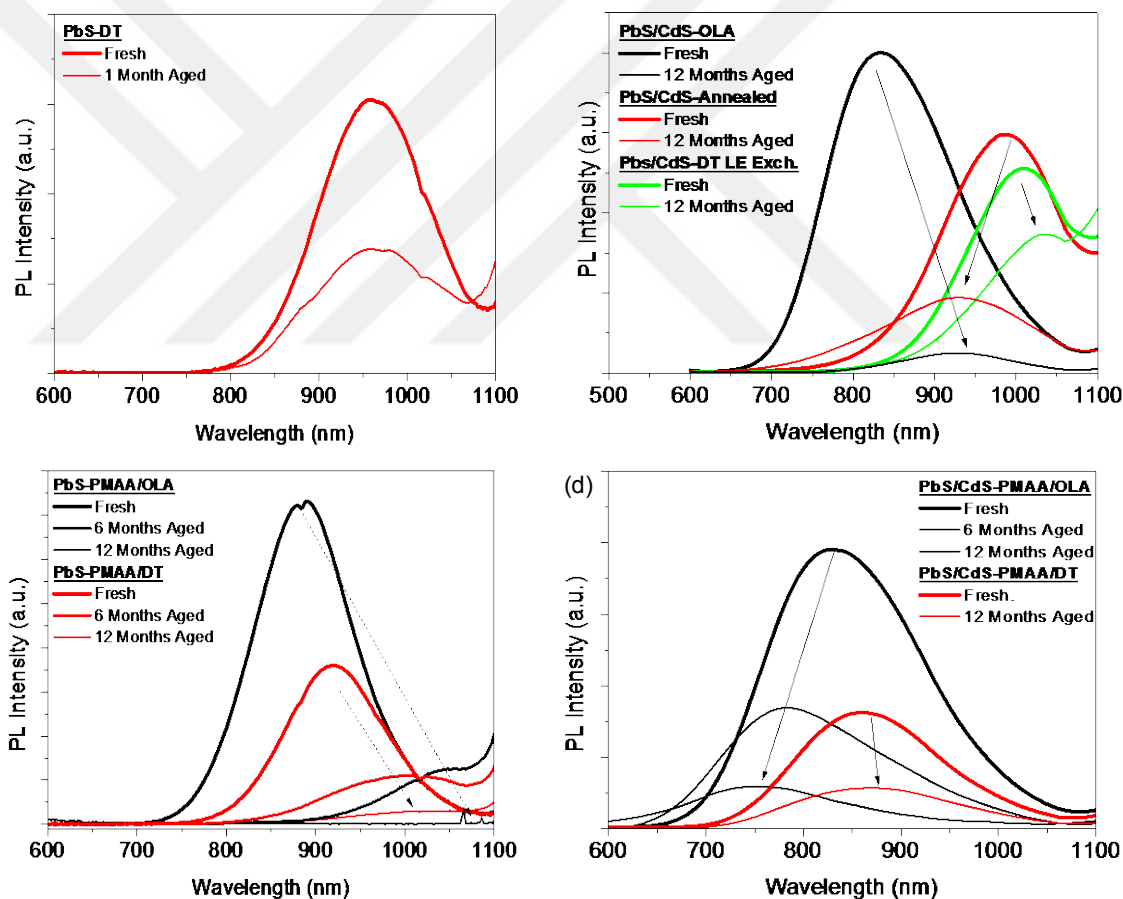


Figure 4. 9 Comparison of stability of (a) PbS-DT, (b) PbS/CdS-X, (c) PbS-PMAA/X, (d) PbS/CdS-PMAA/X (X=OLA, DT) in chloroform up to a year.

PbS-DT is the colloiddally least stable one so stability in chloroform was tested for 1 month storage. It showed a minimal spectral shift in 1 month with about 55% reduction in the emission intensity (Figure 4. 9). When optical stability is concerned, PbS/CdS provided the most favorable compositions and with PMAA coating followed by DT exchange both spectral shift and loss in intensity can be reduced compared to the other composition in 1 year. Annealed PbS/CdS QDs with DT ligand exchanged showed a minimal change in their properties: 30 nm red shift and only 31% losing the emission intensity after 1 year. In case of PbS-PMAA/OLA, large red shift with almost complete loss of emission intensity was detected after 1 year. Stability was enhanced by DT ligand exchange. PbS-PMAA/DT showed 104 nm redshift and 91% decrease in the emission intensity. In case of PbS/CdS-PMAA/X, stability of both annealed QD and QDs subjected to annealing and DT ligand exchange was studied. A 77 nm blue shift with 84% emission intensity loss was detected without DT ligand exchange. DT ligand exchange minimized the shift to 9 nm (to longer wavelengths) and resulted in 65% decrease in the emission intensity in one year (Table 4. 1).

Table 4. 1 QDs stored in chloroform

QD-TYPE	Store Duration	PL Shift	PL Intensity
PbS-DT	1 month	5 nm	-54.5%
PbS/CdS-DT	1 year	30 nm	-31%
PbS-PMAA/DT	1 year	104 nm	-91%
PbS/CdS-PMAA/DT	1 year	77 nm	-84%

