ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

DEVELOPMENT OF NANO-ALLOYED CdTeS QUANTUM DOTS VIA TWO-PHASE SYNTHESIS METHOD

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

İKİ FAZ YÖNTEMİYLE NANO-ALAŞIM CdTeS KUANTUM NOKTACIKLARININ SENTEZİ

YÜKSEK LİSANS TEZİ

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Sacide Melek KESTİR, a **M.Sc.** student of **ITU Graduate School** student ID 513191027, successfully defended the thesis entitled **“DEVELOPMENT OF NANO-ALLOYED CdTeS QUANTUM DOTS VIA TWO-PHASES SYNTHESIS METHOD”**, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission **: 17 June 2022**

Date of Defense **: 1 July 2022**

To all my future journeys,

FOREWORD

First of all, I am grateful for my past journeys that ended up in Istanbul Technical University Nano Science and Nano Engineering master degree programme. I have learned many unique, new not only theory but also the techniques that comprises the nano world.

Secondly, I want to thank you Assoc. Prof. Caner Ünlü, who accepted me into his laboratory and allowed me to study there, for his priceless guidance and support during the thesis. He gave the opportunity to be part of the BeeDot research group and I learned so many things during that period not only about quantum dots but also being scientific researcher in a laboratory which were amazing experiences. Thank you for everything. I feel so lucky to be your student.

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June 2022 Sacide Melek Kestir

(Chemist)

TABLE OF CONTENTS

Page

ABBREVIATIONS

C-dot : Carbon Dot
Cd-MA : Cadmium Myristate
CYS : L-cysteine
FWHM : Full Width at Half Maximum
IR : Infrared
NM : Nanometer
NAC : N-acetyl L-cysteine
OA : Oleic Acid
PL : Photoluminescence
QDs : Quantum Dots
QY : Quantum Yield
HR-TEM : High-Resolution Transmission Electron Microscopy
UV : Ultraviolet
XPS : X-ray Photoelectron Spectroscopy
XRD : X-ray Diffraction

SYMBOLS

Au	**:** Gold
CdO	**:** Cadmium Oxide
CdS	**:** Cadmium Sulfur
CdSe	**:** Cadmium Selenide
CdTe	**:** Cadmium Tellurium
CdTeS	**:** Cadmium Tellurium Sulfur
$NaHB_4$	**:** Sodium Borohydride
NAHTe	**:** Sodium Hydrogen Telluride
NaOH	**:** Sodium Hydroxide
PbS	**:** Lead Sulfur
S	**:** Sulphur
Te	**:** Tellurium

LIST OF FIGURES

DEVELOPMENT OF NANO-ALLOYED CdTeS
QUANTUM DOTS VIA TWO-PHASE SYNTHESIS METHOD

SUMMARY

The 20th century was called as the golden age for the science since the significant discoveries that is going to affect human life was made in that century. The science around that time opened the new gate to the mysterious world that humankind had been take advantage of it without even realizing but they had never been able to discover. The humankind had tried to explore and investigate the unfamiliar materials which came from especially nano scale at that time. The new characterization techniques like X-ray lead to finding of properties of these novel materials which is not visible to human eye. They have only from 1 to 100 nm dimensions, however; their surface and physical properties are way better than bulk materials that no one can argue. Therefore, since then the interest to the nano science have been increased day by day. And this new world has named as nanomaterials for last 30 years.

The main cause for unique properties of nanomaterials comes from the confinement of electrons which bulk materials don't display. As a result of the confinement, discrete energy levels are formed due to interaction between valance and conjugation band under Bohr radius. On other words, it can be said that electrons have no freedom to move in nano dimension, their motion is confined. One type of the quantum nanostructures are zero-dimensional materials which named after restriction in all dimensions. Quantum dots which is zero-dimensional nano structure displays exclusive physical properties like high photoluminescence, wide adsorption and narrow emission.

QDs in other words semiconductor nanocrystals, which synthesized for the first time in 1981 by Ekimov and was took its name in 1984, used 2000 years ago by Romans and Greeks and due to its discrete energy levels in their structure, they also are named as artificial atoms. Besides the discrete energy levels in QDs, high surface-to-volume-ratio properties makes them ideal candidate from diagnostic to photovoltaic cells. Their adsorption wavelength is broad from infrared to ultraviolet which means different size of the QDs can be excited with the same wavelength. At the same time, they have narrow emission wavelength that are altered with QDs' size and composition. In other words, QDs can emit different kind of wavelength with the same composition by changing the size. They are generally composed of II-VI and III-V elements from periodic table. Among these properties, QDs are more stable and brighter than organic dyes.

As the properties of these nanomaterials have been understood, the attraction for these materials have increased especially last 20 year. There has been more attempt to use it for treatment, diagnosis of illness and for the solar cells to increase efficiency of photovoltaic cells. According to application area, different types of QDs, having diverse size, composition and structures, can be desired which is achievable with the help of the different types of the fabrication techniques. However, the main challenge

part is to fabricate them effectively under the mild conditions without giving harm to the nature. Today, the manufacture methods are divided into two parts: top-down and bottom-up. Both have its own advantages and drawbacks. Bottom-up methods mean the self-assembly of the atom or molecules to constitute desired structure. Self-assembly is the key part of these methods. Method starts with the nucleation and goes on with the self-assembly and when the free energy reaches the maximum level, the production finishes.

Bottom-up methods also divided into chemical and physical parts. However, chemical bottom-up fabrication is more advantageous in respect to temperature, time, usage of device etc. Two-phase method is type of chemical bottom-up which is invented in 1984 for Au nanocrystals. As can be understandable from the name, there are two-immiscible-phase in this method. The nanocrystals constitute interlayer between these two-phase. Two-phase method occurs in one tank, one step and mild conditions regarding other ones. As result of the reaction, QDs that have high quantum yield and narrow emission band, arises.

The main disadvantages of QDs, they are so reactive when they are bare nanocrystals. Bare QDs are affected from the external sources so easily that damage their optical properties. Therefore, the surface of the QDs are always coated with organic or non-organic capping agents. Organic agents can be organic molecules that involves functional groups at the both ends, and inorganic ones are generally other QDs which have higher band gap. On the other hand, hydrophobicity gives the QDs better optical properties than hydrophilicity. Having hydrophobic character, QDs are mainly not suitable for the biological application while they need to be water-soluble. Thus, there are some attempts to make them hydrophilic. Exchange of the surface with hydrophilic agent or coating it with functional groups like silica are two examples to build water-soluble QDs.

In this thesis, the CdTeS QDs were synthesized with the two-phase method and its optical and structural characteristic are investigated. The two-immiscible phase were the toluene and water in the reaction. Oleic acid was used as capping agent to passivate the surface. Later, the effect of the water-phase precursors was examined. The amount of the Te was doubled and cut in half to observe the effect. Lastly, these synthesized QDs were made hydrophilic by ligand exchange method and its optical properties are investigated.

The characterization of the CdTeS QDs was both optical and structural. The structural one was made with HR-TEM, XPS and XRD. The optical characterization was made with UV-Vis and Fluorescence spectroscopy.

From the HR-TEM, the structure of the QDs observed as monodisperse and homogenous. XPS gave the insight through the type of the QDs which is the gradient alloy due to Te rich center. XRD proved the CdTe characteristic of the QDs. Excitation graphs demonstrated the brightness of the QDs at both polar and non-polar phase. Also, the half amount of the Te had the highest intensity among them; however, the normal amount of Te had highest wavelength. Absorbance peak of different amount of Te was the same.

İKİ FAZ YÖNTEMİYLE NANO-ALAŞIM
CdTeS KUANTUM NOKTACIKLARININ SENTEZİ

ÖZET

20. yüzyıl daha sonraları insanlığı çok büyük etkileyen buluşlar yapılması bakımından bilimin altın çağı olarak adlandırılır. Bu dönemki bilim, insanlığın o döneme kadar keşfedemediği ama farkında olmadan yararlandığı esrarengiz bir kapıya açılır. Tanımadığı ve özellikle nano boyutundan gelen bu malzemeleri, insanoğlu bu dönemde tanımaya ve incelemeye çalıştı. X ışınları gibi yeni karakterizasyon teknikleri insanın gözle göremediği bu malzemelerin özelliklerinin keşfine yol açtı. Bu malzemeler sadece 1'den 100 nanometreye kadar bir boyutları olsa da fiziksel ve yüzeysel özellikleri tartışmasız bir şekilde kullanılan büyük boyutlu malzemelerden çok daha iyiydi ve bu yüzden nano bilime olan ilgi gün geçtikçe arttı. Son 30 yılda ise bu yeni diyara nano-malzemeler denilmiştir.

Nano malzemelerin bu benzersiz özellikleri, büyük boyutlu malzemelerin göstermediği kuantum sınırlama özelliğinden gelmektedir. Kısıtlamanın sonucu olarak, Bohr yarıçapının altında, değerlik ve iletkenlik bantları arasında oluşan etkileşim sonucunda kesikli enerji düzeyleri oluşur. Başka bir sözle söylersek, nano boyutta elektronların hareketi serbest değildir, sınırlıdır. Kuantum nano yapıların bir çeşidi olan sıfır-boyutlu malzemelere adı, elektronun hareketi üç boyutta da sınırlanınca verilir. Sıfır-boyutlu kuantum nano yapılardan biri olan kuantum noktacıklar yüksek fotoluminesan, geniş adsorpsiyon ve dar emisyon gibi özel fiziksel özellikleri gösterir.

