

**RENDERING OPTICAL AND STRUCTURAL
PROPERTIES OF SEMICONDUCTOR
NANOCRYSTALS BY CHEMICAL DOPING**

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ABSTRACT

RENDERING OPTICAL AND STRUCTURAL PROPERTIES OF SEMICONDUCTOR NANOCRYSTALS BY CHEMICAL DOPING

Semiconductor nanocrystals are widely used in technologic applications because of their unusual and tunable optical properties. In this study we synthesized two type of semiconductor nanocrystals by the aqueous synthesis method. Colloidal HgCdTe semiconductor nanocrystals were synthesized by cation exchange reaction at room temperature. The absorption and photoluminescence spectra of water dispersible semiconductor nanocrystals appeared in NIR range of the electromagnetic spectrum. Aging process showed higher shift to red region in absorption and fluorescence spectra for HgCdTe nanocrystals. Increasing the initial Hg: Cd mole ratio spectral tuning was achieved. The size of the semiconductor nanocrystals was controlled between 8 nm to 44 nm by selecting the size of initial CdTe nanocrystals. Water dispersible Gd doped CdTe nanocrystals were also studied by changing initial Cd:Gd mole ratio. CdS shell was formed in order to make more compact and stable Gd doped CdTe nanocrystals. Size of Gd doped CdTe/CdS nanocrystals was tuned up to 38 nm by increasing initial Gd content. The optical spectra of Gd doped CdTe nanocrystals were in the range from 535 nm to 555 nm after 4 hours reaction time. Photoluminescence quantum efficiencies of Gd doped CdTe nanocrystals were measured and found out that doping Gd, decrease the quantum yield of nanocrystals. We concluded that CdTe nanocrystals can be used to synthesize doped nanocrystals by chemical doping. We demonstrated that optical and structural properties of Hg and Gd doped CdTe can be rendered by chemical doping.

ÖZET

YARI İLETKEN NANOKRİSTALLERİN OPTİK VE YAPISAL ÖZELLİKLERİNİN KİMYASAL KATKILANDIRMA YLA DÜZENLENMESİ

Yarı iletken nanokristaller ayarlanabilir ve farklı optik özelliklerinden dolayı teknolojik bir çok alanda geniş bir kullanım alanına sahiptirler. Bu çalışmada optik özellikleri farklı iki ayrı yarıiletken nanokristal su içinde sentezlenmiştir. Bunlardan biri yakın kızılötesi bölgede ışıma yapan HgCdTe nanokristalleri savunma sanayisinde gece görüş sistemlerinde kullanılabilmesinden dolayı çok tercih edilen malzemelerdir. Kolloidal HgCdTe yarıiletken nanokristalleri oda sıcaklığında katyon yerdeğiştirme reaksiyonuyla sentezlenmiştir. Suda dağılılabilen HgCdTe yarıiletken nanokristallerinin soğurma ve ışıma spektrumları, başlangıç Hg: Cd mol oranının artmasıyla NIR bölgeye kaymıştır. Yaşlandırma işlemi HgCdTe nanokristallerinin soğurma ve ışıma spektrumlarında daha çok kırmızı bölgeye kayma göstermiştir. Nanokristallerin büyüklükleri, başlangıçtaki CdTe nanokristallerinin büyüklüğünün kontrolüyle, 8 nm ile 44 nm arasında değiştirilemektedir. Bu çalışmada ayrıca Gd katkılı CdTe nanokristalleri de sentezlenmiştir. Gd katkılı nanokristallerin üzerine CdS kabuğu oluşturularak, nanokristallerin daha küçük ve kararlı olmaları sağlanmıştır. Başlangıç Cd:Gd mol oranı değiştirilerek nanokristallerin büyüklüğü Gd başlangıç miktarının artırılmasıyla 38 nm'ye kadar büyümüştür. Fotoluminesans kuantum verimleri ölçülmüş ve Gd katkılılandırıldığında kuantum verimlerinin düştüğü gözlemlenmiştir. Bu çalışmada CdTe nanokristalleri kullanılarak kimyasal katkılandırma ile katkılı nanokristallerin sentezlenebileceği sonucuna vardık. Hg ve Gd katkılı CdTe nanokristallerinin kimyasal katkılandırma ile optik ve yapısal özelliklerinin değiştirilebileceğini gösterdik.

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CHAPTER 1

INTRODUCTION

1.1. Nanotechnology and Nanocrystals

Today's one of the most developing science field is the nanotechnology which deals with the nanoscale materials like atoms and molecules. Origin of the nanotechnology is discussible but the lecture called "Plenty room in the bottom" by Richard Feynman (Feynman 1960) is the most accepted one about birth of the nanotechnology. He claimed that scalable materials could be replicated itself in miniature to molecular scale. Various techniques use nanotechnology for the manipulation of particles on the nanometer scale (Hughes 2000).

Nanotechnology and nanoscience are the combinations of the study of nanoscale objects and systems. Nanoscale obejects are smaller molecules than structures that are used in microtechnologies which provides the useful physical behaviours like quantum confinement efect. An important science field in the development of nanoscience is chemistry which able to form this nanoscale structures like nanospheres, nanorods, nanowires etc.. with different compositions like metals, oxides, organics and semiconductors. These nanostructures could be used in electronic and optical devices, medicine as drug delivery systems, or catalysts (Love et al. 2005).

Nanocrystals, which are the backbone in nanotechnology, are semiconductor quantum dots (QDs) which are tiny, light emitting nanometer scale particles with unique optical and electronic properties. Colloidal semiconductor nanocrystals are single cystals which has a few nanometer diameter size. The size and the shape of the nanocrystals are controlled by the temperature, stabilizers used in the synthesis etc. Quantum dots are also preferred than organic dyes and fluorescent proteins because of their 10 - 50 times larger molar extinction coefficients. This property makes them brighter in photon-limited applications (Nie et al. 2007).

Quantum dots could be synthesized by the semiconductor materials from periodic table group II-VI as CdS, CdSe, group III-V as InP, InAs.. group IV-VI as PbSe.

Figure 1.1 shows the experimental data from literature which depends on the emission maxima and the sizes of different types of nanocrystals with different composition. They have different bulk band gap energies. The emission wavelengths ranges between 400 to 1340 nm, and the size varies from 2 to 9.5 nm (Michalet et al. 2005). Especially cadmium based nanocrystals have tunable optical properties as shown in Figure 1.1 that these types of quantum dots are very attracted by researches nowadays.

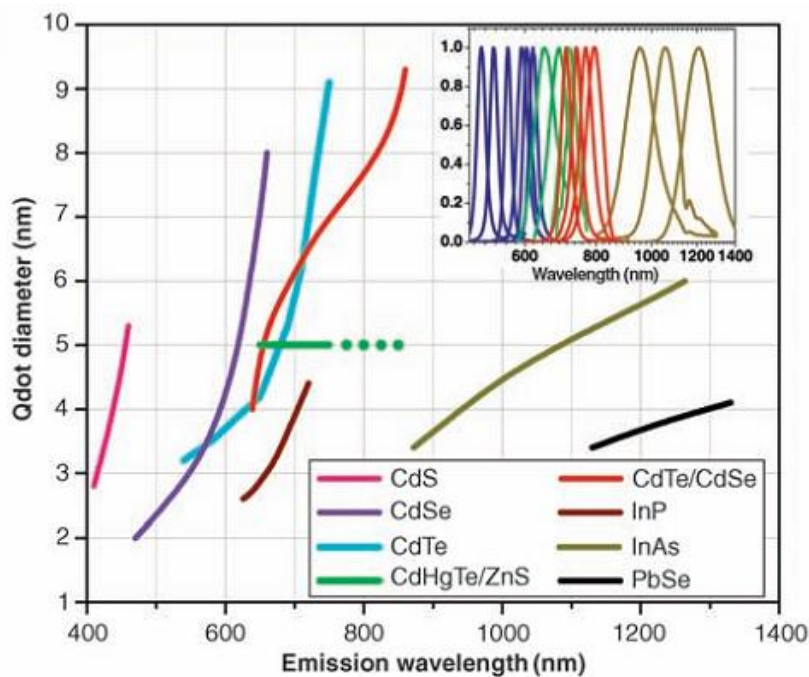


Figure 1.1. Emission maxima and sizes of nanocrystals of different composition.
(Source : Michalet et al. 2005)

Quantum dots could be classified in to three group as doped quantum dots, core and core / shell type quantum dots. Core type semiconductor nanocrystals contains at least two atoms like CdTe, CdSe, CdS, ZnTe, ZnS, PbS etc.. Alloy nanocrystals also exist as HgCdTe, ZnCdTe, CdSeTe etc.. Different synthesis methods for these kind of quantum dots exist before 1980, however in 1993, Murray et al. developed a new synthesis method to obtain monodisperse, high quality CdS, CdSe and CdTe nanocrystallites. The synthesis is basically the pyrolysis of organometallic reagents by injection into solvent by heating. The size of the crystallities lies between 12 Å and 115 Å (Murray, Norris, and Bawendi 1993). In core / shell quantum dots, core nanocrystal coated with a shell which contains different types of atoms. CdTe/CdS, CdSe/ZnS,

ZnCdTe/CdS etc... are the some of the examples for core / shell quantum dots. Covering with a shell provides an enhancement in optical properties of nanocrystals. Both photostability and photoluminescence quantum efficiency increase by means of shell part. In a study, CdSeTe nanocrystals were covered with ZnS shell as shown in Figure 1.2. Synthesized nanocrystals had high photoluminescence quantum efficiencies, photostability and biocompatibility. These properties provides utility in cell imaging and biosensing with great sensitivity (Liang et al. 2010).