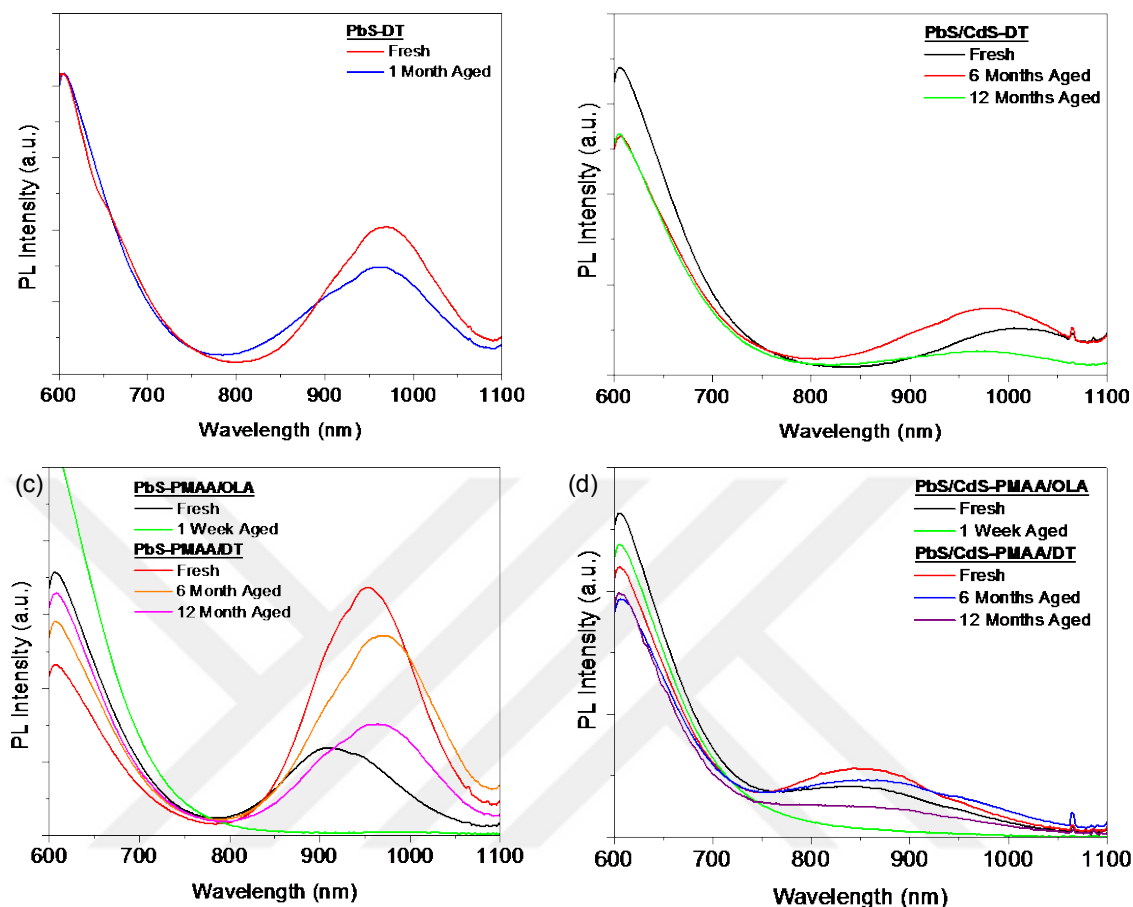


Figure 4. 10 Comparison of stability of (a) PbS-DT, (b) PbS/CdS-DT, (c) PbS-PMAA/X, (d) PbS/CdS-PMAA/X (X=OLA, DT) in petroleum product type 1 up to a year.

Stability in petroleum product type 1: None of the particles maintained their emission property without DT ligand exchange up to 1 week in the harsh condition of petroleum product type 1. In addition, strong emission of type 1 product at around 600 nm is higher than the luminescence intensity of our QDs which was added in 100ppm concentration (Figure 4.10). Type 1 product contains active phosphines to enhance efficiency of the product, but these phosphine groups may cause degradation of QD by attacking surface of QDs. PbS-DT QDs were still luminescent after 1 month, with a slight blue shift and

36% decrease in emission intensity (Figure 4. 10). No emission was detected after 6 months. Interestingly, emission intensity increased with slight blue shift in case of DT exchanged PbS/CdS QD in 6 months but a 44 nm blue shift and 51% emission intensity decrease was recorded after one year. PMAA coated QDs showed better stability in type 1 product. Interestingly, unlike QDs without PMAA, there was no blue shift (oxidation) observed with PMAA coated QDs. PbS-PMAA/DT displayed minimal amount of red shift (10 nm) and 55% emission intensity loss in one year. PbS/CdS-PMAA/OLA, which is the composition before DT ligand exchange, did not show significant shift but again 55% emission intensity decrease (Table 4. 2). So, it seems like multidentate attachment of the PMAA on particle surface seems to enhance stability even without DT. Core/shell structure does not provide a dramatic improvement, yet DT ligand exchange is essential.

Table 4. 2 QDs stored in type 1 petroleum product

QD-TYPE	Store Duration	PL Shift	PL Intensity
PbS-DT	1 month	5 nm	-36%
PbS/CdS-DT	1 year	44 nm	-51%
PbS-PMAA/DT	1 year	10 nm	-55%
PbS/CdS-PMAA/DT	1 year	no	-55%

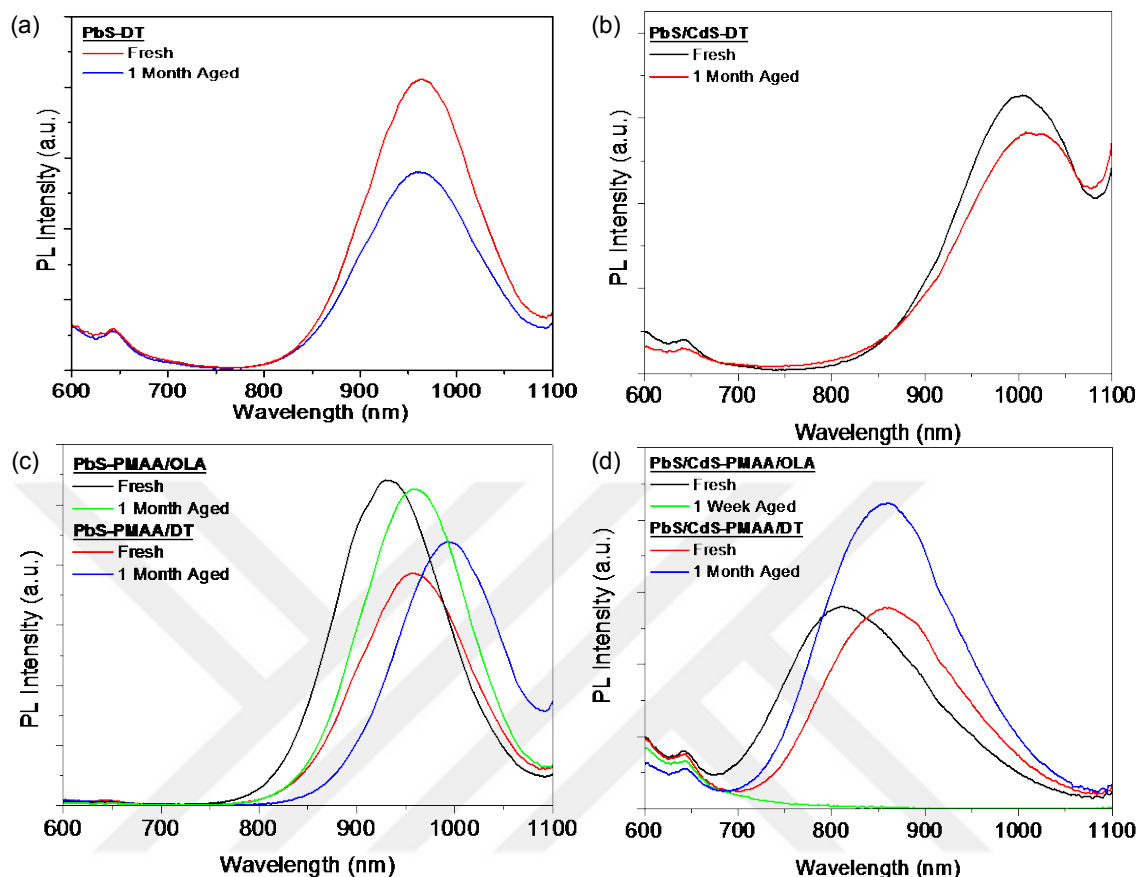


Figure 4. 11 Comparison of stability of (a) PbS-DT, (b) PbS/CdS-DT, (c) PbS-PMAA/X, (d) PbS/CdS-PMAA/X (X=OLA, DT) in type 2 petroleum product up to a month.