İlk defa 1981 yılında Ekimov tarafından üretilen ve 1984'te adını alan kuantum noktacıklar başka bir deyişle yarı iletken nano kristaller, 2000 yıl önce Romalılar ve Yunanlılar tarafından kullanılmıştır ve yapısındaki kesikli enerji seviyeleri nedeniyle yapay atomlar adıyla da adlandırılır. Periyodik cetvelin 2-6 veya 3-5 grubundaki elementlerden oluşurlar. Kesikli enerji seviyeleri dışında, yüzeyin hacme olan oranı yüksek olduğundan, teşhisten fotovoltaik hücrelere kadar geniş bir kullanım alanları vardır. Kuantum noktacıklar kızılötesinden mor ötesi ışığa kadar geniş bir aralıkta absorpsiyon yapması aynı dalga boyuyla farklı boyuttaki kuantum noktacığı uyarılabilme özelliği verir. Aynı zamanda da organik boyalara göre dar bir emisyon aralığına sahiptirler. Ayrıca aynı yapıdaki malzeme, boyutları değişerek farklı dalga boylarında emisyon yaparlar. Bu özelliklerinin dışında, kuantum noktacıklar organik boyalardan hem daha parlak hem de daha foto stabillerdir.

Son yirmi yılda, nano malzemelerin özellikleri anlaşıldıkça, bu malzemelere olan ilgi de git gide arttı. Bu malzemeleri hastalıkların tanı ve iyileştirilmesinde veya fotovoltaik hücrelerin verimini arttırmak gibi girişimler artarak devam etmektedir. Kullanılmak istenen alana göre kuantum noktacıkları istenilen boyutta ve yapıda elde etmek çeşitli üretim yollarıyla bugün mümkündür. Ama kullanım alanından önce bu malzemelerin asıl zorluğu onların üretim yoludur. Buradaki asıl zorluk ise bu malzemeleri üretirken doğaya zarar vermeden, olabilecek en ılıman koşullarda ve

verimli bir şekilde üretmektir. Bugün, üretim metotları aşağıdan-yukarıya ve yukarıdan-aşağıya olmak üzere iki bölüme ayrılır. Her iki üretim çeşidinin de kendine göre avantajları ve dezavantajları vardır. Yukarıdan-aşağıya metodu daha çok fiziksel yollar kullanılarak büyük moleküllerin nano boyuta küçültülmesidir. Aşağıdan-yukarıya metodu ise, atom veya moleküllerin bir araya gelerek istenilen yapını oluşturmasıdır. Kendiliğinden bir araya gelme durumu burada malzemenin özelliklerini belirleyen önemli bir faktördür. Bu metot atom veya moleküllerin bir araya gelerek çekirdek yapıyı oluşturmasıyla başlar, bu yapıların kendiliğinden bir araya gelmesiyle de devam eder ve serbest enerjinin maksimum değere ulaşmasına kadar devam eder.

Aşağıdan-yukarıya metodu da fiziksel ve kimyasal olmak üzere ikiye ayrılır. Ama kimyasal metotlar zaman, sıcaklık, alet kullanımı gibi konularda fiziksel metotlardan daha avantajlıdır. Kimyasal bir aşağıdan-yukarıya yöntemi olan iki faz yöntemi 1984 yılında altın nano-kristalleri için icat edilmiştir. Adından da anlaşılacağı gibi birbirine karışmayan iki farklı faz vardır ve nano-kristaller bu iki fazın arasında oluşur. Bu yol tek basamakta ve kapta ılıman koşullar altında istenilen malzeme elde edilir. Sonuçta elde yüksek kuantum verimli, dar emisyon aralığına sahip kuantum noktacıkları oluşur.

Kuantum noktacıkların dezavantajlarından biri ise, yalın olarak üretilenler yüzeylerinin çok reaktif olmasından dolayı hemen bozulurlar ve bu yüzden optiksel özellikleri hemen değişir. Bu yüzeyleri hemen fonksiyonel bir grup içeren organik veya yüksek enerji bant aralığına sahip başka bir kuantum noktacık ile inorganik kaplama etkin maddeyle kaplanırlar. Bu kaplama hem yüzeyi kontrol altına almanın yanı sıra kuantum noktacığın küme olmasını engellemek hem de daha sonra fonksiyonel gruplar ekleyerek farklı alanlarda kullanımını sağlar. Bunun yanı sıra, kuantum noktacıklar suda çözünmedikleri zaman daha iyi optiksel özellikleri olur. Suyu sevmeyen malzemeler ise biyolojik kullanım için uygun değildir. Bu yüzden çeşitli yollarla bu malzemeler suda çözülebilir hale getirilir. Yüzeyin slika gibi suyu seven malzeme ile kaplanması veya yüzeyin suyu seven bir etken madde ile değiştirilmesi iki yoldur.

Bu tezde, iki-faz yöntemiyle üretilen CdTeS kuantum noktacıklarının optiksel ve yapısal özellikleri incelenmiştir. İki-faz yönteminde polar faz olarak su, apolar olarakta tolüen ve yüzeyi pasifleştirmek için ise oleik asit kullanılmıştır. Sulu fazın etkisni görmek için, sulu fazda çözdürülen tellürün miktarı bir yarıya kesilip, bir de iki katına çıkartılmıştır. Son olaraktan, sentezlenen hidrofobik kuantum noktacıklar ligand değiştirme metoduyla hidrifilik yapılıp, optik olarak incelenmiştir.

Bu kuantum noktacıkların karakterizasyonu hep optiksel hem de yapısal olarak yapılmıştır. Yapısal analiz için HR-TEM, XPS ve XRD kullanılırken, optik için UV-Vis ve floresan spektrometresi kullanılmıştır.

HR-TEM sonuçlarına göre, homojen ve tek dağılımlı kuantum noktacıklarını kanıtlamıştır. XPS sonucuna göre merkezde Te karakterinin fazla olması ve 1 gün sonra bunun değişerek S karakterinin artması nedeniyle kuantum noktalarının yapısının nano-alaşım heterojen şeklinde olduğu görülmüştür ve XRD ise CdTe kristal çinko-blend kübik yapıyı kanıtlamıştır. Ayrıca bu yapısal sonuçlara göre, yapıdaki tellür miktarı arttıkça yapının saf CdTe kübik yapısına yaklaştığı ve pikin giderek daha genişlediği gözlemlenmişti. Buna göre yapıya fazladan tellür eklediğimizde kristal yapıyı bozulduğu anlaşılmıştır. Daha sonra optik özellikleri incelendiği zaman, floresan spektrumu ise polar ve apolar fazda bulunan kuantum noktacıklarını parlaklığını kanıtlamış ve normal miktar tellüre sahip olan kuantum noktacıklar en yüksek dalga boyunu vermiştir. Yarı miktara sahip kuantum noktacık ise en yüksek yoğunluk pikini vermiştir. Absorban piki ise normal miktar tellür sahip olanlarda en fazla olduğunu gözlemlenmiştir.

1. INTRODUCTION

1.1 Nanotechnology

In 1974, Norio Taniguchi used the term ‘nanotechnology’ for the first time. He described the term as the separation, consolidation and deformation of the materials by one atom or one molecule [1]. However, that definition for the nanotechnology revised due to the improvement in sciences recently. Nowadays nanotechnology is used as the design, characterization, production and application of materials, structures, devices and systems in nanometer scale which means manipulation of at least one or more dimensions from 1 to 100 nanometer (nm) [2]. According to this definition, it can be said that nanotechnology covers different types of the sciences and engineering, as schemed in Figure 1.1, to solve difficulties that human faced on earth.

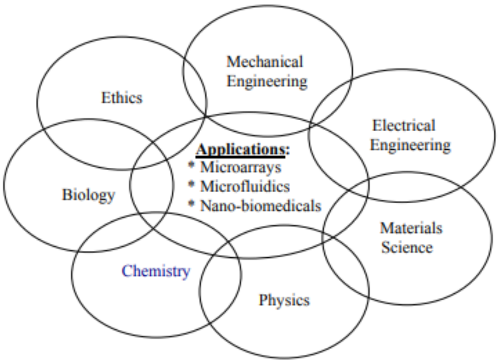


Figure 1.1: Different scientific areas of nanotechnology [3].

Although the term was used last century for the first time, humankind have been using the advantage of the nanotechnology from forth-century A.D. For example, Lycurgus cup resides from that time, which is presented in British Museum in London, includes gold and silver nanoparticles which cause to change in color under light source [4]. Since then, nanotechnology has improved, and diverse types of the nanomaterials have been synthesized with different types of approaches. Moreover, the number of scientific articles published about the nanotechnology has increased from early 1990s as schemed in Figure 1.2 [5].

Nanomaterials have gained extreme interest lately due to their unique properties. Surface properties and quantum effects are the two main factors which cause the nanomaterials to behave differently from bulk materials in terms of chemical reactivity, mechanical, optical, electrical and magnetic properties [6].

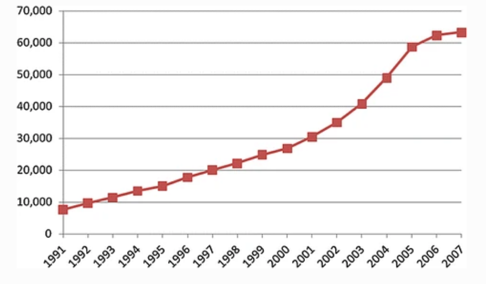


Figure 1.2: Scientific nanotechnology articles published per year [5].

1.2 Quantum Nanostructures

Nanostructures are classified into three main groups as schemed in Figure 1.3, which are two-dimensional, one-dimensional and zero-dimensional, due to number of freedoms experienced by electrons and holes inside the material [7]. One of the most important properties that nanoscale materials display is the confinement of the electrons. This leads to raise of unique properties like optoelectronic, mechanical and magnetic characteristic which bulk materials do not display. If the electrons have 2 dimensions to move freely and the other dimension is restricted to move, the material is defined as two-dimensional. Quantum well is an example of this type of material. According to this definition, one-dimensional materials like quantum wire have only one direction to move for electrons. Lastly, in zero-dimensional materials like quantum dots (QDs) electrons are quantized in all three directions [8]. It can be said that there is no restriction for the movement of the electron in bulk materials, in other words, the movement of electron is continuous. However, in nano level, this phenomenon alters to discrete levels as can be seen in Figure 1.4.