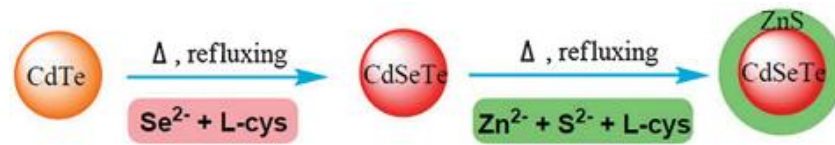


Figure 1.2. Schematic illustration of the synthesis of water-soluble CdSeTe/ZnS nanocrystals. (Source : Liang et al. 2010)

Doped semiconductor nanocrystals are simply quantum dots modified by adding small percentage of different atoms in order to change optical, electrical and compositional properties of nanocrystals.

In literature semiconductors were doped with Mn, Cu etc. In a study, color tunable Mn doped ZnSe nanocrystals were synthesized by aqueous synthesis. First of all MnSe core was formed then, Zn(Oac)₂ solution and 3- mercaptopropionic acid (MPA) were added to the solution several times in order to obtain Mn doped ZnSe quantum dots. PL spectroscopy was used to control growth of the nanocrystals. Stable quantum dots had tunable fluorescence spectra between 572 nm to 602 nm (Shao et al. 2011).

Organometallic method also studied for Cu and MnSe doped ZnSe nanocrystals. ZnSe core nanocrystals had tunable PL emission spectra. According to the articles MnSe doping to ZnSe nanocrystals increase the usage of these quantum dots interest in spintronics. Cu doped ZnSe nanocrystals could be used to study about confinement effect (Pradhan et al. 2005).

1.2. Synthesis of Nanocrystals

Various synthesis methods for semiconductor quantum dots were studied nowadays. Choosing the proper synthesis method is important to obtain quantum dots with desirable optical and compositional properties.

Quantum dots were synthesized mainly by four different chemical synthesis, which are organometallic approach, two phase approach, solvothermal approach and one pot aqueous approach.

1.2.1. Two Phase Approach

Two phase approach is more preferable method in case of low toxicity and easy-performing. Lower temperature requirement is an advantage for two phase method, however reaction goes slowly. Two phase method was firstly used to synthesize 1 - 3 nm gold nanocrystals. Thiol capped gold nanocrystals were formed by the reduction of AuCl_4 by sodium borohydride in the presence of an alkanethiol solution (Brust et al. 1994). Some noble metal nanocrystals were synthesized by this method successfully. However semiconductor nanocrystals started to synthesize by two phase method with Pan et al. in 2004. They synthesized highly luminescent, monodisperse CdS nanocrystals. Nanocrystals occurred in the toluene – water interface easily and safely (Pan et al. 2004). The reaction mechanism for two phase synthesis of CdS nanocrystals were shown in Figure 1.3.

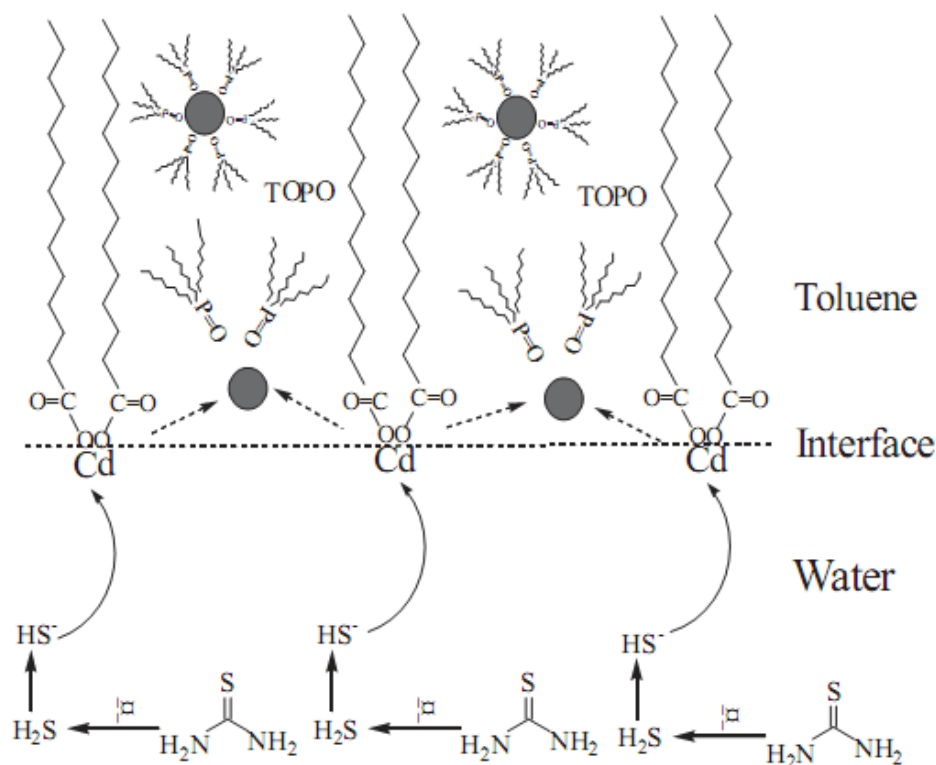


Figure 1.3. The mechanism for forming CdS nanocrystals with two phase method.
(Source : Pan et al. 2004)

1.2.2. Solvothermal Approach

In solvothermal synthesis, reaction occurs in stainless steel autoclave. Reaction mixture is prepared and put into teflon lined stainless steel autoclaves. Reaction temperature is adjusted for proper reaction time. Then the autoclaves are cooled to room temperature for characterization parts of the nanocrystals. Reaction temperature, reaction time, types of solvent, surfactant and precursors could be arranged to get desired nanocrystals. A simple and general one step surfactant – assisted solvothermal synthesis method was developed to synthesize three different kinds of metal tellurides which are CoTe, Ag₂Te/Ag and CdTe. These nanostructures were synthesized in the presence of Na₂TeO₃, ascorbic acid, PVP (polyvinylpyrrolidone) or CTAB (cetyltrimethylammonium bromide) in ethanolamine and water mixture. The reaction mixture was prepared and the autoclave was sealed. Reaction time was 24 hours, reaction temperature was 200°C (Jiang and Zhu 2010), (Jiang, Zhu, and Cui 2010).

1.2.3. Organometallic Approach

Organometallic synthesis is an earlier synthesis method in which hydrophobic surfactants like TOPO (trioctylphosphine oxide) and TOP (Trioctylphosphine) were used. Disadvantage of this method could be count as its high temperature requirement. One of the earlier example for organometallic approach is the study of synthesis of CdTe by pyrolysis of bis(4-methyphenyltelluro)cadmium in the solid state with 98 % yield (Steigerwald and Sprinkle 1987). Then, CdTe nanocrystals were synthesized with a novel organometallic approach. Different tellerium precursors were reacted with dimethylcadmium as Cd precursor. A mixture of dodecylamine and trioctyphosphine was used as organic solvent. The size of the cubic CdTe nanocrystals were between 2.5 and 7 nm. Highly luminescence CdTe nanocrystals showed strong and wide range in electromagnetic spectrum. Photoluminescence quantum efficiencies of nanocrystals was observed as up to 65 % (Talapin et al. 2001).

1.2.4. One Pot Aqueous Approach

An alternative to organometallic synthetic routes was developed by Gaponic et al. They synthesized thiol capped CdTe nanocrystals with higher photoluminescence quantum efficiency as up to 40 % by one pot aqueous sytnesis. This method is the most used synthesis method because it is less toxic and less expensive. Reaction occurs in aqueus medium, so the particles are water dispersible. Different groups like amine, mercapto groups are used as capping agents. Schematic presentation of the synthesis of thiol capped CdTe nanocrystals are shown in Figure 1.4. H_2Te which was formed by the reaction of H_2SO_4 and Al_2Te_3 , used as Te precursor and it was injected to the Cd precursor. Different Te precursors could be used, too. Formation and growth of CdTe nanocrystals occurs in the reflux. Schematic presentation of the synthesis of thiol capped CdTe nanocrystals were shown in Figure 1.4.

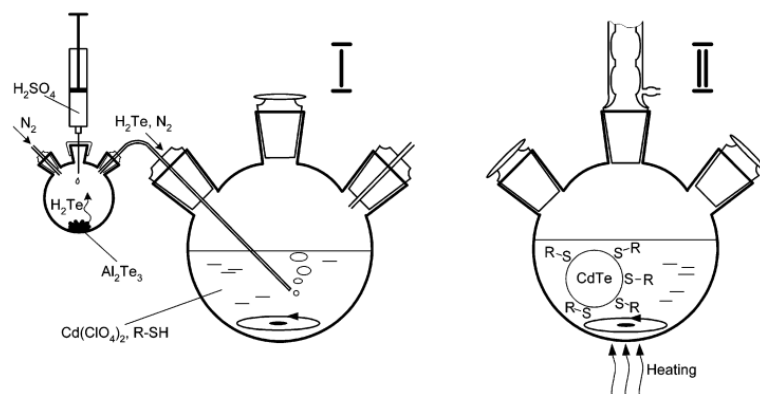


Figure 1.4. Schematic presentation of the synthesis of thiol capped CdTe nanocrystals.