Stability in petroleum product type 2: Shelf life of product 2 is maximum 1 month, hence stability up to a month is satisfactory in this product. These QDs show better stability in petroleum product 2 than other petroleum products. Only 3 nm blue shift with 23% loss in the emission intensity and 14 nm red shift with 13.3% loss in the emission intensity of PbS-DT and PbS/CdS-DT after 1 month, respectively, was recorded in type 2 petroleum product (Figure 4. 11). The week emission at around 650 nm is coming from the petroleum product. PbS-PMAA/OLA QD showed a minimal spectral shift (31 nm red

shift) with almost no loss in emission intensity (3 %) after 1 month, which is an important evidence of better surface passivation with PMAA ligands, and positive impact of such on stability in product type 2. This is an important achievement. When it is subjected to ligand exchange, PbS-PMAA/DT, 12% emission intensity increase with 16 nm red shift was observed. Interestingly, CdS shell on such particles, disturbed such stability or CdS is more vulnerable to the constituents of type 2 product. Emission of PbS/CdS-PMAA/OLA disappeared after 1 week, but emission intensity was enhanced (34.3%) after 1 month with 5 nm blue spectral shift (Figure 4. 11d). All changes in the emission properties are summarized in Table 4. 3.

Table 4. 3 QDs stored in type 2 petroleum product			
QD-TYPE	Store Duration	PL Shift	PL Intensity
PbS-DT	1 month	3 nm	-23%
PbS/CdS-DT	1 month	14 nm	-13.3%
PbS-PMAA/DT	1 month	16 nm	12%
PbS/CdS-PMAA/DT	1 month	5 nm	34.3%

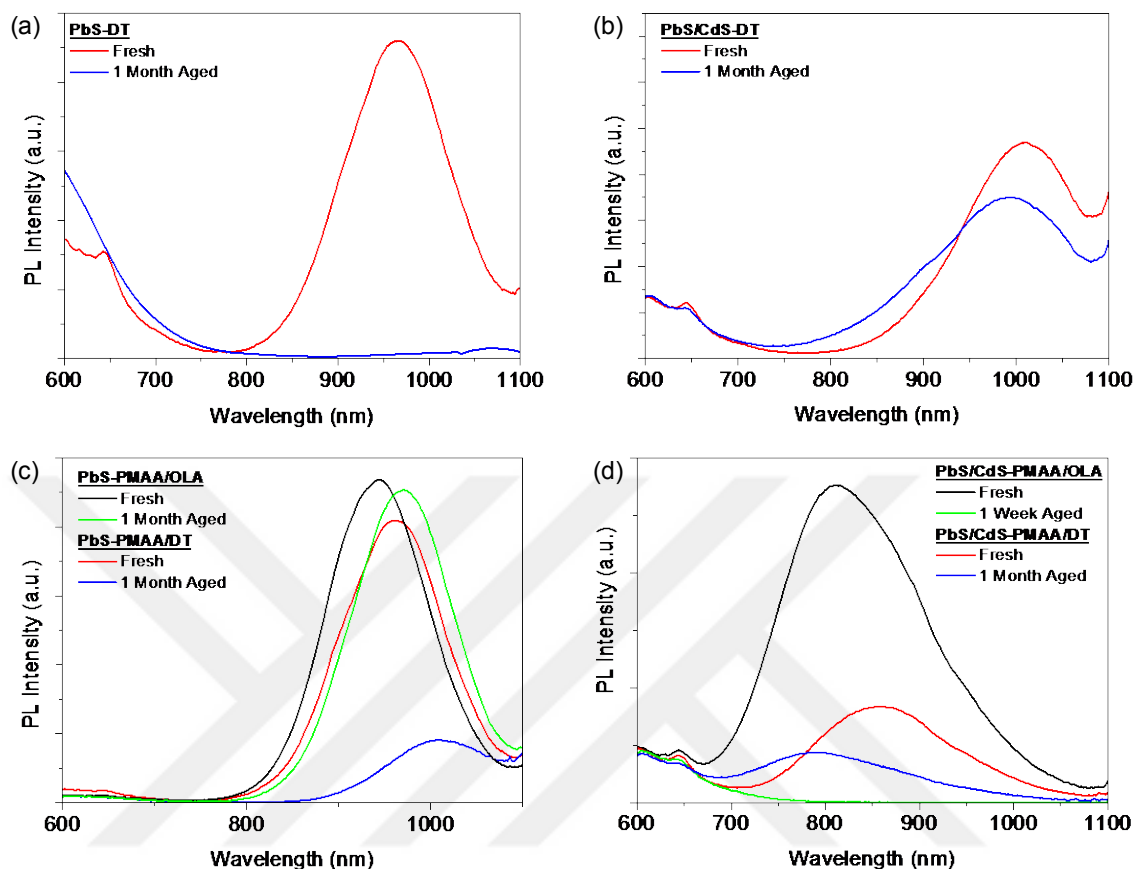


Figure 4. 12 Comparison of stability of (a) PbS-DT, (b) PbS/CdS-DT, (c) PbS-PMAA/X, (d) PbS/CdS-PMAA/X (X=OLA, DT) in petroleum product type 3 up to a month.

Stability in petroleum product type 3: This product has a shelf life shorter than 1 month as well so stability of QD in type 2 product up to a month was tested. These QDs showed the worst stability in petroleum product type 3 (Figure 4. 12). Without DT ligand exchange, QDs were not stable in petroleum product type 3 after one week, except PMAA coated core PbS-PMAA/OLA QD. PMAA seems to be critical to stability in petroleum product type 3. Type 3 product has emission at around 650 nm wavelength, as well. In case of PbS-DT, emission diminished almost completely with strong redshift in 1 month.

PbS/CdS-DT experienced a 25.3% loss in the emission intensity with 17 nm blue shift. PMAA coated PbS-OLA is the only stable QD without DT ligand exchange in petroleum product type 3. PL emission intensity reduced by 3.2% and 29 nm red shift was observed in 1 month. In case of PbS-PMAA/DT, we have seen 49 nm red shift and 77.6% emission intensity loss. Emission of OLA/PMAA coated core-shell QD diminished after one week. For PbS/CdS-PMAA/DT, we have seen 75 nm blue shift with 48.9% emission intensity decrease in one month. Interestingly, we have observed a blue shift for both core-shell QDs, while just PbS showed a red shift. Additives in type 3 product may cause oxidation of the CdS shell more than PbS. In addition to that, OLA/PMAA ligand for core PbS QD provides better stability than DT/PMAA (Table 4. 4). This either related to defects generated during ligand exchange or reaction of thiol with the additives of the type 3 product.