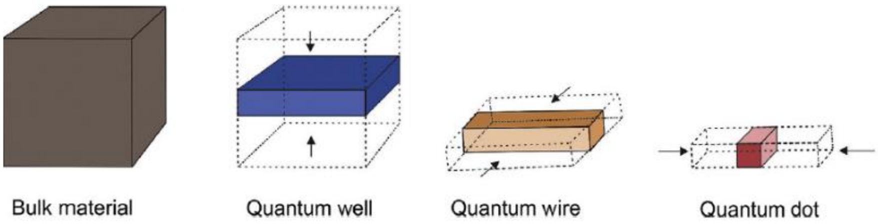


Figure 1.3: Schematic diagram for quantum nanostructures [8].

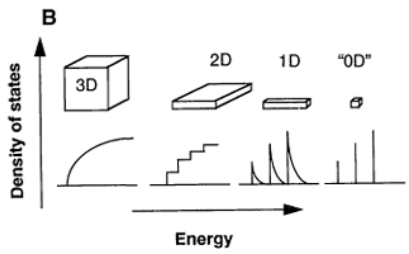


Figure 1.4: Density of states in quantum nanostructures and bulk material [9].

1.3 Quantum Dots

One type of the zero-dimensional quantum nanostructures is the quantum dots. They are described as semiconductor nanocrystals which consist of 100-100.000 atoms in very small size range [10]. Its ingredients are generally II-VI or III-V elements. Their physical dimensions are smaller than the Bohr radius and as a result they display unique luminescence characteristic and electronic properties like wide absorption, narrow emission and high stability toward light [11]. Depending on their size and chemical compositions, they emit diverse wavelength from infrared (IR) to visible region as indicated in Figure 1.5 [12]. Furthermore, the surface-to-volume-ratio of quantum dots is so high that 20% of its atom on the surface of material which has a 5 nm diameter [13]. This property makes the QDs perfect candidates to bind covalently to bio recognition molecules such as peptides, antibodies [12].

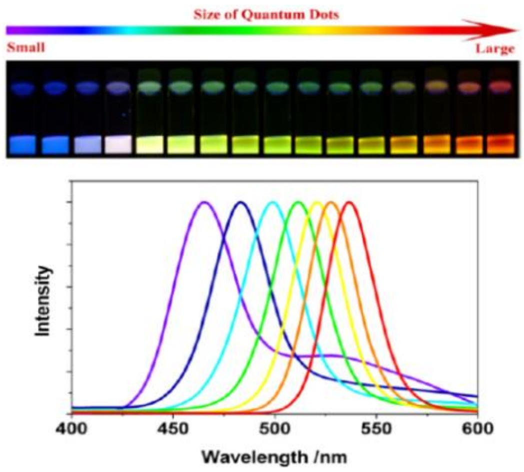


Figure 1.5: View of sixteen distinct emission of CdSe QDs under ultraviolet (UV) lamp and photoluminescence spectra of different sized CdSe QDs [14].

Although quantum dots took its name in 1920, the ancient Greeks and Romans used lead salts and calcium hydroxide more than 2000 years ago to dye their hair with the help of PbS QDs [15]. In 1981, a new class of material were discovered for the first time by Ekimov. He had synthesized three-dimensional microscopic crystals of semiconducting compound which was copper chloride (CuCl) in a transparent dielectric matrix [16]. Then the attention to the QDs had started around the beginning of 20th century, CdS and CdSe QDs embodied to glasses to obtain red-yellow color. Then, Rooksby used XRD for the first time to investigate the structure of CdS and CdSe which altered the color of glass in 1932 [17]. The term QDs was first defined by Ekimov and Onushenko in 1984 [16].

1.4 Quantum Confinement Effect

The most important property of quantum dots is the quantum confinement effect which comprises the other feature of them. As a result of this, it has distinctive optical, electronic and chemical characteristic that the other nanomaterials don’t have [18].

All the materials have the conduction and valance band which are separated each other by band gap. Insulator materials have a so wide gap between two bands that they can’t transfer their electrons when they excite from an external energy like photon or light. However, this band gap energy becomes less in the semiconductor bulk materials and for the conductor materials, they are no band gap between conduction and valance band. This situation alters when materials fall to nano dimensions. When electrons are stimulated by an external agent in nano dimension and excite to conduction band, weak bond between hole and electron forms under the size of Bohr radius. The weak attraction between these electron and electron hole by the Coulomb force is called exciton. Every single semiconductor has its own Bohr radius below which band energies turn into discrete levels in QDs as can be seen in Figure 1.6 [8]. In other words, electrons have no mobility between valance and conjugation band in all three dimensions. It is called quantum confinement effect [19].

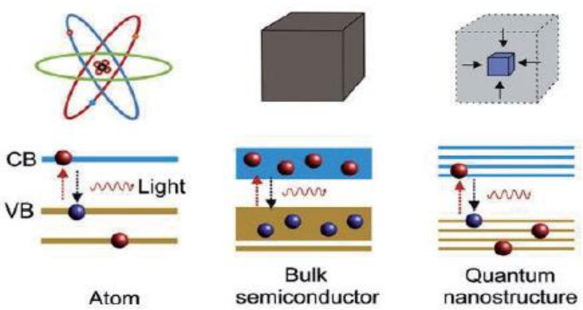


Figure 1.6: Schematic of energy band structures in atom, bulk semiconductor and quantum nanostructure [20].

With the decreasing size of QDs, there is a widening of the bandgap in quantum confinement [7]. Under the Bohr radius, the energy band gap can be altered with the size of nanoparticles which can be seen in Figure 1.7. The composition of the QDs is another significant factor which affects this bandgap.

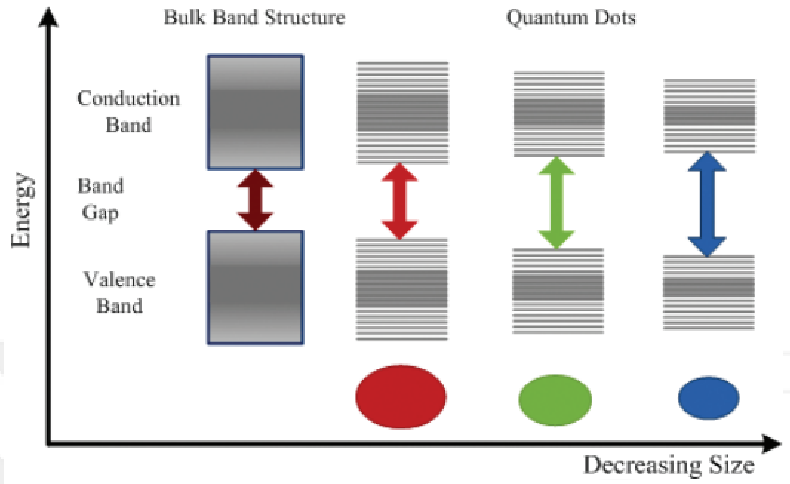


Figure 1.7: Schematic of an energy band structures changing with the size [21].

Moreover, these discrete energy levels make the QDs perfect candidate for the different kind of application areas from photovoltaic, light emitting diodes to quantum computing [8]. The use of the QDs for spotting the cells for plant bio imaging have become profitable in consequence of their small size, luminance, independence of emission on the excitation wavelength and stability under rough conditions [11]. Also, they display fast switching speed, low-energy operation, long state retention and high reproducibility for the memory devices and quantum computing with high surface-to-volume ratio property [22]. Due to these discrete energy level as in atoms and molecules, semiconductor nanocrystals also can be named as “artificial atoms”.

1.5 Optical Properties of QDs

As discussed before, an electron can be excited with the different kind of an external sources like photon or light. Later, the excited electron returns to the ground state and recombines with the hole. Electron emits this excess energy as light at certain wavelength while it is turning back to the ground state which is called luminescence as schemed in Figure 1.8. When semiconductor materials release these excess energy (or part of it) via photon emission, it is called photoluminescence (PL) [23]. One example of photoluminescence materials is the quantum dots [24].

For the QDs, these emission wavelengths can be determined with the size and composition. As the size of the QDs get bigger, the energy for the excitation becomes less and they emit photons in red wavelength. The color alters blue wavelength as the size of QDs get smaller. In other words, QDs can emit any color of light with the changing of the size from same composition of the nanocrystal [8]. Due to sharper spectra, photo stability and high quantum yield (QY), which is the consequence of bright PL QDs with the large molar extinction coefficient, makes them perfect candidate for the biological applications [24-25].

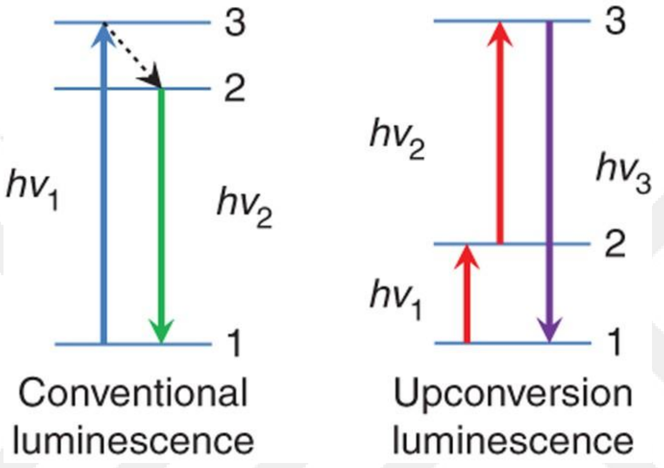


Figure 1.8: Schematic representation of the conventional and up-conversion luminescence processes [26].