1.3. Characterization of Nanocrystals

1.3.1. Optical Characterization

Excitation of electrons in atoms and molecules from ground state to excited states is termed as absorption of UV-Visible radiation. Absorbance (or optical density) is basically a logarithmic ratio of initial radiation to transmitted radiation through the material. It is directly proportional with the concentration, the extinction coefficient of the material and length of the light path. Each compound absorbs the light according to its chemical structure.

Compounds that have absorbed the light, emitted it at different wavelength. This process is called fluorescence. Generally, the fluorescence emission wavelength is larger than the absorption wavelength.

Absorption and fluorescence spectroscopies provide fast, non-destructive and contactless options (Drbohlavova et al. 2009). Also qualitative and quantitative information could be obtained from these optical characterization techniques.

Varian Cary 50 UV-Vis Spectrometer and Varian Cary Eclipse Fluorescence Spectrometer are used at room temperature in order to investigate the optical properties of synthesized HgCdTe and Gd-doped CdTe nanocrystals. Aliquots were taken from the reaction flask at different time periods and their optical characterization was recorded to control the growth of quantum dots.

Photoluminescence quantum efficiency (PL QE) could be calculated by absorption spectra and fluorescence emission spectra. Basically, quantum yield is the ratio of the number of emitted photons to the number of absorbed photons as shown in the equation below (Fery-Forgues and Lavabre 1999).

$$QY = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}} \quad (1.1)$$

Quantum yield and lifetime measurements could be understood by Jablonski diagram as shown in Figure 1.5. In this figure the absorption of sample is not shown in detail, however it is clearly seen that the emission of sample could be occurs by radiative and non radiative processes (Lakowicz 2006).

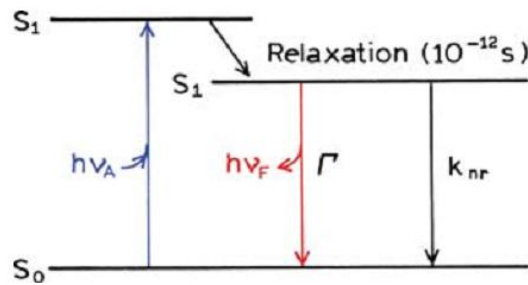


Figure 1.5. An example of Jablonski diagram
(Source: Lakowicz 2006)

Quantum yield could also be defined as the ratio of radiative and non-radiative processes as shown in equation below. k_r and k_{nr} are the rate constants of radiative and non-radiative processes of the sample, respectively (Fery-Forgues and Lavabre 1999).

$$QY = \frac{k_r}{k_r + \sum k_{nr}} \quad (1.2)$$

In order to calculate the quantum yield of the nanocrystals, a standard dye with a well-known quantum yield is used to compare. It is important to choose the proper dye for the calculation. Absorption and PL spectra of the reference dye should overlap with absorption and PL spectra of the nanocrystals. In this study, Rhodamine 6G is used as

reference dye for calculating the quantum yield of Gd doped CdTe nanocrystals. The absorption and fluorescence spectrum of Rhodamine 6G are shown in Figure 1.6.

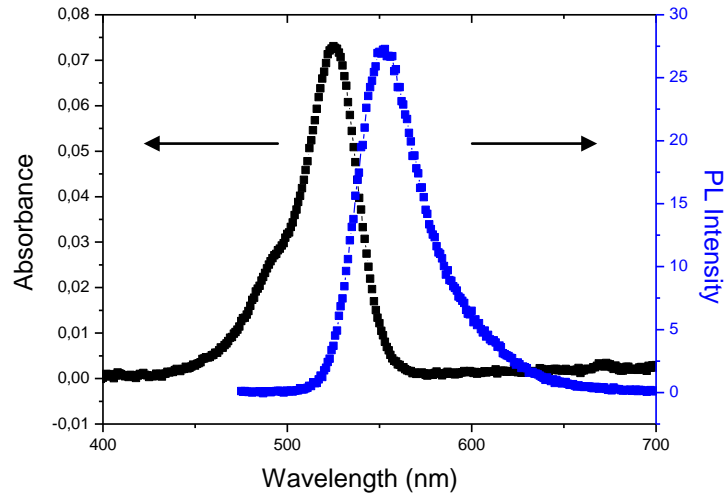


Figure 1.6. Absorption and fluorescence spectrum of Rhodamine 6 G which is a reference dye.

Both absorption and PL emission spectra of reference dye and nanocrystals were performed, then optical density (OD) from absorption spectra and integrated area (I) of fluorescence peak from fluorescence emission spectra were obtained. Quantum yield of the nanocrystals were calculated by the equation given below. η corresponds to refractive index of the medium (Fery-Forgues and Lavabre 1999).

$$QY = Q_{ref} \frac{I}{I_{ref}} \frac{OD_{ref}}{OD} \frac{\eta^2}{\eta_{ref}^2} \quad (1.3)$$

Time-resolved measurements are also an important part of fluorescence spectroscopy. In many cases like the overlap of emission and absorption spectra, time-resolved measurements provide more information than steady-state measurements. Most of these measurements are performed by time correlated single photon counting (TCSPC). The principle of TCSPC is simply, the excitation of sample by a pulse of light and then the measurement of time between excitation of sample and observation of photons (Lakowicz 2006). Lifetime measurements were recorded by FLS 920P, Edinburgh Instruments in Solar Energy Institute, Ege University. Photodynamic information about the synthesized quantum dots were obtained from fluorescence decay traces.

1.3.2. Structural Characterization

Structural characterization of synthesized semiconductor quantum dots was carried out by using X-Ray Diffraction (XRD), Dynamic Light Scattering (DLS) technique, Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) Scanning Transmission Electron Microscopy (STEM), Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM-EDS), Transmission Electron Microscopy (TEM) and X-Ray Fluorescence (XRF) Instrument techniques.

X-Ray Diffraction (XRD) measurements were carried out by Philips X-pert Pro Powder Diffractometer at IYTE-MAM (Material Research Center). XRD is one of the non destructive technique to reveal information about the chemical composition and crystal structure of the nanocrystals. Basically, XRD technique is based on observing the intensity of scattered X-Ray beam which hits the sample. Nanocrystals were purified with isopropanol and centrifugation technique, then powdered form of the nanocrystals were used for XRD analysis.

Scanning Electron Microscopy was used to obtain compositional information about the nanocrystals. In order to do this, Energy Dispersive X-Ray Detector (EDS), the most common accessory of SEM was used. Philips XL 30S FEG Scanning Electron Microscope at IYTE-MAM is used for the analysis. Also Scanning Transmission Electron Microscopy (STEM) at IYTE-MAM and Transmission Electron Microscopy (TEM) at Muğla Sıtkı Koçman University were used to display nanocrystals.

The size of the nanocrystals were investigated by Dynamic Light Scattering (DLS) Measurements by Malvern Zetasizer Nanoseries -Nano-ZS. Generally, the results obtained from DLS was bigger than the results obtained from TEM or STEM. It is exceptable because TEM measures the hard core of the nanocrystal but DLS measures both the hard core and the hydrodynamic diameter of the nanocrystals (Qian et al. 2007).

Elemental analysis was carried out by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) which is a kind of mass spectrometry. It is able to detect metals at the lowest concentrations by ionizing the sample with inductively coupled plasma and separating them by mass spectrometer. Inductively Coupled Plasma – Atomic Emission Spectroscopy was also used for compositional analysis. Difference from ICP-

MS is that in ICP-AES separation of the ionized sample analyzed by Atomic Emission Spectroscopy. Gadolinium and Cadmium ions were prepared by their standards to form calibration curve. 1% HNO₃ was used to disintegrate the nanocrystals to obtain compositional information. Gadolinium and Cadmium mole ratio was obtained by Agilent 7500ce Inductively Coupled Plasma/Mass Spectrometer and Varian ICP 96 model Inductively Coupled Plasma Atomic Emission Spectrometer

X-Ray Fluorescence (XRF) Instrument was also used to achieve compositional information. In this technique, material is excited by bombarding with high energy X-Rays. Then the material emits the characteristic fluorescent X-Rays. Spectro IQ II X-Ray Fluorescence Instrument was used at IYTE-MAM.

1.4. Purpose of This Study

The purpose of the study is to modify the optical properties of nanocrystals by chemical doping. Chemical modification of CdTe nanocrystals by Hg²⁺ and Gd³⁺ precursors were studied.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF NIR EMITTING HgCdTe NANOCRYSTALS

2.1. Introduction

Semiconductor nanocrystals are widely used in technologic applications because of their unusual and tunable optical properties. Various types of nanocrystals were synthesized with different synthesis methods as mentioned in Section 1.2. According to the size and composition, nanocrystals emit the light at different wavelengths in the electromagnetic spectrum. Compare to visible emitted nanocrystals, NIR emitted quantum dots such as HgCdTe nanocrystals are preferable in order to use materials for IR detector in defence industry, solar cells, bioimaging agents to improve tissue penetration, lower background interference, and reduced photochemical damage (Smith and Nie 2010). Also therapeutics and optoelectronics industry have been interested in NIR region emitted nanocrystals (Tang et al. 2007).