In overall, PMAA coating with DT ligand exchange provide better stability in type 1 and type 2 petroleum products, as we presumed. PMAA covered QDs show the minimal spectral shift, which is required for our industrial application. CdS shell layer provides better photodegradation resistance almost in all solution.

Table 4. 4 QDs stored in type 3 petroleum product

QD-TYPE	Store Duration	PL Shift	PL Intensity
PbS-DT	1 month	105 nm	-98%
PbS/CdS-DT	1 month	17 nm	-25.3%
PbS-PMAA/OLA	1 month	29 nm	-3.2%
PbS-PMAA/DT	1 month	49 nm	-77.6%
PbS/CdS-PMAA/DT	1 month	75 nm	-48.9%

4.5 Conclusion

In this chapter, PMAA coated colloidal PbS and core-shell PbS/CdS NIR QDs were synthesized successfully. Annealing and DT ligand exchange processes were performed to obtained QDs with improved stability.

Addition of PMAA to the PbS-OLA synthesis affected the nucleation and growth. Higher amount of PMAA resulted in smaller particle size. Investigation of Pb:PMAA ratio on luminescence properties indicated the Pb:PMAA -1:1.2 ratio as the optimum for appropriate surface passivation, due to higher amount of carboxyl units. This ratio provided 4-fold stronger emission intensity compared to Pb:PMAA-1:0.4, with smaller particle size.

Influence of DT addition on optical properties of PbS-OLA/PMAA during the reaction and exchange of OLA with DT after the synthesis was studied as, well. DT addition before nucleation, increased solubility of the precursors and enabled ultrasmall PbS QDs

with brighter emission. DT addition to PMAA covered particles provides 152 nm blue shift with roughly 3.5-fold intensity increase. So, PMAA/DT combined effect provides better surface passivation and even smaller crystals relatively PbS-OLA/DT (see chapter 1). In addition, improved solubility allows reactions at low temperatures, e.g. 65 °C, which help production of smaller crystals. Amount of DT is critical to quality as well, and it was optimized as 1.0 mL DT in 7 mL OLA to provide smallest particles with highest intensity.

Influence of the molecular weight of PMAA on the luminescence of PbS-OLA/PMAA was studied, as well. Studies performed with PMAA of 5000 and 131500 g/mol, revealed no significant effect on the size but 2.5-fold better emission intensity with the higher molecular weight one, possibly due to better surface passivation and stabilization.

PbS/CdS-OLA/PMAA QDs obtained by cation exchange method successfully. Produced particles are 2.28 nm in diameter, which is one of the smallest in literature. Due to no change in emission intensity of QD after shell growth process, we concluded that PMAA ligands passivates surface of QD well. Comparison of annealing of PbS/CdS-OLA and PbS/CdS-OLA/PMAA QDs confirmed better passivation with PMAA with significantly reduced red shift in the emission peak.

DT ligand exchange performed on PMAA coated core and core-shell QDs improved stability further. Little red shift during ligand exchange indicates better passivation of PMAA relative to OLA. Core-shell QDs experienced even smaller red shift. QDs with different ratio Pb:PMAA (1:0.4-1:0.8) stored in chloroform for three months after DT

ligand exchange. We have seen QDs with higher PMAA ligands, experienced much less emission intensity drop and wavelength shift.

Stability of QDs (PbS-DT, PbS/CdS-X, PbS-PMAA/X and PbS/CdS-PMAA/X (X=OLA, DT)) were analyzed by storing them in chloroform and three different petroleum products up to 1 year. We compared stability of different QDs in terms of emission intensity change and emission shift overtime. Stability results show that, (i) PMAA coating with DT ligand exchange provide better stability in type-1 and type-2 petroleum products, (ii) PMAA provides minimal spectral shift, which is required for our industrial application (iii) CdS shell layer provides better resistance to photodegradation almost in all liquids.

Highly stable and strongly luminescent PMAA coated colloidal PbS and core-shell PbS/CdS NIR QDs were synthesized for the first time in the literature. Produced QDs were smaller than those reported in the literature which can be detected with Si-detector. Emission was managed to shifted to shorter wavelengths, as short as 790 nm.

Chapter 5

5 Conclusion

Pb-chalcogenides are one of the most popular NIR QDs. There is a great amount of work in photovoltaics with PbS and some in optical imaging. Long term instability, lack of ultra-small sized PbS with emission detectable by most instruments using PMT or Si-detector, and difficult, expansive synthetic methods using toxic and oxidatively unstable precursors are major problems of PbS. If these problems can be resolved, there may be a dramatic increase in its industrial use both in PV and in luminescent tagging. The ultimate application of these QDs targeted in this thesis is optical tagging/barcode, hence optical and colloidal stability of these particles at low concentrations (100 ppm), and availability of as many QDs as possible satisfying such criteria were necessary.

This thesis described four different approaches which worked in a synergistic way to solve all these problems to meet the requirements.

The first and most important contribution of this thesis to literature is the green synthesis of multiple, ultrasmall, stable PbX QDs with improved emission intensity between 868-1015 nm (size of particles between 2.4-3.2 nm) range. In the first chapter, this new synthetic method was discussed in detail. Two major hypothesis of this method was (1) the use of strongly binding DT to the reaction mixture which provided two

advantages: solubilization of the precursors hence more homogenous reaction mixture, and better passivation of the crystal surface. The later not only contributed to size reduction but enhancement of the luminescence intensity by providing better surface passivation. Better solubilization of precursors allowed reactions at lower temperature (as low as 65 °C) which helps to slow down crystal growth and reduce the stable crystal size. (2) Diluting solution with non-coordinating toluene and vacuum drying to enhance homogeneity.

By changing the reaction parameters such as temperature, stoichiometry, concentration, DT amount, Pb:S ratio, different PbS QDs with strong emission below 1100 nm was demonstrated. The PbS with 2.4 nm diameter is the smallest one achieved with elemental S in OLA in the literature. These methods produced multiple PbSe QDs with emission below 1100 nm, as well, which is rare in the literature. Post-synthetic exchange of OLA with DT improved the optical stability tested in 3 months (only 47 nm red shift) but with initial loss in the intensity. Improved stability was attributed to strong binding of DT to surface and elimination/reduction of surface defects.