As mentioned earlier in the definition of the QDs, they have not only wide adsorption but also narrow emission spectra. On the other hand, having been compared lately with QDs, conventional dyes have large emission spectra which cause intersection with different dyes. Therefore, there is a limit about the usage of these dyes, especially when it is needed for the labelling biological molecules. In contrast, the narrow emission spectra of QDs, which is controllable with size, composition and surface coating, can emit light at exact wavelength which is variable of from IR to UV [27]. Furthermore, dyes need a precise wavelength to excite its electrons due to narrow excitation spectra. In semiconductor nanocrystals, a single wavelength of light excites many sizes of QDs, resulting in different emission color because of wide adsorption spectra [28]. Also, QDs are bright nanomaterials. They are 20 times brighter than traditional fluorescent materials [29].

Another important issue for the fluorescence materials is the photo stability. In this regard, QDs have significant advantage over organic fluorophores which blench in a few minutes after exposure to light [27]. QDs are more stable than some of organic dyes and stand to excitation and fluorescence for hours with their high level of brightness and photo blenching threshold [9, 29-31].

1.6 Synthesis Types of Quantum Dots

In the beginning of these thesis, it was said that Romans and Greeks were the first civilizations that use these novel nanostructures according to discoveries from their residual. Since then there have been more attempts to develop more feasible synthesis methods of QDs to get better properties for the application areas as their novel physical features have been started to bring into light. Today, the synthesis types of QDs are categorized into two parts: top-down or bottom-up methods as schemed in Figure 1.9 for the carbon dot (C-dot) preparation. According to desired size and structure, one technique can be advantageous than the other one because both techniques have its own drawbacks. The choice of the fabrication type of the QDs is the vital part for the usage area of them because it determines its intrinsic properties like size, shape and crystallinity [7].

The objective behind the top-down approaches is the thinning the bulk materials to nanometer dimension [11]. These methods also divided into categories like ball milling, lithography and other processes according to their instrumentation [8]. Among them, the most common top-down methods [11] are the electron beam lithography [32] and reactive-ion etching [33] and/or wet chemical etching [34]. The other methods like focused ion [35] or laser beam [36] are also being used for the synthesis of zero dimensional dots. The most important disadvantages of these techniques are the impurities inside the QDs and structural failure which formed by patterning [7].

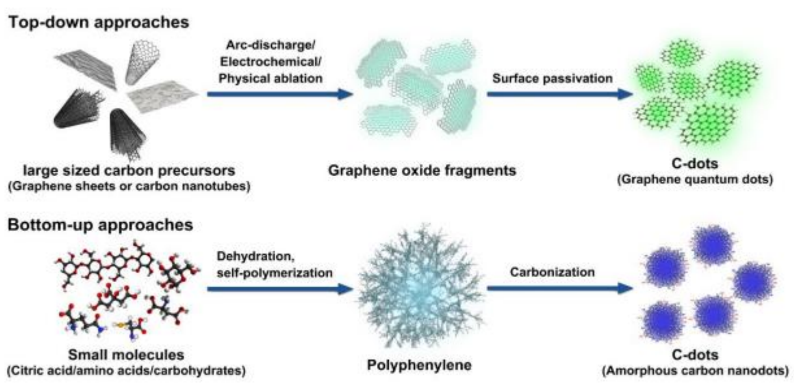


Figure 1.9: Schematic representation of the top-down and bottom-up fabrication of C-dot [37].

1.6.1 Bottom-up approaches

The main strategy in bottom-up synthesis is the self-assembly of atom or molecules into the desired structure [8]. The process of self-assembly consists of three part. Firstly, precursors are added to system with controlled reaction parameters to produce the monomers. Then, these monomers come together irreversibly and start the nucleation part until the free energy becomes the maximum. And nucleation starts right after the particle growth period, ending up to formation of QDs with desired size [22]. The nucleation process can be homogeneous, heterogeneous and secondary [38]. In the last step, the production and consumption of the monomers reaches out the balance with the desired nanostructure and the self-assembly finishes.

The bottom-up techniques also categorized into two parts as physical and chemical methods. As clear from the name, physical methods use the physical properties like vaporization, condensation, sublimation and sputtering for the preparation of nano structural materials. The types of some physical methods are inert gas condensation [39], physical vapor deposition [40] and laser ablation [41].

On the other hand, chemical methods have enormous advantages over physical methods like; being simple techniques with less instrumentation, able to perform high or low temperatures, feasibility of the doping of other atoms and lastly feasibility of various sized and shaped QDs with large quantity [8]. The types of some chemical methods are sol-gel techniques [42], chemical vapor deposition [43], colloidal synthesis [44], microwave assisted synthesis [45] and two-phase method [46].

1.6.2 Two-phase synthesis method

In 1994, Brust *et al* introduced the two-phase synthesis method for the alkanethiol-capped Au nanocrystals with %93 reaction yield. The toluene-water, which are two immiscible liquids, was their two-separate liquid-liquid interfaces [47]. Since then, different kind of interfaces and materials have been experimented to synthesize outstanding nanocrystals [48].

The main strategy in two-phase synthesis method is to constitute two immiscible phase which can be polar and non-polar as schemed in Figure 1.10. The precursors dissolves in either polar or nonpolar phase. The reaction, which results in nanocrystals, occurs in the interlayer between two phases and then the nanocrystals goes to upper phase. The reaction occurs in one tank and one step.

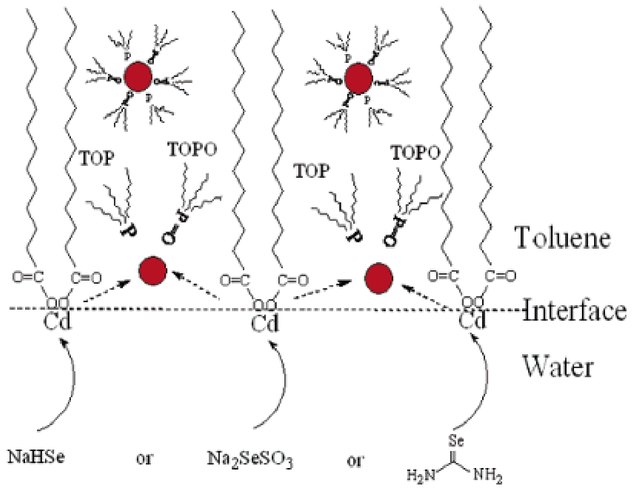


Figure 1.10: Schematic representation of two-phase synthesis method for CdSe nanocrystals at toluene-water interface [49].

Compared with other ones, the major benefits of these method are the mild and controllable conditions and reaction agents are environmentally friendly and less toxic [48, 50]. Furthermore, these nanocrystals display excellent properties like high luminescent and monodisperse [51] also they have narrow emission gap.

1.7 Surface Passivation and Functionalization of QDs

It was said that QDs has a high surface-to-volume ratio and this high surface sites can lead to enhanced or reduced transfer rate of charge carriers [7]. Therefore, surface states, which originate from unsatisfied bonds on the surface, can modify the optical properties like absorption, quantum efficiency and luminescent intensity of QDs [52]. The energy of these states is formed in the bandgap of QDs [53]. This can lead to trap the charge carrier which are electron or hole and QDs starts to behave like reducing or oxidizing agent which reduces the QY [7]. According to this, it can be said that surface states have notable importance on the optical properties of QDs.

In the light of the importance of surfaces, today QDs haven't produced uncovered since bare core nanocrystals have significant two disadvantages. At first, the surface of bare QDs extremely reactive [54] because of high surface-to-volume ratio; therefore, the structure can be easily damaged by external factors which leads to additional trapping pathways and unstable structure [27, 55]. Secondly, imperfections [54] and blinking, which cause to chance of single QDs between fluorescent and non-fluorescent states [56] can be formed. These imperfections on the surface cause to emission irregularities which are non-productive and non-emissive [27, 55].

For the acquiring the photo stable QDs, surface passivation is the crucial step which can be done some coating with an extra layer. Coating are divided into two part as either depositing an organic or inorganic capping agent as can be seen in Figure 1.11. The most common organic agents, which adsorbed on the surface, are phosphenes and mercaptans [7]. And inorganic capping means that the adding another semiconductor to QDs with a higher bandgap which have similar structure with QDs [24]. This strategy opens new type of structure which is called core-shell QDs with higher QY and photochemical stability [57, 58].

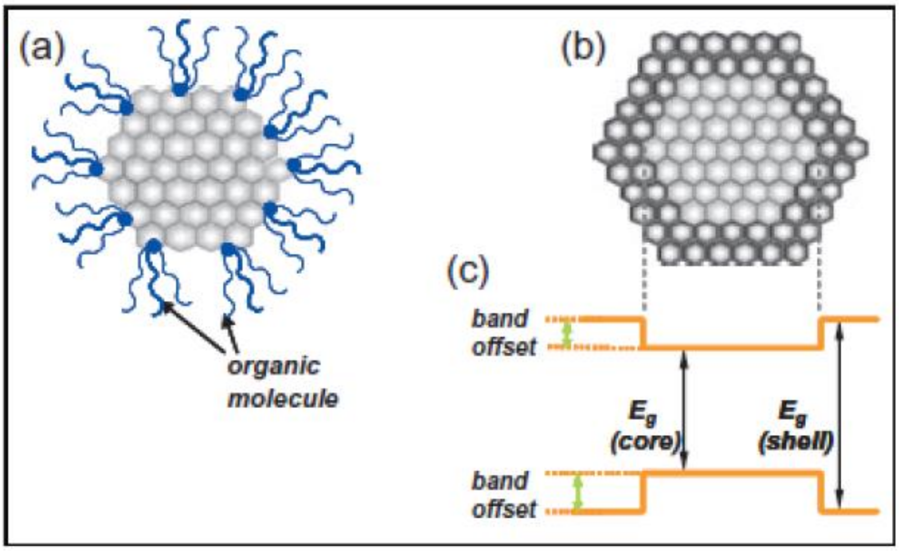


Figure 1.11: (a) Organically capped QDs, (b) Inorganically capped QDs (core/shell) and (c) Band-gap difference of core and shell [59].