In literature NIR emitted nanocrystals have been mentioned widely. One of the mostly used synthesis method for HgCdTe nanocrystals is solvothermal approach. Facile, low-cost HgCdTe nanostructures was synthesized at different shapes such as nanorods, cubes and quantum dots with different size and compositions. The emission wavelength of the sample with composition $\text{Hg}_{0.2}\text{Cd}_{0.8}\text{Te}$ was 0.5 – 0.9 eV which is useful for optoelectronic applications. The average size of the HgCdTe nanostructures varied between 20 and 500 nm (Khatei, Pendyala, and Rao 2011). Smaller HgCdTe alloy nanocrystals could be synthesized in aqueous medium. Synthesis of HgCdTe nanocrystals by one pot aqueous approach were also studied. Thioglycolic acid capped HgCdTe nanocrystals had emission between 640 to 1600 nm in electromagnetic spectrum. This spectral region covers the second and third telecommunication windows. Photoluminescence quantum efficiencies of these particles were calculated as 55 %. Size of the nanocrystals were obtained from TEM as 4.2 nm after 22 hours reaction time (Lesnyak et al. 2009).

In our study, we practiced on cation exchange reactions in aqueous reaction medium. Thioglycolic acid capped CdTe nanocrystals were synthesized with one pot aqueous synthesis as mentioned before. Then, mercury precursor is added to the reaction flask to make cation exchange reaction between Cadmium and Mercury ions. Several articles are published according to the similar synthesis. Thiol-capped CdTe nanocrystals were covered with subsequent layers of HgTe and CdTe. Room temperature photoluminescence measurements showed that the nanocrystals gave emission between 800 to 1100 nm in electromagnetic spectrum according to the composition of nanocrystals (Rogach et al. 2001). Smith and Nie also studied on the synthesis of alloy HgCdTe nanocrystals by cation exchange reactions. CdTe nanocrystals were synthesized as seed for HgCdTe nanocrystals. Cd^{2+} replaced with Hg^{2+} as shown in Figure 2.1. Organic non polar solvents were preferred because of their advantage in controlling the growth process of nanocrystals with narrow size distribution and high crystallinity. Lattice parameters of cubic CdTe and HgTe nanocrystals are nearly identical. This causes that mercury cadmium cation exchange does not effect the size of the nanocrystals. Nanocrystal size was obtained from TEM as 6.5 nm and the hydrodynamic diameter was 10 nm for synthesized HgCdTe nanocrystals (Smith and Nie 2010).

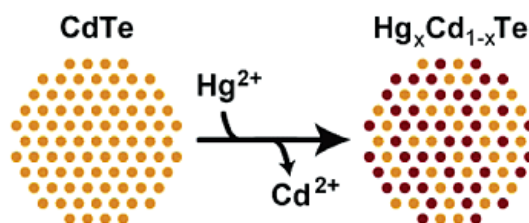


Figure 2.1. Schematic illustration of cation exchange reaction in HgCdTe nanocrystals.
(Source : Smith and Nie 2010)

2.2. Experimental

HgCdTe nanocrystals were synthesized by two step procedure. Firstly CdTe nanocrystals were performed and used as seed, then Hg precursor is added to synthesized CdTe nanocrystals by cation exchange reaction in order to synthesize HgCdTe nanocrystals.

2.2.1. Reagents

Metal sources, Mercury(II) perchlorate hexahydrate and Cadmium chloride were purchased from Sigma Aldrich. Thioglycolic acid (TGA, Merck), Sodium borohydride (NaBH₄, Merck) Tellurium powder (Fluka) were used throughout the synthesis. 2-propanol (Sigma Aldrich) was used to precipitate the HgCdTe nanocrystals.

2.2.2. Synthesis of CdTe Nanocrystals

In a typical synthesis of CdTe nanocrystals, cadmium and tellurium precursors are prepared individually.

2.2.2.1. Preparation of Te Precursor

Sodium hydrogen telluride (NaHTe) was prepared by the reaction in which sodium borohydride (NaBH₄) is oxidized by tellurium. The charge of Te changes from 0 to -2 as seen in the reaction below.



The reaction occurred under nitrogen or argon gas at 60°C. Resulted NaHTe could be oxidized with air easily, it should be synthesized just before the each experiment.

2.2.2.2. Preparation of CdTe Nanocrystals

One pot aqueous method was used to synthesize CdTe nanocrystals (Rogach et al. 2007). Cadmium precursor, CdCl₂, was dissolved in 110 mL of ultra pure water in two-necked flask with a septum. Thioglycolic acid was added as the thiol stabilizer. pH of the solution was adjusted to 11 by dropwise addition of 1 M of NaOH solution. The flask was attached to the condenser with deaerating by N₂ bubbling for an hour at 80°C. After an hour Te precursor was injected into the two-necked flask and the temperature

increased to 110°C. CdTe nanocrystals started to form. Formation and growth steps are proceed upon reflux. Growth of the nanocrystals were controlled by sampling at different time intervals. Dynamic Light Scattering (DLS) instrument, UV-Vis absorption and fluorescence spectroscopies were used to characterize the aliquots. The growth was stopped by cooling the solution to the room temperature.

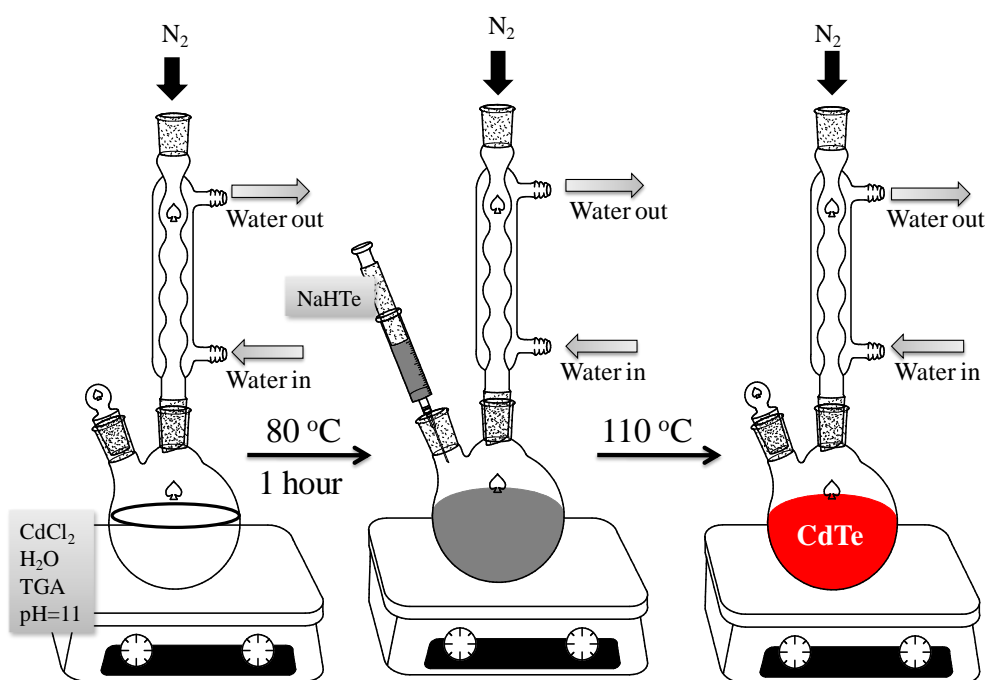


Figure 2.2. Schematic illustration of synthesis of CdTe nanocrystals

2.2.3. Synthesis of HgCdTe Nanocrystals

HgCdTe nanocrystals were formed by using CdTe nanocrystals. 0.03 M Hg(ClO₄)₂ solution was prepared as Hg precursor. Different amount of Hg was injected to the desired amount of CdTe nanocrystals in a flask with constant stirring at room temperature under open-air conditions with a condenser attached. Color of the solution turned to brown or black from orange/red according to the amount of Hg content. Growth steps were proceed in the flask. Purification steps were applied when desired size and absorption wavelengths were obtained. DLS technique and Absorption spectra were performed to control the growth of the nanocrystals.