In the second chapter, to improve the optical stability of QDs further, PbS/CdS core-shell structure was suggested. A very thin CdS shell was obtained via RT CE process. CE method was performed at elevated temperatures in the literature. We achieved to perform CE process at RT for OLA and OA coated QDs, which has failed in case of OA coated PbS QDs in the literature. Surface defects and high surface/volume ratio of ultrasmall sizes of PbS QDs allow efficient CE at room temperature. RT CE has many advantages for industrial use, such as it is self-limiting and time independent. In addition, shell

passivation applied by RT CE process provides 5.8-9 fold increase (increase amount is related with surface properties of QD) in the emission intensity with roughly 100 nm blue shift in the emission maxima. So, shell growth process enables further size tunability in the range of 800-1020 nm with increased emission intensity. PL lifetime studies revealed PbS/CdS QDs have increased lifetime compared with PbS QD, which supports formation of thin CdS layer and confinement of the exciton in the core. In order to improve the crystallinity of the core/shell structure low temperature solid state annealing was performed. This method is a unique contribution of this thesis to ultrasmall PbS/CdS QD synthesis, since it does not cause a dramatic aggregation of the particles. Optimum annealing temperature was determined as 50 °C. Lastly, DT ligand exchange on PbS/CdS QDs improved stability dramatically up to 1 year. Overall, emission tunability, control of shell thickness and quality was demonstrated in a very simple and economic RT CE followed by a low temperature annealing processes which is highly applicable to industrial scale.

In the last chapter, PMAA coated, highly stable and luminescent colloidal PbS and PbS/CdS NIR QDs were synthesized following the methods developed in previous chapters. Influence of reaction parameters such as temperature, duration, Pb:PMAA ratio, amount of DT and PMAA and molecular weight of PMAA, on the optical properties were studied. Multidentate binding of PMAA in addition to OLA and DT, improved stability and reduced size further. Presence of PMAA coating did not prevent RT CE process. However, shell growth did not improve the luminescence intensity as in case of the PbS/OLA-DT. This confirms better surface passivation with PMAA and less non-

radiative coupling events. PbS/CdS QDs with emission at 790 nm were achieved. These are the smallest PbS/CdS QDs reported in the literature. In addition, both PMAA coated core and core-shell QDs showed minimal change in the emission intensity and wavelength upon DT ligand exchange.

Stability of the produced QDs (PbS-DT, PbS/CdS-X, PbS-PMAA/X and PbS/CdS-PMAA/X (X=OLA, DT)) were tested in petroleum products in the last chapter at 100 ppm level as well as in chloroform up to 1 year in ambient conditions. All of the produced QDs show great colloidal stability over 2-3 years. In general, PMAA coated QDs show better stability and combined effect of PMAA and CdS shell provides highest stability in terms of resistance to spectral shift and intensity loss.

Overall, we achieved to develop highly stable, bright, monodisperse PbS and PbS/CdS QDs with different coatings and with emission in the range of 790-1100 nm. We have developed a green, scalable and cheap synthesis route for these particles. These QDs are not as stable as desired for petroleum products but are dramatically more stable than particles used in PV and biological applications. By using thiolated polymeric ligands and other Pb salts, stability and optical properties of proposed QDs can be improved further.

5.1 Publications & Conferences

E.Durmusoglu, F. Acar, “Zero Dimensional Semiconductor Nanocrystals; Quantum Dots” at 2. NanoKon 27-28 September, Istanbul, Turkey, 2012- Oral Presentation

E. Durmusoglu, P. Dagtepe, Y. Türker and F. Acar, “Room Temperature Synthesis and Characterization of Stable, Highly Luminescent PbS/CdS Core-Shell Quantum Dots with

Emission Below 1100 nm” at Nanotech France 2015 International Conference & Exhibition June 15 – 17 June, Paris, France, 2015- Oral Presentation

E. Durmusoglu, P. Dagtepe, Y. Türker and F. Acar, “CdS Shell Growth upon PbS QDs at Room Temperature via Cation Exchange Process”, at 9th International Summer Schools "N&N, OE & Nanomedicine" (ISSON15) 4-11 July held in Thessaloniki, Greece, 2015- Poster Presentation

E. Durmusoglu, P. Dagtepe, Y. Türker and F. Acar, “Room Temperature Synthesis and Characterization of Stable, Highly Luminescent PbS/CdS Core-Shell Quantum Dots with Emission Below 1100 nm” at 12th International Conference on Nanosciences & Nanotechnologies (NN15) 7-10 July held in Thessaloniki, Greece, 2015-Oral Presentation

E.Durmusoglu, F. Acar, “Investigation of the Influence of Heat-Treatment on the Properties of Colloidal PbS/CdS Quantum Dots” at E-MRS 2016 Spring Meeting 2-6 May held in Lille, France, 2016- Oral Presentation

E.Durmusoglu, F. Acar, “Enhancing Optical Properties of PbS@CdS QDs by Room Temperature Cation Exchange Process” at 1. Science Fair in Koc University 16 June held in Istanbul, Turkey, 2016- Poster Presentation

E.Durmusoglu, “Fundamentals of Nanoscience” at Interdisciplinary Colloquium in Geneva University 20-24 June held in Geneva, Swiss, 2016- Oral Presentation

Duman, F. D.; Khodadust, R.; Durmusoglu, E. G.; Yagci, M. B.; Acar, H. Y. Impact of reaction variables and PEI/l-cysteine ratio on the optical properties and cytocompatibility of cationic Ag₂S quantum dots as NIR bio-imaging probes. *RSC Adv.* 2016, 6, 77644-77654

Durmusoglu, E. G.; Turker, Y.; Acar, H. Y. An Improved Synthesis of Highly Luminescent and Stable Ultrasmall PbS and PbSe Quantum Dots (under review)

Unal, O.; Khodadust, R.; Durmusoglu, E.G.; Erdem, E.; YAGCI, M.; Yurtsever, E.; Acar, H. Y. Strongly Blue Luminescing bPEI-SPION as a New Theranostic Nanoparticle for Gene Delivery with Dual Imaging Modality (under review)

Durmusoglu, E. G.; Acar, H. Y. Influence of Heat-Treatment on the Properties of Colloidal PbS/CdS Quantum Dots (in preparation)



A Appendix

A. Calculation of Particle Size for PbS QDs

Size of these QDs were calculated by following equation which is developed by Cademartiri et al. using different size PbS QDs;

$$D(nm) = 0.85 + \sqrt{0.7225 + (1243/\lambda(nm) - 0.41) * 3.84} / (1243/\lambda(nm) - 0.41) \quad [35]$$

The following formulas used to calculate valance band energy (E_{vb}), conduction band energy (E_{cb}) and Band Gap (E_0);

$$VB = -4.76 - 0.64 * D^{(-0.9)} \quad [55]$$

$$CB = -4.35 + 5.12 * C2^{(-1.27)} \quad [55]$$

$$E_0 (Ev) = E_{cb}(Ev) - E_{vb}(Ev)$$

Table A.1 Particle size of PbS QDs with respect to absorbance maximum

Abs. Max (nm)	D (nm)	VB (eV)	CB (eV)	Band Gap (eV)	Abs. Max (nm)	D (nm)	VB (eV)	CB (eV)	Band Gap (eV)
600	2,12	-5,09	-2,37	2,71	801	2,72	-5,02	-2,92	2,10
601	2,12	-5,09	-2,38	2,71	802	2,73	-5,02	-2,92	2,10
602	2,12	-5,09	-2,38	2,71	803	2,73	-5,02	-2,92	2,10
603	2,12	-5,08	-2,38	2,70	804	2,73	-5,02	-2,92	2,10
604	2,13	-5,08	-2,39	2,70	805	2,74	-5,02	-2,92	2,09
605	2,13	-5,08	-2,39	2,69	806	2,74	-5,02	-2,93	2,09
606	2,13	-5,08	-2,39	2,69	807	2,74	-5,02	-2,93	2,09