Nanocrystals with narrow emission spectra and photo stability properties can used as the fluorescent probe for the diagnostic of the diseases [28]. Many QDs, with high luminescent property, are soluble in organic solvent. However, solubility is a key factor for the biological applications of QDs [27]. In other word, these QDs, that have hydrophobic characteristic, must be modified to make them hydrophilic [10].

There have been many attempts to make them water-soluble. The main two principle to make them water soluble are either exchange of a surface with a hydrophilic layer as can be seen in Figure 1.12 [60] which leads to degeneracy especially in the QY and coating of the surface with another layer which can carry functional group like silica [61]. Having some disadvantages, these two methods have been tried to develop in order to use the QDs for the biological areas to treat and diagnose the diseases.

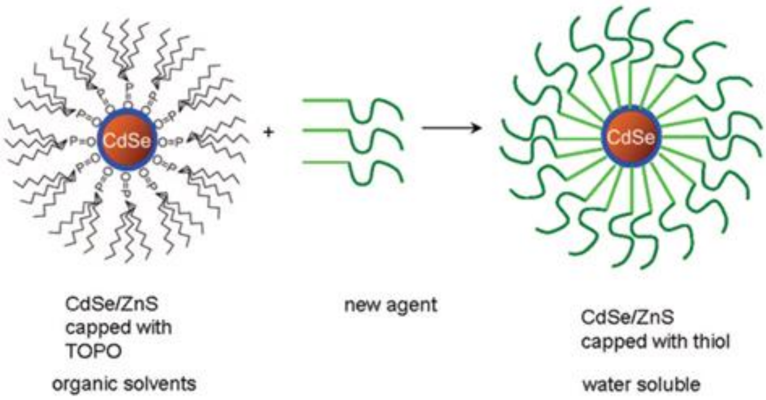


Figure 1.12: Schematic representation of ligand exchange process [60].

1.8 Purpose of Thesis

Among the other QDs, CdTe is the most studied and investigated one due to its unique properties like high luminescent and QY and it has multiple application areas from photovoltaic cells to bio-imaging. However, the photo physical properties of CdTe must be improved in order to make it photo stable. This improvement can be made with adding extra inorganic layer to acquire core/shell structure with ZnS or CdS which showed high photo luminescence and photo stability properties at room temperature [57]; nevertheless, it requires extra step in the fabrication.

On the other hand, photo physical properties of nanocrystals can be developed by adding an extra atom like Se or S to make nano alloyed QDs. Furthermore, two-phase method for synthesizing the core/shell nanocrystals can be used also for the nano alloys QDs fabrication.

The purposes of this thesis are to advance the photo physical features of CdTe QDs with another atom, sulfur and create alloyed nanomaterial. In this thesis, highly luminescent and photo stable CdTeS nano alloyed QDs were produced with two-phase synthesis method. Moreover, the effect of the water phase precursors, which are Te and S, was investigated by alteration the quantity of Te. The reaction conditions were mild and the QDs produced at room temperature at single shot. Later, the characterization tests were made to the samples, which were taken at different times and were comprised different amount of Te-S, to understand its structural and optical properties. Lastly, in order to use in biological application these QDs were capped with hydrophilic agent with ligand exchange procedure and luminescence properties of water-soluble QDs were investigated.

2. MATERIALS AND METHOD

In recent years, different kinds of synthesis approach for the quantum dots have enhanced especially as their unique and novel features have been discovered. Among the QDs, CdTe is one of the most studied types due to its wide range of application areas from photovoltaic cells to bio-scanning.

In this thesis, highly luminescent CdTeS QDs were synthesized by two-phase synthesis approach at single step and at low temperatures. Afterwards, these QDs were investigated to understand their optical and structural properties.

2.1 Synthesis of Precursors

Before the synthesis of QDs, the materials cadmium myristate and NaHTe must be prepared as explained below. Resource of cadmium myristate was synthesized as stock and kept away from the moisture and the heat to use it later. However, NaHTe material was so sensitive to oxygen that it couldn't be possible to protect it from oxidation. Therefore, NaHTe was synthesized every time freshly when QDs were produced.

2.1.1 Synthesis of cadmium myristate (Cd-MA)

The cadmium precursor was prepared according to method by Pan *et al* [62]. 20 mmoles of myristic acid and 10 mmoles of cadmium oxide (CdO) were mixed and heated at 200^{o}C until the clear solution was obtained. Then the material was recrystallized in toluene and dried in an oven. The structure of Cd-MA can be seen in Figure 2.1.

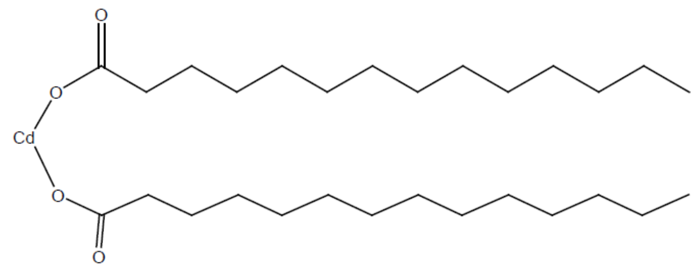


Figure 2.1: Molecular structure of cadmium myristate

2.1.2 Synthesis of NaHTe as Te precursor

The tellurium precursor was synthesized according to a previously published article [63]. 10 mg of Te was weighed carefully and putted 50 ml reaction flask and it was purged with N_2. Then, 15 mg of $NaBH_4$ was dissolved in 10 ml distilled water under N_2 atmosphere. Later, this solution was transferred to tellurium flask fast with the help of syringe. The reaction mixture was heated to 60^{o}C until all Te solids were dissolved and by the end of the reaction NaHTe was obtained. Formation of NaHTe was observed due to change of color of the synthesis medium (purple color was observed.).

Furthermore, impact of the Te-S amount in other words materials in the non-polar phase was investigated. Amount of the Te-S was doubled and cut in half and their optical and structural features were compared with the one that has normal amount of Te-S.

2.2 Synthesis of Quantum Dots

2.2.1 Synthesis characteristics of CdTeS QDs

In this thesis, highly luminescent CdTeS QDs were produced. All the experiments were made with a three necked 250 ml flask. Three necks were utilized for the N_2 gas flow, addition of non-polar phase after the polar phase and cooling tube. In all experiments, polar phase was water and non-polar phase was toluene. The starting time of the formation of QDs was accepted as the polar and non-polar phase were mixed.

Oleic acid (OA) was used as a surfactant in the thesis to get monodisperse nanocrystal since the temperature was not enough parameter for the producing monodisperse crystal structures. Its molecular structure can be seen in Figure 2.2.

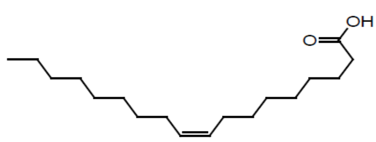


Figure 2.2: Molecular structure of oleic acid

2.2.2 Synthesis of CdTeS QDs

Firstly, 0.1 g of Cd-MA and 1.50 g of OA was weighed for non-polar phase. Then, these materials were dissolved in 50 ml of toluene in the 100 ml glass flask and the solution was purged with N_2 atmosphere until the Cd-MA was dissolved.

Later, 60.0 mg of thiourea was dissolved in 45 ml distilled water in the three-necked flask under the N_2 gas for the polar phase. After all solution was saturated with N_2, the prepared NaHTe solution was added with the help of the syringe in order to keep the solution away from the oxygen.

Lastly, the solution of Cd-MA and OA in other word non-polar phase was added to three-necked flask to start the formation of the quantum dots under N_2 at 100°C. After these mixing the two phases, the 1-2 ml of the sample was taken every thirty minutes to investigate the formation of the quantum dots under UV light. The reaction was stopped according to the color of the quantum dots after the 1, 2 or 3 day. Different colors emission of QDs under UV lamp can be seen in Figure 2.3. The green, yellow and red color obtained after one, two and three-day reaction started, respectively.

In order to investigate the effect of the Te-S amount, the quantity of Te precursor was changed. All the steps were the same. The only difference was that the amount of Te, and $NaBH_4$ was doubled or cut in half and dissolved in appropriate liter of distilled water.

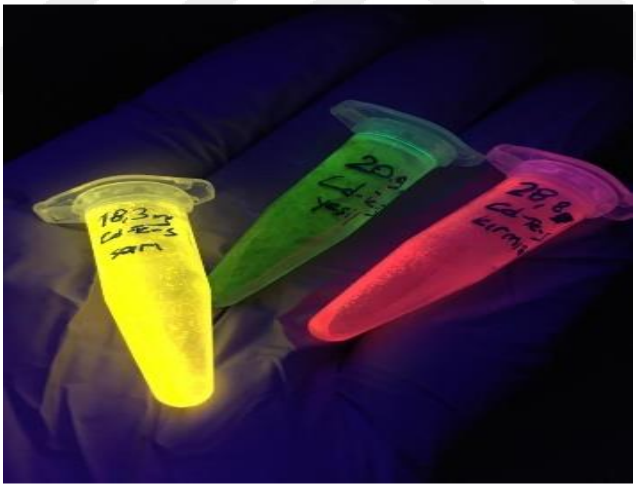
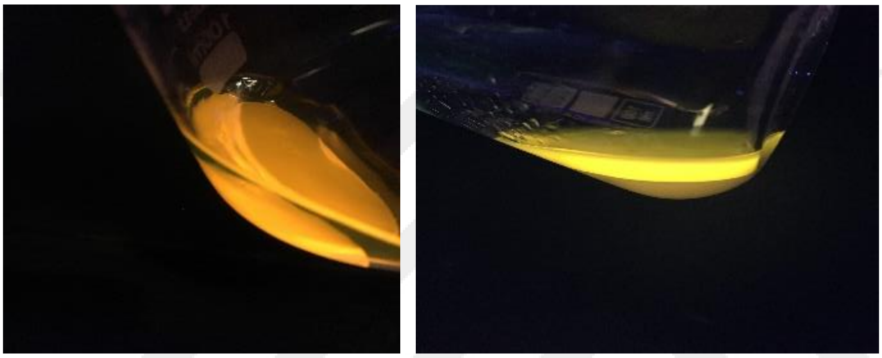


Figure 2.3: The emission colors of CdTeS QDs under UV light (366 nm) irradiation for samples obtained at 1, 2 and 3 day.