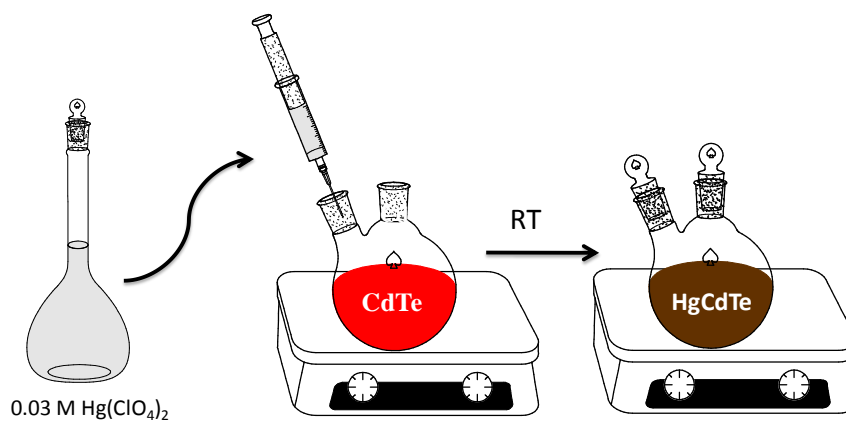


Figure 2.3. Schematic illustration of synthesis of HgCdTe nanocrystals

2.2.4. Precipitation of HgCdTe Nanocrystals

Isolation of HgCdTe nanocrystals were needed to remove excess reactants and impurities. For this process, precipitation was performed with isopropyl alcohol in centrifuge. After centrifugation, supernatants are extracted and resulted precipitate were left to dry at room temperature. The dried HgCdTe nanocrystals could be stored after saturation with an inert gas at refrigerator for months.

2.3. Results and Discussion

2.3.1. Optical Characterization

Optical characterization of HgCdTe nanocrystals were performed by Ultraviolet-visible absorption and fluorescence spectroscopies which are mostly used to control how the reaction proceeds.

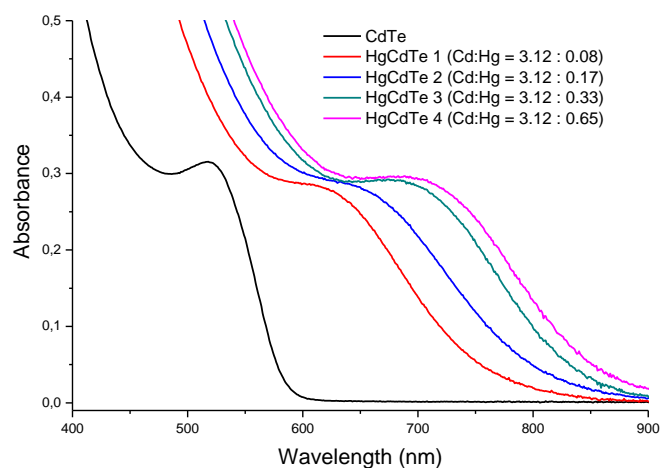


Figure 2.4. Absorption spectrum of HgCdTe nanocrystals with different initial Cd:Hg mole ratio. Increasing the Hg content resulted shifts to NIR range.

Figure 2.4 shows the absorption spectra of water dispersible CdTe and colloidal HgCdTe nanocrystals. Significant red shift was observed toward the NIR range. While CdTe nanocrystals absorb light at 520 nm, Hg addition resulted to shift of spectra between 615 and 700 nm according to the different Cd:Hg mole ratio. Higher Hg content resulted more shift in spectra.

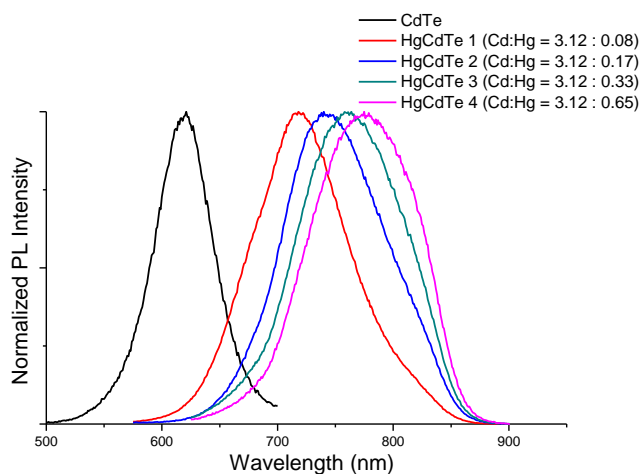


Figure 2.5. Normalized fluorescence spectrum of CdTe and HgCdTe nanocrystals with different initial Cd:Hg mole ratio. Spectra shifted to NIR range with increasing Hg content.

As such in absorption spectra, fluorescence emission spectra also showed the red shift as shown in Figure 2.5. CdTe nanocrystals emitted light at 620 nm. Following the addition of Hg precursor, emission peak of the nanocrystals shifted up to 720 nm for the nanocrystal with lower initial Hg:Cd mole ratio, 720 nm for the one with higher mole ratio.

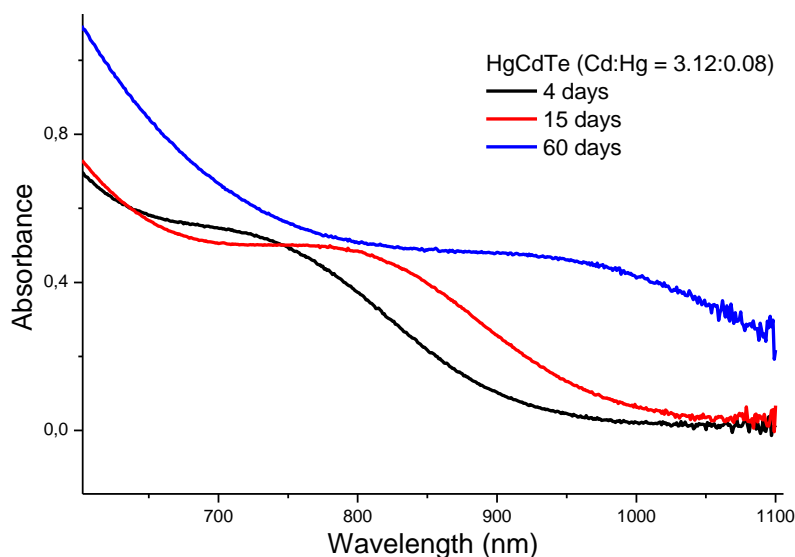


Figure 2.6. Absorption spectra of HgCdTe nanocrystals with aging. Spectra shifted to NIR range for nanocrystals which kept in reaction flask with significant time period.

Some of HgCdTe nanocrystals stored in reaction holder. Absorption spectra was taken in different periods. It showed that nanocrystals shifted to near infrared region with aging. Freshly synthesized HgCdTe absorbed the light at 715 nm. However, fifteen days after the synthesis absorption maximum shifted to 785 nm, two months later it shifted to 950 nm. The significant difference in absorption spectra with aging is showed in Figure 2.6.

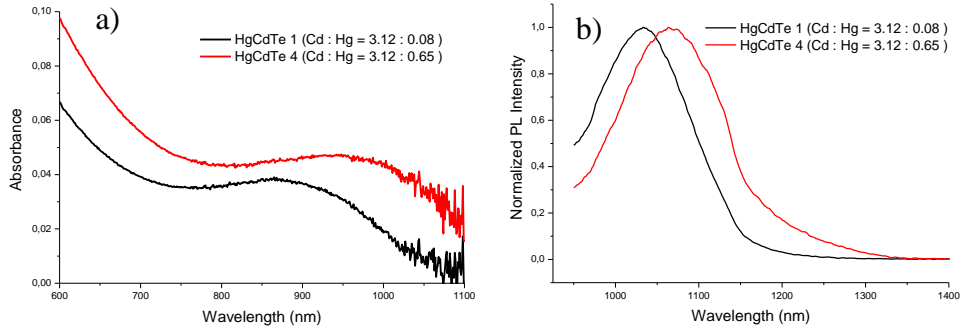


Figure 2.7. (a) Absorption and (b) normalized PL spectra for aged HgCdTe nanocrystals. NIR ranged absorption and fluorescence spectra shifted to red with high Hg content.

Taken absorption and photoluminescence spectra for aged nanocrystals showed that HgCdTe nanocrystals shifted toward near infrared region as shown in Figure 2.7. Nanocrystal with initial Cd:Hg mole ratio is 3.12 : 0.08 absorbed the light at 870 nm and emitted at 1030 nm. As it is expected, the nanocrystal with initial Cd:Hg mole ratio is 3.12 : 0.65 showed more shift in both absorption and PL spectra. Higher Hg content aged nanocrystal absorbed light at 960 nm and emitted at 1070 nm.

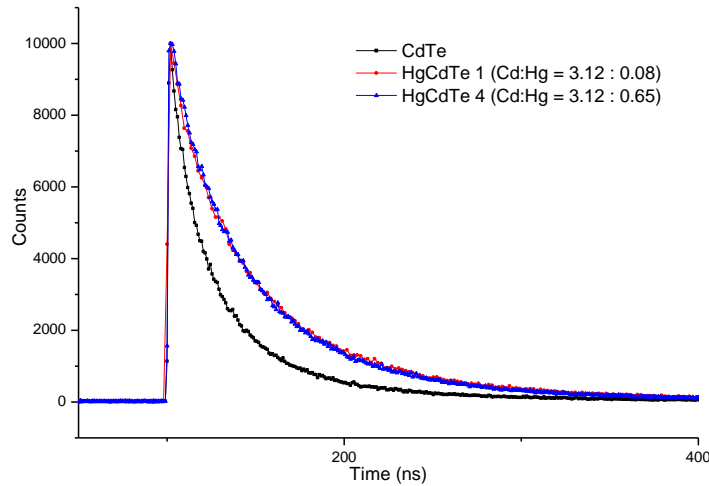


Figure 2.8. Fluorescence decay traces for CdTe and HgCdTe nanocrystals. HgCdTe nanocrystals have longer lifetimes than CdTe nanocrystals.