607	2,14	-5,08	-2,40	2,69	808	2,75	-5,02	-2,93	2,09
608	2,14	-5,08	-2,40	2,68	809	2,75	-5,02	-2,93	2,08
609	2,14	-5,08	-2,40	2,68	810	2,75	-5,02	-2,93	2,08
610	2,14	-5,08	-2,41	2,68	811	2,76	-5,02	-2,94	2,08
611	2,15	-5,08	-2,41	2,67	812	2,76	-5,02	-2,94	2,08
612	2,15	-5,08	-2,41	2,67	813	2,76	-5,02	-2,94	2,08
613	2,15	-5,08	-2,42	2,66	814	2,77	-5,02	-2,94	2,07
614	2,16	-5,08	-2,42	2,66	815	2,77	-5,02	-2,95	2,07
615	2,16	-5,08	-2,42	2,66	816	2,77	-5,02	-2,95	2,07
616	2,16	-5,08	-2,43	2,65	817	2,77	-5,02	-2,95	2,07
617	2,16	-5,08	-2,43	2,65	818	2,78	-5,02	-2,95	2,06
618	2,17	-5,08	-2,43	2,65	819	2,78	-5,01	-2,95	2,06
619	2,17	-5,08	-2,44	2,64	820	2,78	-5,01	-2,96	2,06
620	2,17	-5,08	-2,44	2,64	821	2,79	-5,01	-2,96	2,06
621	2,18	-5,08	-2,44	2,63	822	2,79	-5,01	-2,96	2,05
622	2,18	-5,08	-2,45	2,63	823	2,79	-5,01	-2,96	2,05
623	2,18	-5,08	-2,45	2,63	824	2,80	-5,01	-2,96	2,05
624	2,19	-5,08	-2,45	2,62	825	2,80	-5,01	-2,97	2,05
625	2,19	-5,08	-2,46	2,62	826	2,80	-5,01	-2,97	2,05
626	2,19	-5,08	-2,46	2,62	827	2,81	-5,01	-2,97	2,04
627	2,19	-5,08	-2,46	2,61	828	2,81	-5,01	-2,97	2,04
628	2,20	-5,08	-2,47	2,61	829	2,81	-5,01	-2,97	2,04
629	2,20	-5,07	-2,47	2,61	830	2,82	-5,01	-2,98	2,04
630	2,20	-5,07	-2,47	2,60	831	2,82	-5,01	-2,98	2,03
631	2,21	-5,07	-2,48	2,60	832	2,82	-5,01	-2,98	2,03
632	2,21	-5,07	-2,48	2,60	833	2,83	-5,01	-2,98	2,03
633	2,21	-5,07	-2,48	2,59	834	2,83	-5,01	-2,98	2,03
634	2,21	-5,07	-2,48	2,59	835	2,83	-5,01	-2,99	2,03
635	2,22	-5,07	-2,49	2,58	836	2,84	-5,01	-2,99	2,02
636	2,22	-5,07	-2,49	2,58	837	2,84	-5,01	-2,99	2,02
637	2,22	-5,07	-2,49	2,58	838	2,84	-5,01	-2,99	2,02
638	2,23	-5,07	-2,50	2,57	839	2,85	-5,01	-2,99	2,02
639	2,23	-5,07	-2,50	2,57	840	2,85	-5,01	-3,00	2,01
640	2,23	-5,07	-2,50	2,57	841	2,85	-5,01	-3,00	2,01
641	2,24	-5,07	-2,51	2,56	842	2,86	-5,01	-3,00	2,01
642	2,24	-5,07	-2,51	2,56	843	2,86	-5,01	-3,00	2,01
643	2,24	-5,07	-2,51	2,56	844	2,86	-5,01	-3,00	2,01
644	2,24	-5,07	-2,52	2,55	845	2,87	-5,01	-3,01	2,00

645	2,25	-5,07	-2,52	2,55	846	2,87	-5,01	-3,01	2,00
646	2,25	-5,07	-2,52	2,55	847	2,87	-5,01	-3,01	2,00
647	2,25	-5,07	-2,52	2,54	848	2,88	-5,01	-3,01	2,00
648	2,26	-5,07	-2,53	2,54	849	2,88	-5,01	-3,01	1,99
649	2,26	-5,07	-2,53	2,54	850	2,88	-5,01	-3,01	1,99
650	2,26	-5,07	-2,53	2,53	851	2,88	-5,01	-3,02	1,99
651	2,26	-5,07	-2,54	2,53	852	2,89	-5,01	-3,02	1,99
652	2,27	-5,07	-2,54	2,53	853	2,89	-5,01	-3,02	1,99
653	2,27	-5,07	-2,54	2,52	854	2,89	-5,01	-3,02	1,98
654	2,27	-5,07	-2,55	2,52	855	2,90	-5,01	-3,02	1,98
655	2,28	-5,07	-2,55	2,52	856	2,90	-5,01	-3,03	1,98
656	2,28	-5,06	-2,55	2,51	857	2,90	-5,01	-3,03	1,98
657	2,28	-5,06	-2,55	2,51	858	2,91	-5,00	-3,03	1,97
658	2,29	-5,06	-2,56	2,51	859	2,91	-5,00	-3,03	1,97
659	2,29	-5,06	-2,56	2,50	860	2,91	-5,00	-3,03	1,97
660	2,29	-5,06	-2,56	2,50	861	2,92	-5,00	-3,04	1,97
661	2,29	-5,06	-2,57	2,50	862	2,92	-5,00	-3,04	1,97
662	2,30	-5,06	-2,57	2,49	863	2,92	-5,00	-3,04	1,96
663	2,30	-5,06	-2,57	2,49	864	2,93	-5,00	-3,04	1,96
664	2,30	-5,06	-2,58	2,49	865	2,93	-5,00	-3,04	1,96
665	2,31	-5,06	-2,58	2,48	866	2,93	-5,00	-3,05	1,96
666	2,31	-5,06	-2,58	2,48	867	2,94	-5,00	-3,05	1,96
667	2,31	-5,06	-2,58	2,48	868	2,94	-5,00	-3,05	1,95
668	2,32	-5,06	-2,59	2,47	869	2,94	-5,00	-3,05	1,95
669	2,32	-5,06	-2,59	2,47	870	2,95	-5,00	-3,05	1,95
670	2,32	-5,06	-2,59	2,47	871	2,95	-5,00	-3,05	1,95
671	2,32	-5,06	-2,60	2,46	872	2,95	-5,00	-3,06	1,95
672	2,33	-5,06	-2,60	2,46	873	2,96	-5,00	-3,06	1,94
673	2,33	-5,06	-2,60	2,46	874	2,96	-5,00	-3,06	1,94
674	2,33	-5,06	-2,60	2,45	875	2,96	-5,00	-3,06	1,94
675	2,34	-5,06	-2,61	2,45	876	2,97	-5,00	-3,06	1,94
676	2,34	-5,06	-2,61	2,45	877	2,97	-5,00	-3,07	1,93
677	2,34	-5,06	-2,61	2,45	878	2,97	-5,00	-3,07	1,93
678	2,34	-5,06	-2,62	2,44	879	2,98	-5,00	-3,07	1,93
679	2,35	-5,06	-2,62	2,44	880	2,98	-5,00	-3,07	1,93
680	2,35	-5,06	-2,62	2,44	881	2,98	-5,00	-3,07	1,93
681	2,35	-5,06	-2,62	2,43	882	2,99	-5,00	-3,07	1,92
682	2,36	-5,06	-2,63	2,43	883	2,99	-5,00	-3,08	1,92