2.3 Functionalization of QDs

The quantum dots which produced here was soluble in organic solvent like toluene, chloroform etc. However, water soluble quantum dots are also needed according to application areas. There are some methods to make the QDs water soluble like ligand exchange, silica encapsulation and hydrophobic interaction. In this thesis, ligand exchange method was utilized according to Zhang *et al* [64] method to get the water soluble QDs since this method does not alter immensely the optical properties of the quantum dots.

In order to make the QDs water soluble, 5 mg of solid QDs were taken as they precipitated from toluene to methanol. Then solid QDs were dissolved in 5 ml of chloroform. At the same time, 5 ml of N-acetyl-L-cysteine (NAC) or L-cysteine (CYS) were dissolved in freshly prepared 5 ml of 1 M NaOH to adjust the pH 10. These two solutions were putted together in a flask and were mixed for 3-4 hours in a shaker. At the beginning, QDs were in the chloroform phase, after shaking QDs went up to the polar phase as in the Figure 2.4 for the bright yellow QDs.



a b

Figure 2.4: The emission of QDs under UV; a) before and b) after ligand exchange process. Lower phase is chloroform, upper one is NaOH solution.

2.4 Characterization of Quantum Dots

2.4.1 Optical characterization

The characterization of QDs involves optical and structural group. For the optical characterization, UV Visible and fluorescence spectroscopy were used. Varian Cary Eclipse fluorescence spectroscopy was used for the emission and excitation spectrums. The excitation wavelength was 350 nm for the synthesized QDs. The absorption properties of QDs were investigated with the Scinco-Neosys-2000 Double-Beamed UV-Vis spectrophotometry.

2.4.2 Structural characterization

High-Resolution Transmission Electron Microscopy (HR-TEM), X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD) were used for the structural characterization of QDs. To understand the size and shape of the QDs, JEOL JEM-

ARM200CFEG UHR-TEM was used. XPS measurements were taken with Thermo Scientific K-Alpha with a monochromatic 1486.68 eV Al Kα X-ray line source and a 400 μm beam size for the elemental and formation analysis. XRD analysis was made with Rigaku Smartlab X-Ray Diffractometer with CuKα radiation (λ = 1.5406^0 A). The XRD data was collected in a step scanning mode in the rage from 10^0 to 60^0.

3. RESULTS AND DISCUSSION

Firstly, the condition of the QDs were investigated under UV lamp with a wavelength of 336 nm every 30 minutes after the mixing the two immiscible phases. The 1-2 ml samples from the reaction were taken to understand the emission wavelength of the QDs with naked eye. The color of the QDs were seen under UV lamp which can be seen in the Figure 3.1. First one on the left were taken after 3 hours from starting which is bright green. The bright yellow and orange ones in the middles were taken after 1 and 2 days respectively and lastly the red on the right one was taken after 3 days.

From the figure 3.1, it can be said that the size of the QDs are getting bigger and the color of the QDs shifts to red from blue as the reaction occurs. However, these results are only depending on the naked human eye. For the confirmation of this phenomena, other optical measurement depends on fluorescent and absorption were made.

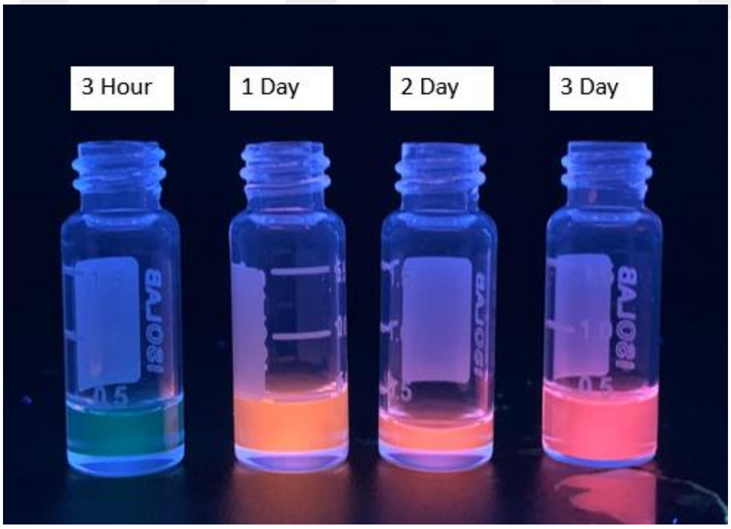


Figure 3.1: Size-tunable emission colors of CdTeS QDs under UV light in toluene. From left to right, size is getting bigger.

3.1 Optical Results

The CdTeS QDs were solved in toluene to investigate the luminescence intensity. The samples from QDs were taken in 1, 2 and 3 days at same hour. The wavelength vs luminescence intensity graph can be seen in Figure 3.2.

According to graph, intensity and line width of the emission spectra of both 1, 2 and 3 days are the same which indicates that they have same grown tendency. Also, the sharp and narrow peak of spectra points out size distribution of QDs. After one day, the wavelength is around 560 nm and this shifts to 640 nm one day later. However, there is no enormous change after 2 days because of the saturation of QDs with Te. The maximum wavelength of the CdTeS QDs, which is achievable after 3 days, is around 660 nm.

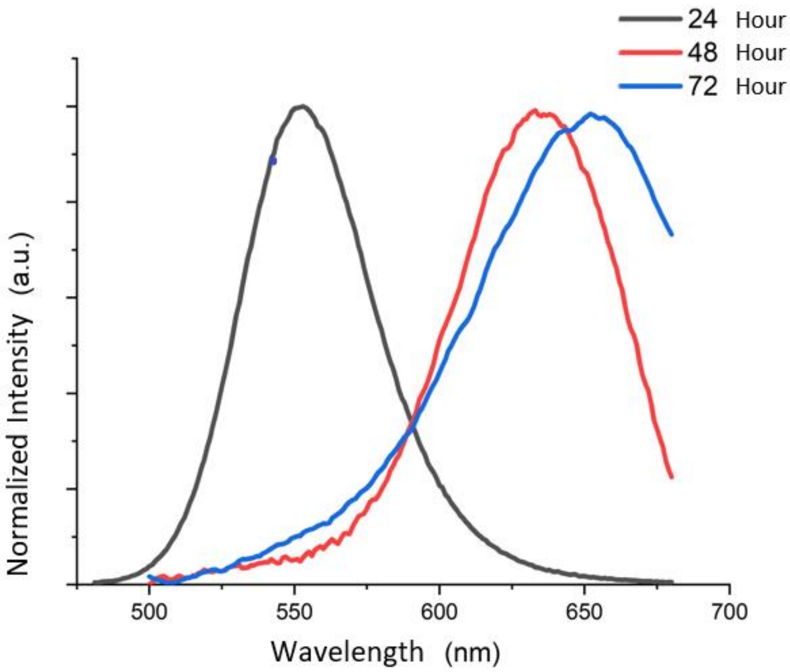


Figure 3.2: The emission spectra of CdTeS QDs at different reaction time.

Furthermore, photo luminesce of CdTe and CdS QDs are compared with CdTeS one. According to results from literature, highest wavelength of the CdTe and CdS QDs is only around 617 and 545 nm, respectively [65-66]. In the light of these findings, CdTeS QDs has higher emission wavelength than the CdTe and CdS ones. Addition of the sulphur atom to CdTe QDs with two-phase synthesis method cause the shifting of the emission wavelength to the red region.

After that, the emission spectra are investigated for the 1 and 3 hours. Normal amount of Te is excited at 350 nm as in Figure 3.3. There is no intensity 1 and 3 hour after the starting, in other words QDs doesn't come into existence. As a result, it can be said that the constitution of CdTeS starts after one day which is slow.

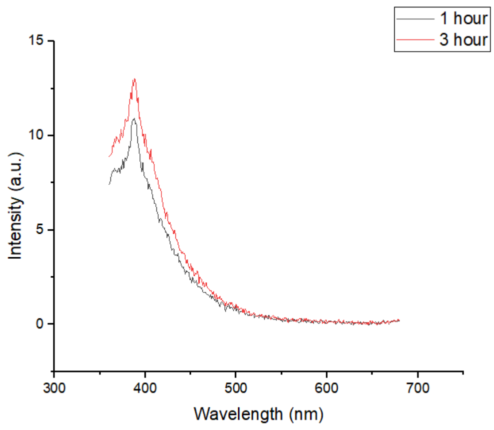


Figure 3.3: The emission spectra of CdTeS QDs at 1 and 3-hour with normal amount of Te at 350 nm excitation wavelength.