Lifetime measurements were carried out for both CdTe and HgCdTe nanocrystals in order to understand the photodynamics of the nanocrystals. Three exponential fitting procedure was applied for all measurements to obtain best χ^2 value

which is close to 1.0. There is a significant difference in lifetime values between CdTe and HgCdTe nanocrystals as shown in Figure 2.8. Lifetime values for CdTe nanocrystals are 14.5 ns, 33.5 ns and 132.5 ns with relative percent 44.5, 45.2 and 10.3 respectively. Lifetime values for lower Hg percentage in the HgCdTe nanocrystal (Cd:Hg = 3.12:0.08) are 26.1 ns, 62.2 ns and 178.3 ns with relative percent 15.6, 69 and 15.5 respectively. Lifetime values for the nanocrystal with higher Hg content (Cd:Hg = 3.12:0.65) showed the similar trend. Values are 19.8 ns, 49.3 ns and 114.5 ns with relative percent 10.1, 65.1 and 24.8 respectively. Average lifetime values were calculated by relative percentages and lifetime values for each content. While average lifetime of CdTe nanocrystals was 35.42 ns, values are 73.7 ns and 62.49 ns for HgCdTe nanocrystals with low and high Hg content, respectively. Another set of experiment with initial Cd:Hg mole ratios 3.12:0.16, 3.12:0.31 and 3.12:0.62 was done and lifetime values were obtained. The lifetime values for each component and average values was shown in Table 2.1. The trend is similar with previous results that, CdTe nanocrystals have shorter lifetime than HgCdTe nanocrystals. In HgCdTe nanocrystals, it is shown that when initial Cd:Hg mole ratio decrease, lifetimes of nanocrystals decrease, too. Fluorescence decay traces for the second set HgCdTe nanocrystals were shown in Figure 2.9. χ^2 values are 1.014, 1.980 and 1.079 for sample HgCdTe-1, HgCdTe-2 and HgCdTe-3 respectively.

Table 2.1. Fluorescence lifetime values for CdTe and HgCdTe nanocrystals. χ^2 values are between 0,980 and 1,079. HgCdTe nanocrystals have longer lifetime values.

Sample	Initial Cd:Hg mole ratio	τ_1 (ns)	Rel %	τ_2 (ns)	Rel %	τ_3 (ns)	Rel %	τ_4 (ns)	Rel %	τ_{average} (ns)
CdTe	3.12:0	3,44	3,96	11,29	38,29	26,13	44,54	93,21	13,21	28,41
HgCdTe-1	3.12:0.16	6,12	1,66	31,24	29,76	65,70	57,72	182,08	10,87	67,11
HgCdTe-2	3.12:0.31	15,62	9,98	49,17	68,93	128,06	21,08	---	---	62,44
HgCdTe-3	3.12:0.62	10,80	7,85	42,01	68,80	103,92	23,35	---	---	54,01

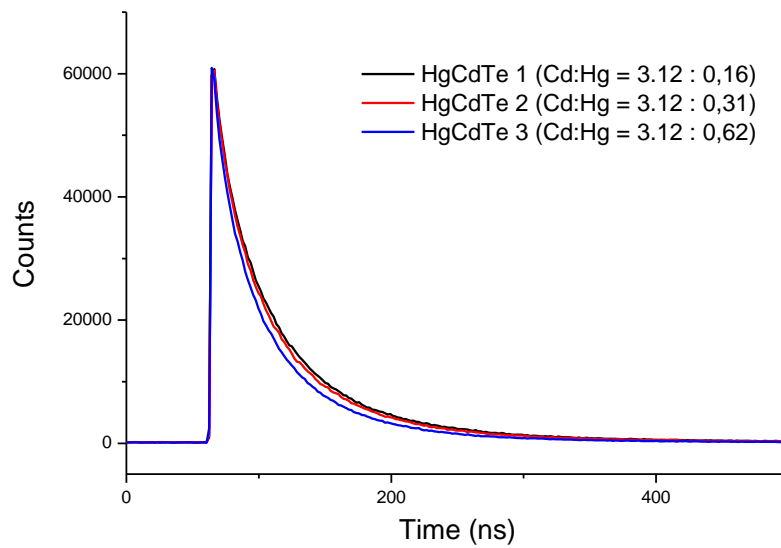


Figure 2.9. Fluorescence decay traces for HgCdTe nanocrystals. Increasing Hg content resulted shorter lifetime values.

2.3.2. Structural Characterization

Structural characterization was completed by Dynamic Light Scattering (DLS) instrument to obtain size of the nanocrystals, X-Ray diffraction (XRD) analysis to understand the structure of the nanocrystal and Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDS) and X-Ray Fluorescence (XRF) Instrument to get information about composition of the HgCdTe nanocrystals. Scanning Transmission Electron Microscopy (STEM) and Transmission Electron Microscopy (TEM) were also used.

Size of HgCdTe nanocrystals could be controlled by adjusting the size of CdTe source, initial mole ratio and reaction time. In order to obtain smaller colloidal HgCdTe nanocrystals, initial CdTe should be small. Figure 2.10 shows the size distribution of smaller CdTe and HgCdTe nanocrystals.

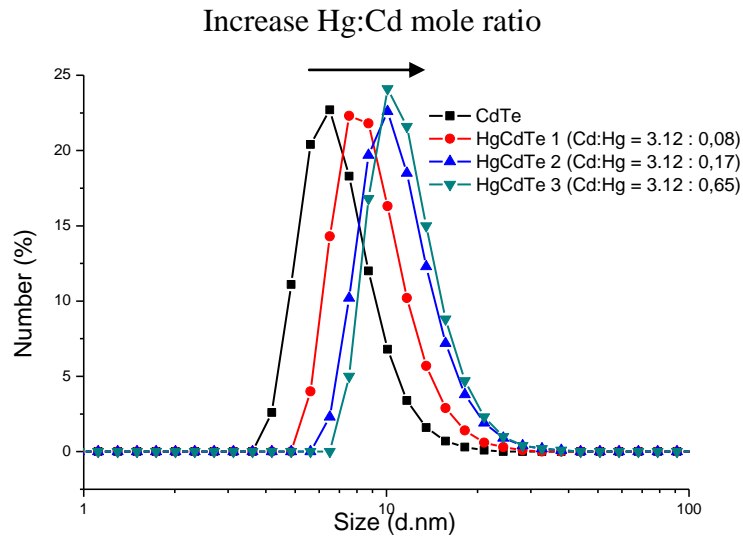


Figure 2.10. Size distribution of smaller CdTe and HgCdTe nanocrystals with different initial Cd:Hg mole ratio. Increasing Hg resulted bigger nanocrystals

Dynamic light scattering measurements showed that the size of previously synthesized CdTe nanocrystals was 6 nm. The size of HgCdTe nanocrystals are 8 nm, 9,5 nm and 11 nm for the initial Cd:Hg mole ratio is 3.12:0.08, 3.12:0.17, 3.12:0.65 respectively. Size of HgCdTe nanocrystals were increased gradually with increase the initial Hg:Cd mole ratio.

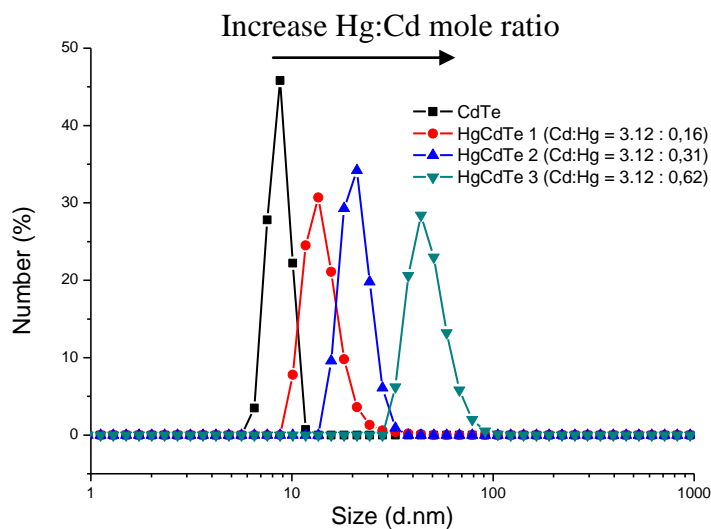


Figure 2.11. Size distribution of bigger CdTe and HgCdTe nanocrystals with different initial Cd:Hg mole ratio. Size of nanocrystals increased with the increase of Hg:Cd mole ratio.

Figure 2.11 shows the size distribution of bigger HgCdTe nanocrystals with different initial Cd:Hg mole ratio. The only difference between Figure 2.10 and Figure 2.11 is the size of CdTe that is used as source. Here the size of the starting CdTe nanocrystal is 9 nm. The size of HgCdTe nanocrystals increased to 12 nm, 20 nm and 44 nm for the initial Cd:Hg mole ratio 3.12:0.16, 3.12:0.31 and 3.12:0.62 respectively.