683	2,36	-5,06	-2,63	2,43	884	2,99	-5,00	-3,08	1,92
684	2,36	-5,06	-2,63	2,42	885	3,00	-5,00	-3,08	1,92
685	2,37	-5,05	-2,63	2,42	886	3,00	-5,00	-3,08	1,92
686	2,37	-5,05	-2,64	2,42	887	3,00	-5,00	-3,08	1,91
687	2,37	-5,05	-2,64	2,41	888	3,01	-5,00	-3,09	1,91
688	2,37	-5,05	-2,64	2,41	889	3,01	-5,00	-3,09	1,91
689	2,38	-5,05	-2,65	2,41	890	3,01	-5,00	-3,09	1,91
690	2,38	-5,05	-2,65	2,40	891	3,02	-5,00	-3,09	1,91
691	2,38	-5,05	-2,65	2,40	892	3,02	-5,00	-3,09	1,90
692	2,39	-5,05	-2,65	2,40	893	3,02	-5,00	-3,09	1,90
693	2,39	-5,05	-2,66	2,40	894	3,03	-5,00	-3,10	1,90
694	2,39	-5,05	-2,66	2,39	895	3,03	-5,00	-3,10	1,90
695	2,40	-5,05	-2,66	2,39	896	3,03	-5,00	-3,10	1,90
696	2,40	-5,05	-2,66	2,39	897	3,04	-5,00	-3,10	1,89
697	2,40	-5,05	-2,67	2,38	898	3,04	-5,00	-3,10	1,89
698	2,40	-5,05	-2,67	2,38	899	3,04	-4,99	-3,10	1,89
699	2,41	-5,05	-2,67	2,38	900	3,05	-4,99	-3,11	1,89
700	2,41	-5,05	-2,68	2,37	901	3,05	-4,99	-3,11	1,89
701	2,41	-5,05	-2,68	2,37	902	3,05	-4,99	-3,11	1,88
702	2,42	-5,05	-2,68	2,37	903	3,06	-4,99	-3,11	1,88
703	2,42	-5,05	-2,68	2,37	904	3,06	-4,99	-3,11	1,88
704	2,42	-5,05	-2,69	2,36	905	3,06	-4,99	-3,12	1,88
705	2,43	-5,05	-2,69	2,36	906	3,07	-4,99	-3,12	1,88
706	2,43	-5,05	-2,69	2,36	907	3,07	-4,99	-3,12	1,87
707	2,43	-5,05	-2,69	2,35	908	3,08	-4,99	-3,12	1,87
708	2,44	-5,05	-2,70	2,35	909	3,08	-4,99	-3,12	1,87
709	2,44	-5,05	-2,70	2,35	910	3,08	-4,99	-3,12	1,87
710	2,44	-5,05	-2,70	2,34	911	3,09	-4,99	-3,13	1,87
711	2,44	-5,05	-2,70	2,34	912	3,09	-4,99	-3,13	1,86
712	2,45	-5,05	-2,71	2,34	913	3,09	-4,99	-3,13	1,86
713	2,45	-5,05	-2,71	2,34	914	3,10	-4,99	-3,13	1,86
714	2,45	-5,05	-2,71	2,33	915	3,10	-4,99	-3,13	1,86
715	2,46	-5,05	-2,71	2,33	916	3,10	-4,99	-3,13	1,86
716	2,46	-5,04	-2,72	2,33	917	3,11	-4,99	-3,14	1,85
717	2,46	-5,04	-2,72	2,32	918	3,11	-4,99	-3,14	1,85
718	2,47	-5,04	-2,72	2,32	919	3,11	-4,99	-3,14	1,85
719	2,47	-5,04	-2,72	2,32	920	3,12	-4,99	-3,14	1,85
720	2,47	-5,04	-2,73	2,32	921	3,12	-4,99	-3,14	1,85