Later, the photoluminescence study is made to the samples that comprise different quantity of Te precursors. There are 2 different samples that each of them has half and double amount of Te respectively. The two of them is excited at 350, 400 and 450 nm. Figure 3.4 displays the photoluminescence intensity vs wavelength graphs for 2 separate samples one day after the starting of reaction. According to results, the first thing that attracts the attention is the decrease of the intensity in half for both 350, 400 and 450 nm as the amount of Te doubles. Also, both graphs of normal and half amount of Te have one peak and means of full width at hall maximum (FWHM) are 38,2 and 89,5 for half and normal amount respectively which indicates half amount of Te has more homogeneous size distribution than normal one. Lastly, double amount of Te has the lowest intensity with lowest peak wavelength in three of them which is 500 nm. It is quite clear that excess amount of Te affects the not only the intensity but also the size of the QDs where both are the smallest.

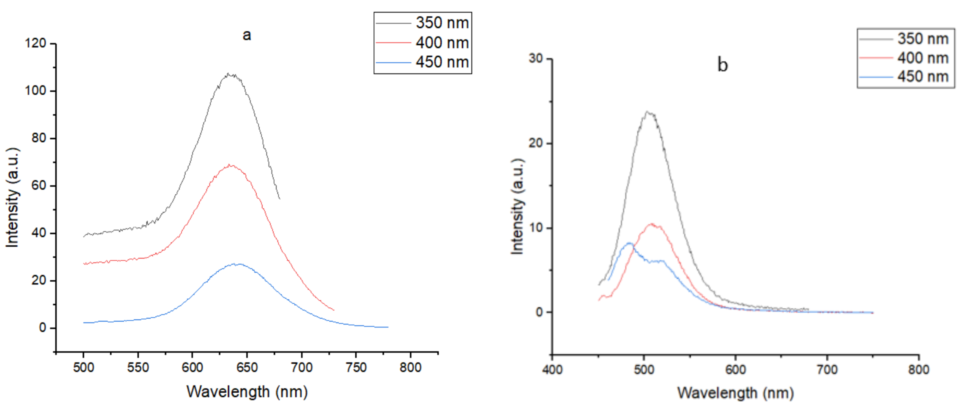


Figure 3.4: The emission spectra of CdTeS QDs with a) half and b) double amount of Te with different excitation wavelengths.

For better comparison, emission spectra of three of them at 350 nm is putted together in Figure 3.5. It is much clear from graph that as the amount of the Te increases, brightness of the CdTeS nanocrystals decreases twice which also affects the QY of the QDs. According to normalized intensity, it is seen that normal amount shifts slightly to the red region despite it has a lower intensity than half amount. The double amount of Te has only one broad peak around 500 nm which also indicates us that the growth tendency is so slow for the double Te amount.

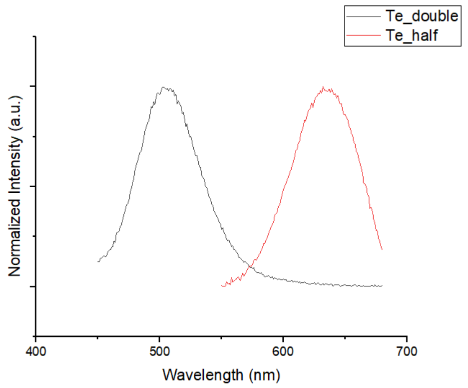


Figure 3.5: The emission spectra of CdTeS QDs excited at 350 nm with normalized intensity.

The excitation spectra of CdTeS QDs are taken for 3 different samples after 24 hours as in Figure 3.6. The graph has one sharp peak around 325 nm for normal and half amount of Te. Due to the normalized graph, it can be also said that normal amount of Te shifts to the red region slightly with respect to half amount. However, there is no sharp peak for the double amount, the peak around 325 nm disappears. Also, intensity of these peak decreases, as the amount of Te increases.

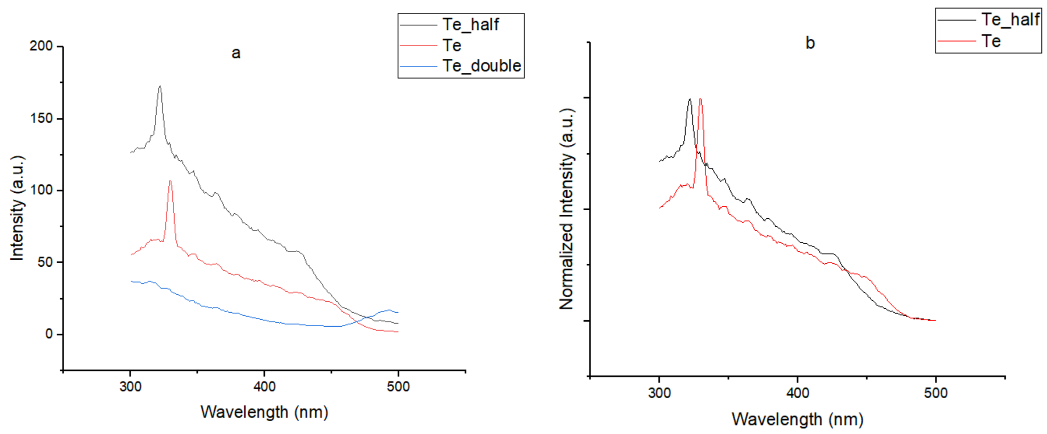


Figure 3.6: The photoluminescence excitation spectra of CdTeS QDs a) measured and b) normalized intensity.

After the optical results of non-polar phase, polar phase is investigated. All the CdTeS QDs are functionalized with NAC or L-cysteine. Firstly, normal amount of Te, which is yellow, are functionalized. Their emission graphs can be seen in Figure 3.7. The intensity of NAC capped QDs gives better intensity than CYS capped ones and both have one peak around 610 nm.

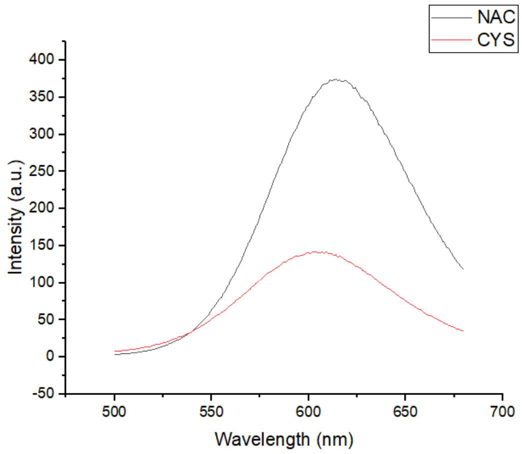


Figure 3.7: Emission spectrum of water soluble yellow QDs excited at 350 nm.

Later, QDs with red color is capped with NAC. Its fluorescence result shows that it has narrow peak around 700 nm which has 13,044 FWHM as in Figure 3.8. This result indicates the narrow size distribution of red QDs in water phase.

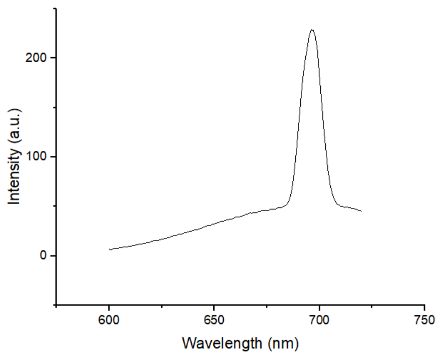


Figure 3.8: Emission spectrum of NAC capped red QDs excited at 350 nm.

For the comparison, the graphs of NAC capped QDs, having two and three-day growth, is putted together in Figure 3.9. As expected, the one-day QDs, which is yellow under UV light has broad peak around 620 nm and the other one has narrow peak around 700 nm which is red under UV. However, the brightness of the yellow one is double than the red one which gives better results for the QY.

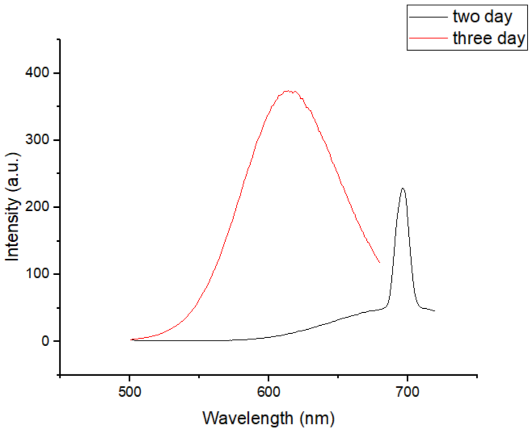
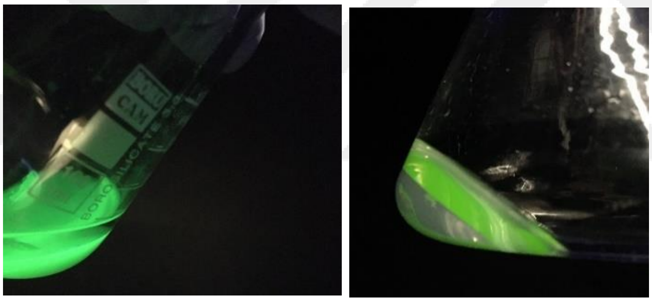


Figure 3.9: The emission spectrum of two and three-day NAC capped QDs excited at 350 nm.

Lastly, the fluorescence properties of the double amount Te is investigated. It is also capped with both NAC and CYS for the comparison which can be seen before and after shaking in Figure 10. According to graphs, they have not only close intensity but also close wavelength around 550 nm for NAC and 575 nm for CYS as in Figure 3.11.



a **b**

Figure 3.10: The emission of double amount of Te under UV lamp; a) before and b) after ligand exchange process

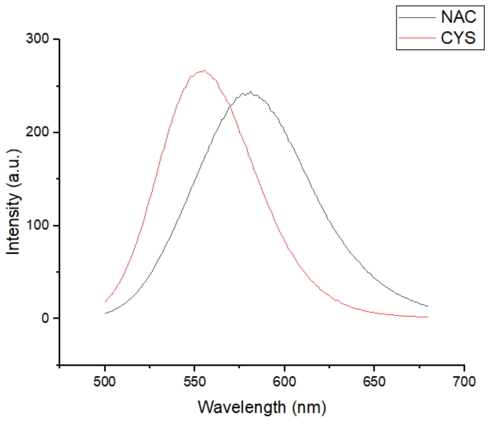


Figure 3.11: The emission spectra of double amount of Te capped with NAC and CYS excited at 350 nm.