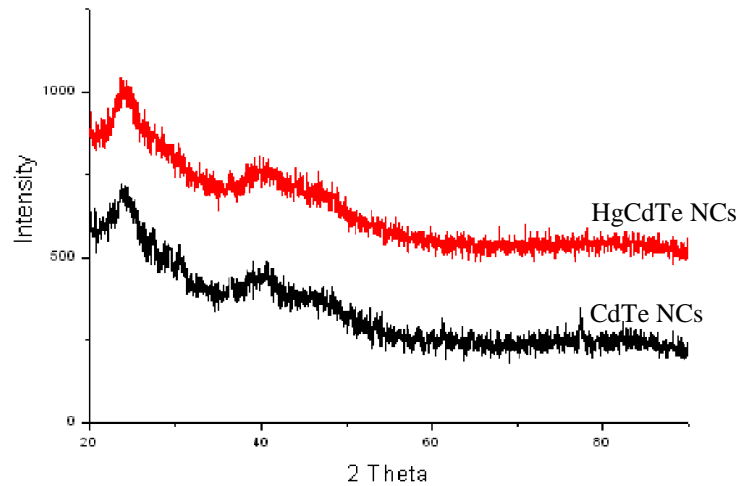


Figure 2.12. XRD diffractometer of CdTe and HgCdTe nanocrystal. Nanocrystals are cubic and have zinc blende structure.

XRD spectroscopy is carried to understand the structure and the composition of the nanocrystals. Figure 2.12 shows that both CdTe and HgCdTe nanocrystals are cubic and have zincblende structure. However, it is not quite simple to identify the nanocrystals compositionally by XRD spectroscopy. Although the electron/hole masses and bulk band gap energies of CdTe and HgTe are very different, their lattice constants are nearly identical. ($a_{\text{CdTe}} = 6.48 \text{ \AA}$ and $a_{\text{HgTe}} = 6.46 \text{ \AA}$) While the bulk band gap energy of CdTe is around 1.5 eV, that of HgTe is almost zero. In HgTe, the bottom of conduction band and the top of the valence band is almost overlapped. That is why HgCdTe nanocrystals able to have a band gap energy between 1.5 eV and 0 eV. Because of this difference in band gap energies, and identical lattice constants, after the cation exchange reaction the size of nanocrystals does not changed so much, but both absorption and fluorescence spectra shifts to red according to Hg content. (Smith and Nie 2010)

The elemental composition was obtained by both SEM-EDS and XRF techniques. The SEM-EDS analysis were carried two weeks and four weeks after the synthesis. First SEM-EDS results are shown in Table 2.2. It shows that independently of initial Cd:Hg mole ratio, the HgCdTe nanocrystals have approximately same Hg content. After a month, the same HgCdTe nanocrystals were analysed with SEM-EDS. The results are shown in Table 2.3. Hg content increases with increase in initial Hg:Cd mole ratio. According to the SEM-EDS interpretation, if the results (in weight %) are between 20-100 %, the error could be up to 5 %. Considering this deviation, XRF results shows the similar trend for these nanocrystals which are shown in Table 2.4.

Table 2.2. SEM-EDS results for HgCdTe nanocrystals two weeks after the synthesis. Compositions of nanocrystals obtained from SEM-EDS are the same independently of initial Cd:Hg mole ratio.

Element	Cd:Hg (Initial mole ratio)	Composition (from SEM-EDS)
HgCdTe 1	3.12 : 0.15	Hg _{0.28} Cd _{0.72} Te
HgCdTe 2	3.12 : 0.31	Hg _{0.24} Cd _{0.76} Te
HgCdTe 3	3.12 : 0.62	Hg _{0.23} Cd _{0.77} Te

Table 2.3. SEM-EDS results for HgCdTe nanocrystals a month after the synthesis. Hg amount in resulted nanocrystals increased with the increase of initial Hg:Cd mole ratio.

Element	Cd:Hg (Initial mole ratio)	Composition (from SEM-EDS)
HgCdTe 1	3.12 : 0.15	Hg _{0.45} Cd _{0.55} Te
HgCdTe 3	3.12 : 0.62	Hg _{0.55} Cd _{0.45} Te

Table 2.4. XRF results for HgCdTe nanocrystals a month after the synthesis. Increasing initial Hg: Cd mole ratio increased the Hg content in composition obtained from XRF.

Element	Cd:Hg (Initial mole ratio)	Composition (from XRF)
HgCdTe 1	3.12 : 0.16	Hg _{0.51} Cd _{0.49} Te
HgCdTe 2	3.12 : 0.31	Hg _{0.50} Cd _{0.50} Te
HgCdTe 3	3.12 : 0.62	Hg _{0.62} Cd _{0.38} Te

STEM images were taken for pure HgCdTe nanocrystals with initial Cd:Hg mole ratio is 3.12 : 0.16. Purification procedure was applied as introduced in experimental section. Purified HgCdTe nanocrystals dispersed in ultra pure water and dropped to TEM grids. Taken images are shown in Figure 2.13.

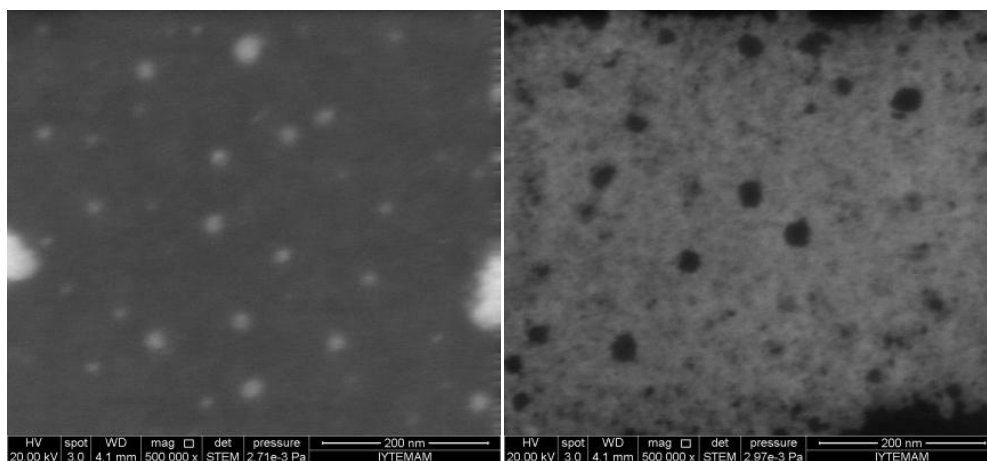


Figure 2.13.STEM images of purified HgCdTe nanocrystals (200 nm scale)

One of the best technique for characterization of nanocrystals is Transmission Electron Microscopy (TEM). Size and structure of nanocrystals could be obtained by TEM. HgCdTe nanocrystals were purified and dropped to TEM grids as done for STEM analysis. TEM images of HgCdTe nanocrystals (initial Cd:Hg mole ratio is 3.12 : 0.16)

are shown in Figure 2.14 that nanocrystals were observed better than STEM images. Size of nanocrystals obtained from TEM is around 5 nm. Dynamic Light Scattering measurements gave the size of nanocrystals as 8 nm. DLS results are larger than TEM results as expected. Because DLS measures both the hard core and the hydrodynamic diameter of nanocrystals. However TEM measures only the hard core of nanocrystals (Qian et al. 2007).

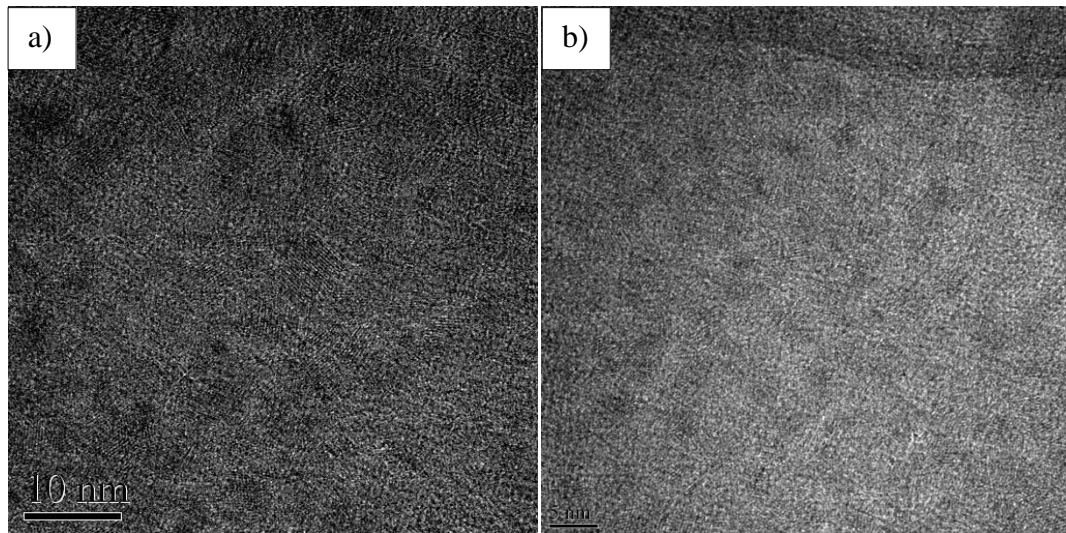


Figure 2.14 TEM images of purified HgCdTe nanocrystals (a) 10 nm and (b) 5 nm scale