721	2,47	-5,04	-2,73	2,31	922	3,12	-4,99	-3,14	1,85
722	2,48	-5,04	-2,73	2,31	923	3,13	-4,99	-3,15	1,84
723	2,48	-5,04	-2,74	2,31	924	3,13	-4,99	-3,15	1,84
724	2,48	-5,04	-2,74	2,30	925	3,13	-4,99	-3,15	1,84
725	2,49	-5,04	-2,74	2,30	926	3,14	-4,99	-3,15	1,84
726	2,49	-5,04	-2,74	2,30	927	3,14	-4,99	-3,15	1,84
727	2,49	-5,04	-2,75	2,30	928	3,14	-4,99	-3,15	1,83
728	2,50	-5,04	-2,75	2,29	929	3,15	-4,99	-3,16	1,83
729	2,50	-5,04	-2,75	2,29	930	3,15	-4,99	-3,16	1,83
730	2,50	-5,04	-2,75	2,29	931	3,15	-4,99	-3,16	1,83
731	2,51	-5,04	-2,76	2,28	932	3,16	-4,99	-3,16	1,83
732	2,51	-5,04	-2,76	2,28	933	3,16	-4,99	-3,16	1,82
733	2,51	-5,04	-2,76	2,28	934	3,16	-4,99	-3,16	1,82
734	2,51	-5,04	-2,76	2,28	935	3,17	-4,99	-3,17	1,82
735	2,52	-5,04	-2,76	2,27	936	3,17	-4,99	-3,17	1,82
736	2,52	-5,04	-2,77	2,27	937	3,17	-4,99	-3,17	1,82
737	2,52	-5,04	-2,77	2,27	938	3,18	-4,99	-3,17	1,82
738	2,53	-5,04	-2,77	2,27	939	3,18	-4,99	-3,17	1,81
739	2,53	-5,04	-2,77	2,26	940	3,18	-4,99	-3,17	1,81
740	2,53	-5,04	-2,78	2,26	941	3,19	-4,99	-3,18	1,81
741	2,54	-5,04	-2,78	2,26	942	3,19	-4,99	-3,18	1,81
742	2,54	-5,04	-2,78	2,25	943	3,20	-4,98	-3,18	1,81
743	2,54	-5,04	-2,78	2,25	944	3,20	-4,98	-3,18	1,80
744	2,55	-5,04	-2,79	2,25	945	3,20	-4,98	-3,18	1,80
745	2,55	-5,04	-2,79	2,25	946	3,21	-4,98	-3,18	1,80
746	2,55	-5,04	-2,79	2,24	947	3,21	-4,98	-3,19	1,80
747	2,55	-5,04	-2,79	2,24	948	3,21	-4,98	-3,19	1,80
748	2,56	-5,03	-2,80	2,24	949	3,22	-4,98	-3,19	1,79
749	2,56	-5,03	-2,80	2,24	950	3,22	-4,98	-3,19	1,79
750	2,56	-5,03	-2,80	2,23	951	3,22	-4,98	-3,19	1,79
751	2,57	-5,03	-2,80	2,23	952	3,23	-4,98	-3,19	1,79
752	2,57	-5,03	-2,81	2,23	953	3,23	-4,98	-3,20	1,79
753	2,57	-5,03	-2,81	2,23	954	3,23	-4,98	-3,20	1,79
754	2,58	-5,03	-2,81	2,22	955	3,24	-4,98	-3,20	1,78
755	2,58	-5,03	-2,81	2,22	956	3,24	-4,98	-3,20	1,78
756	2,58	-5,03	-2,82	2,22	957	3,24	-4,98	-3,20	1,78
757	2,59	-5,03	-2,82	2,21	958	3,25	-4,98	-3,20	1,78
758	2,59	-5,03	-2,82	2,21	959	3,25	-4,98	-3,20	1,78

759	2,59	-5,03	-2,82	2,21	960	3,25	-4,98	-3,21	1,78
760	2,59	-5,03	-2,82	2,21	961	3,26	-4,98	-3,21	1,77
761	2,60	-5,03	-2,83	2,20	962	3,26	-4,98	-3,21	1,77
762	2,60	-5,03	-2,83	2,20	963	3,27	-4,98	-3,21	1,77
763	2,60	-5,03	-2,83	2,20	964	3,27	-4,98	-3,21	1,77
764	2,61	-5,03	-2,83	2,20	965	3,27	-4,98	-3,21	1,77
765	2,61	-5,03	-2,84	2,19	966	3,28	-4,98	-3,22	1,76
766	2,61	-5,03	-2,84	2,19	967	3,28	-4,98	-3,22	1,76
767	2,62	-5,03	-2,84	2,19	968	3,28	-4,98	-3,22	1,76
768	2,62	-5,03	-2,84	2,19	969	3,29	-4,98	-3,22	1,76
769	2,62	-5,03	-2,85	2,18	970	3,29	-4,98	-3,22	1,76
770	2,63	-5,03	-2,85	2,18	971	3,29	-4,98	-3,22	1,76
771	2,63	-5,03	-2,85	2,18	972	3,30	-4,98	-3,22	1,75
772	2,63	-5,03	-2,85	2,18	973	3,30	-4,98	-3,23	1,75
773	2,64	-5,03	-2,85	2,17	974	3,30	-4,98	-3,23	1,75
774	2,64	-5,03	-2,86	2,17	975	3,31	-4,98	-3,23	1,75
775	2,64	-5,03	-2,86	2,17	976	3,31	-4,98	-3,23	1,75
776	2,64	-5,03	-2,86	2,17	977	3,31	-4,98	-3,23	1,75
777	2,65	-5,03	-2,86	2,16	978	3,32	-4,98	-3,23	1,74
778	2,65	-5,03	-2,87	2,16	979	3,32	-4,98	-3,24	1,74
779	2,65	-5,03	-2,87	2,16	980	3,33	-4,98	-3,24	1,74
780	2,66	-5,03	-2,87	2,16	981	3,33	-4,98	-3,24	1,74
781	2,66	-5,03	-2,87	2,15	982	3,33	-4,98	-3,24	1,74
782	2,66	-5,03	-2,87	2,15	983	3,34	-4,98	-3,24	1,73
783	2,67	-5,02	-2,88	2,15	984	3,34	-4,98	-3,24	1,73
784	2,67	-5,02	-2,88	2,15	985	3,34	-4,98	-3,24	1,73
785	2,67	-5,02	-2,88	2,14	986	3,35	-4,98	-3,25	1,73
786	2,68	-5,02	-2,88	2,14	987	3,35	-4,98	-3,25	1,73
787	2,68	-5,02	-2,89	2,14	988	3,35	-4,98	-3,25	1,73
788	2,68	-5,02	-2,89	2,14	989	3,36	-4,98	-3,25	1,72
789	2,69	-5,02	-2,89	2,13	990	3,36	-4,97	-3,25	1,72
790	2,69	-5,02	-2,89	2,13	991	3,37	-4,97	-3,25	1,72
791	2,69	-5,02	-2,89	2,13	992	3,37	-4,97	-3,26	1,72
792	2,70	-5,02	-2,90	2,13	993	3,37	-4,97	-3,26	1,72
793	2,70	-5,02	-2,90	2,12	994	3,38	-4,97	-3,26	1,72
794	2,70	-5,02	-2,90	2,12	995	3,38	-4,97	-3,26	1,71
795	2,70	-5,02	-2,90	2,12	996	3,38	-4,97	-3,26	1,71
796	2,71	-5,02	-2,91	2,12	997	3,39	-4,97	-3,26	1,71

797	2,71	-5,02	-2,91	2,11	998	3,39	-4,97	-3,26	1,71
798	2,71	-5,02	-2,91	2,11	999	3,39	-4,97	-3,27	1,71
799	2,72	-5,02	-2,91	2,11	1000	3,40	-4,97	-3,27	1,71
800	2,72	-5,02	-2,91	2,11					



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VITA

Emek Göksu Durmuşoğlu was born in Fatih in İstanbul, Turkey in 1986. He completed Cağaloğlu Anadolu Lisesi (İstanbul) in 2004. He received his B.S. degree from the Department of Metallurgy and Material Engineering, at Yildiz Technical University (İstanbul) in 2009. He received his MSc degree from the Department of Nanoscience and Nanoengineering at Istanbul Technical University in 2012. In 2012, he started Ph.D. program in the Department of Material Science and Engineering, Koç University (İstanbul).