After the emission analysis, the absorption study was made with UV-Vis spectroscopy. The synthesized QDs were solved in toluene like in florescence spectroscopy. Firstly, the results were taken for the half, normal and double amount of Te. The wavelength versus intensity graph can be seen in Figure 3.12. According to figure 3.12, three of them has peak around 250 nm and the normal amount of Te has the highest intensity among them.

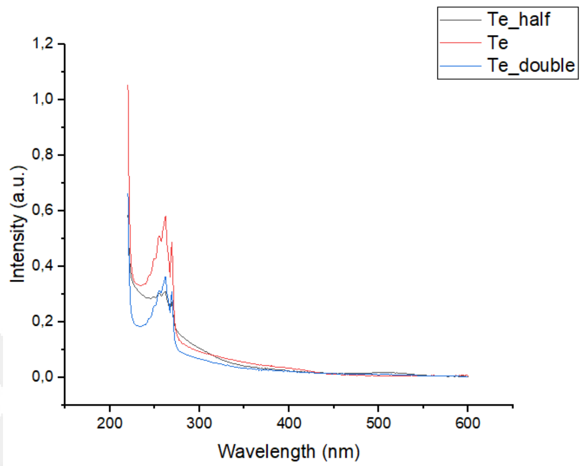


Figure 3.12: The absorption spectrum of half, normal and double amount of Te.

After that, absorption properties of QDs, having 2 and 3-day growth, are compared in Figure 3.13. According to graph, both of 3 and 2-day QDs, which are red and yellow respectively, have same peak around 225 nm. However, the intensity of the yellow QDs s higher than the red ones.

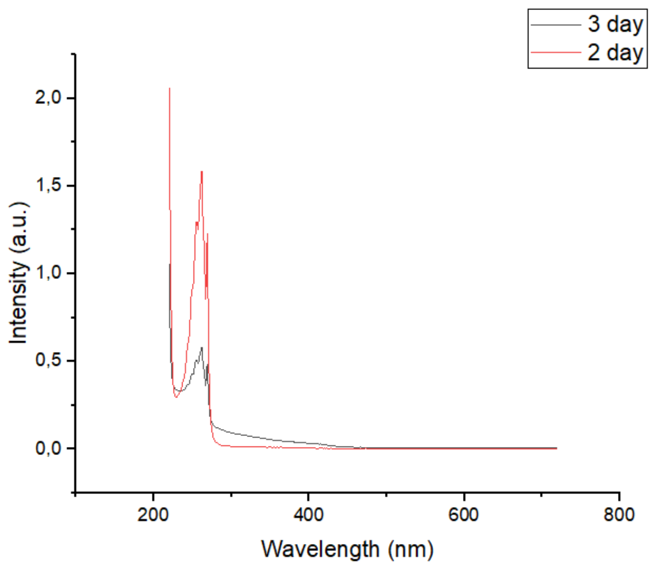
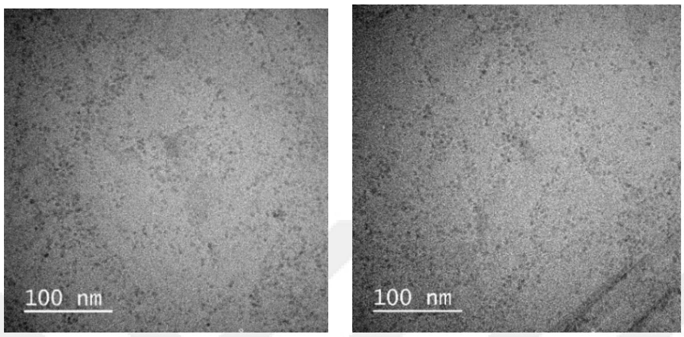


Figure 3.13: The absorption spectrum of QDs after 2 and 3 days.

3.2 Structural Results

Size and mono-dispersity of CdTeS QDs were analyzed by HR-TEM. According to Figure 3.14, both 2 and 3-day QDs, have uniform size distribution without aggregation. It can be also said that these QDs are close to spherical particles with good mono-dispersity. The yellow QDs, which have 2-day growth, range in size from 2 to 3 nm. And the other one, that is red, range from 5 to 6 nm.



a b

Figure 3.14: HR-TEM images of a) 2 and b) 3 days CdTeS QDs.

After that XPS analysis were made to understand the chemical composition of synthesized QDs after 1 and 2 days as shown in Figure 3.15. From the result, it can be said that time has affect not only the size of the QDs but also composition of the QDs. CdTeS QDs is mainly composed of Cd, Te, S, C and O elements. After 1 day, CdTeS QDs have generally Te-rich morphology. However, as the time passes these phenomena alters and the QDs become S rich morphology. According to this, CdTeS QDs are non-homogenous nano-alloy structure. At first, the core and surrounding area are mainly composed of Te and S, respectively. Moreover, as the time went by it becomes S rich.

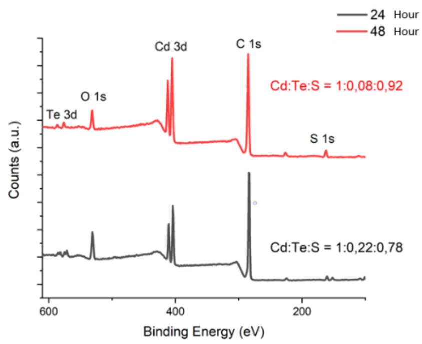


Figure 3.15: XPS spectra of CdTeS QDs after 1 and 2 day begining.

The XRD spectra of the synthetized QDs can be seen in Figure 3.16 which gives the better insight for the crystal structure. The result is compared with the CdTeS QDs that fabricated with other methods and CdTe QDs. The CdTeS QDs has closer diffraction pattern of CdTe QDs than CdSe QDs. It can be said that the structure of these QDs is cubic zinc-blend according to three diffraction peaks which correspond to (111), (220) and (311) peaks starting from lower angles [67-68]. As shown from the graph, the diffraction peaks of (111) plane shifts towards large angles with increasing amount of Te. Furthermore, the patterns shift to pure CdTe as amount of Te increases. The diffraction peaks of (220) and (311) also shifted to from pure CdS to pure CdTe pattern.

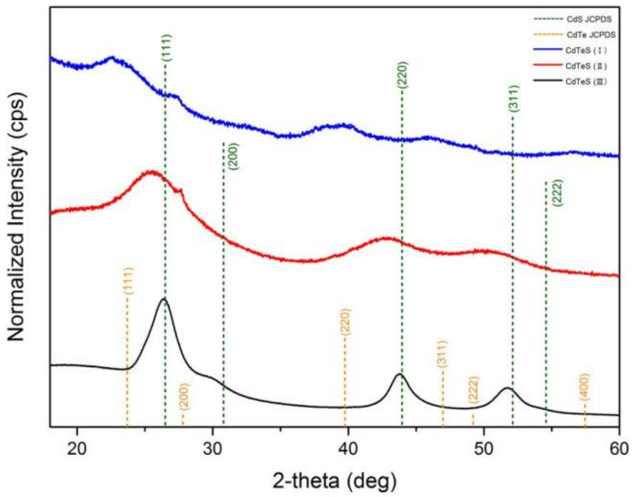


Figure 3.16: XRD spectra of the CdTeS QDs.

4. CONCLUSION

Nanomaterials have gained attraction since last century due to its unique physical properties. Among them, QDs type of nanocrystal have more characteristic properties as a result of the quantum confinement effect. These little materials can be excited with large range of wavelength, but they also emit certain wavelength at the same time due to discrete energy levels under the Bohr radius. In other words, the same composition of the QDs emits the different color as the size of the QDs gets bigger. These unique optical property makes the perfect candidate these material from the photovoltaic cells to biological identification of the molecules.

In these thesis, CdTeS QDs were synthesized with the two-phase method. The different color of the quantum dots was observed as time passed at the same temperature. The color was changed from green to red 3 days after starting of the reaction. The color of them was adjusted according to UV lamp. Later, the investigation of the polar phase precursors, Te, was made as their amount was doubled and cut in half. At the second stage, the synthesized CdTeS QDs was functionalized with NAC and L-CYS to make them bio compatible.

After that optical and structural test were made. The photoluminescence was used to observe emission and excitation peaks of the QDs. The wavelength of the with the normal amount of Te QDs shifted to the red region as it became 3 day after the starting. The amount of the Te decreased intensity of the wavelength as the amount increased, however it didn’t affect the wavelength. After one day, normal amount of Te had the highest wavelength among three of them despite lower intensity than half amount. The luminescence of the polar-phase was better for the NAC capped yellow QDs than L-CYS capped which had normal amount of Te. Also, red QDs displayed narrow peak around 700 nm at polar phase. Furthermore, double amount of Te showed brightness at polar-phase around 500 and 550 nm with L-CYS and NAC, respectively. The absorbance spectrum of the QDs gave only peak around 250 nm for double and normal amount and 2-3 days QDs.

For the structural characterization, HR-TEM results displayed the monodispersity and spherical structure of the CdTeS QDs. According to XPS, QDs had Te dense structure after 1 day; however, S character of the QDs increased after 2 day. It showed that the QDs had CdTe character at the center, CdS at the core which was type of gradient. XRD also revealed the CdTe zinc-blend structure of the QDs as it had similar diffraction pattern with CdTe QDs.

In the light of these findings, the CdTeS QDs were produced by the two-phase method. The synthesized quantum dots also can be used in biological application due to the solubility in polar phase.

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