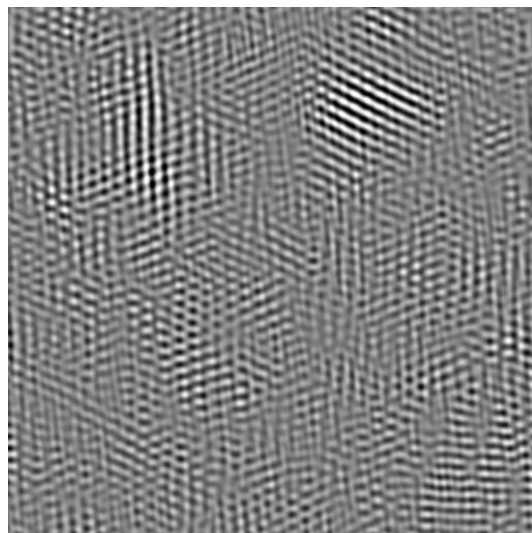


Figure 2.15 Superlattice structure of purified HgCdTe nanocrystals

2.4. Conclusion

Thioglycolic acid capped HgCdTe nanocrystals were synthesized by two step procedure. CdTe nanocrystals were synthesized by one pot aqueous synthesis method. Seed CdTe nanocrystals were used to synthesize HgCdTe nanocrystals by cation exchange reaction. Desired size of HgCdTe nanocrystals from 8 nm to 44 nm were obtained by adjusting initial CdTe nanocrystals. Starting with smaller CdTe nanocrystals forms smaller HgCdTe nanocrystals. If bigger HgCdTe nanocrystals are desired, bigger CdTe nanocrystals are used as seed. Increasing the initial Hg:Cd mole ratio yielded red shifts in both absorption and fluorescence spectra to near infrared region of electromagnetic spectrum. Aging process showed higher shift to red region in absorption and fluorescence spectra for HgCdTe nanocrystals. Lifetime measurements showed a significant difference between CdTe and HgCdTe nanocrystals, HgCdTe nanocrystals have longer lifetime values than CdTe nanocrystals. However, comparison in HgCdTe nanocrystals with different Hg content showed that increasing Hg content caused the decrease in lifetime of nanocrystals. Because of identical lattice parameters of CdTe and HgTe nanocrystals, XRD results only showed that both CdTe and HgCdTe nanocrystals are cubic and have zincblende structure. Compositional information obtained from SEM-EDS and XRF measurements.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF Gd DOPED CdTe NANOCRYSTALS

3.1. Introduction

Doped quantum dots have attracted significant attention because of their specific potential properties. Transition metal ions like Cu and Mn have been used as dopant to nanocrystals in order to enhance the optical properties of quantum dots like minimizing self absorption, having narrower PL emission spectra or provide better thermal stability. Mercaptopropionic acid (MPA) capped, water soluble Mn doped ZnS nanocrystals were synthesized by nucleation doping strategy. Nanocrystals were formed in organic solvent, then high quality water dispersible quantum dots were obtained by ligand exchange reaction (Zheng et al. 2012). Transition metal ions doped core / shell nanocrystals also studied in literature. Mn doped ZnSe / ZnS nanocrystals synthesized by aqueous synthesis. Firstly, Mn doped ZnSe nanocrystals were synthesized then ZnS shell was deposited around the synthesized quantum dots under N₂. UV-Vis absorption and PL spectra was taken in order to control the growth. Nanocrystals with photoluminescence quantum efficiencies as 35 % are preferable in biolabelling applications because of their non-cadmium content (Fang et al. 2010). Rare earth metals like Europium also doped to CdS nanocrystals in order to enhance the electrochemiluminescence (ECL) properties of the nanocrystals by co-precipitation method. Average size of resulted nanocrystals obtained by TEM was 6 nm. It is seen that doping Eu³⁺ facilitates effective energy transfer because of creating new surface state on the CdS nanocrystals which could be use to prepare energy transfer materials (Deng et al. 2012).

In this part of study we focused on Gd doped CdTe nanocrystals because of magnetic properties of Gd ions. Multilayered silica-Gd-silica core-shell nanocrystals were synthesized and their magnetic resonance images were studied by Kobayashi et al in order to enhance the magnetic properties of nanocrystals to obtain a novel magnetic resonance contrast agents. Stöber method was used to synthesized silica nanocrystals

with an average size of 31 nm. Gd doped to synthesized silica nanocrystals by homogeneous precipitation method. Silica shell to Gd doped silica nanocrystals were obtained by TEOS and NaOH. The average size of these multilayered nanocrystals was obtained by TEM as 71 nm (Kobayashi et al. 2007). There is insufficient study about chemical doping especially Gadolinium doped CdTe nanocrystals. For example, Li et al. reported synthesized and stabilized Gd doped CdSe nanocrystals. These nanocrystals were synthesized in organic solvents. Size of the nanocrystals obtained by TEM, for both CdSe and Gd doped CdSe nanocrystals that, Gd addition increased the size of the nanoparticles. XRD measurements were carried out, however it is shown that XRD pattern of Gd doped CdSe nanocrystals had the same diffraction pattern with CdSe nanocrystals. EDS and ICP-AES measurements proved the presence of Gadolinium in CdSe nanocrystals (Li and Yeh 2010).

3.2. Experimental

Gd doped CdTe nanocrystals were synthesized by aqueous synthesis in one step procedure.

3.2.1. Reagents

Metal sources, Gadolinium (III) Nitrate hydrate and Cadmium chloride were purchased from Alfa Aesar and Sigma Aldrich respectively. Thioglycolic acid (TGA, Merck), Sodium borohydride (NaBH_4 , Merck) Tellurium powder (Fluka) were used throughout the synthesis. Thiourea (Sigma Aldrich) is used for core/shell nanocrystals. 2-propanol (Sigma Aldrich) was used to precipitate Gd doped CdTe nanocrystals.

3.2.2. Synthesis of Gd doped CdTe Nanocrystals

Water dispersible Gadolinium doped CdTe nanocrystals were synthesized with the similar method, one pot aqueous approach, that was discussed in section 2.2.2. The precursor was prepared with the same procedure as introduced at section 2.2.2.1. Gadolinium (0.001 M $\text{Gd}(\text{NO}_3)_3$ solution and Cadmium (CdCl_2) precursors were mixed

with ultra pure water in the beginning of the synthesis. Thioglycolic acid (TGA) was used as stabilizer and the pH of the solution was adjusted to 11 by 1 M of NaOH solution. The solution was deaerated by N_2 at $80^\circ C$. Te precursor was injected into the reaction flask after an hour and the temperature increased to $90^\circ C$. Gd doped CdTe nanocrystals started to form under reflux at $90^\circ C$. Schematic illustration of synthesis of Gd doped CdTe nanocrystals are shown in Figure 3.1. Experimental set up of nanocrystals are also shown in Figure 3.2 that it is possible to carry out six experiment at the same time and at the same conditions like temperature, rate of stirring etc. Sampling was performed to control formation and growth steps of nanocrystals. The growth was stopped by cooling the reaction flask to the room temperature.

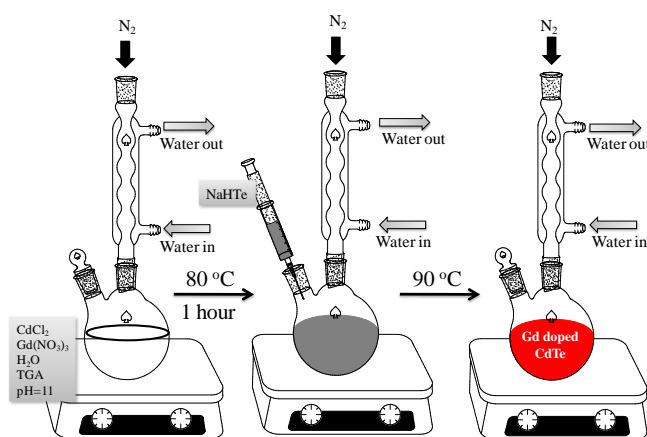


Figure 3.1. Schematic illustration of synthesis of Gd doped CdTe nanocrystals



Figure 3.2. Experimental set up of synthesis of Gd doped CdTe nanocrystals

Gadolinium mole ratio was increased from 0,01 mmol to 0,09 mmol for 3,12 mmol Cadmium ion. 9 different reactions were studied by changing different initial Cd:Gd mole ratio.

3.2.3. Synthesis of Gd doped CdTe/CdS Nanocrystals

Gd doped CdTe nanocrystals were covered by CdS shell in aqueous synthesis in one step procedure. The beginning of the synthesis is the same with the synthesis of Gd doped CdTe nanocrystals as mention in Section 3.2.2. CdS shell was formed by injection of 6 ml thiourea-ultra pure water solution after injection of tellerium precursor (NaHTe) to the reaction flask at 90°C.

3.3. Results and Discussion

3.3.1. Optical Characterization

Optical characterization of Gd doped CdTe nanocrystals were performed by lifetime measurements, UV-Vis Absorption and fluorescence spectroscopies. Aliquots were taken in different time intervals to control the reaction.

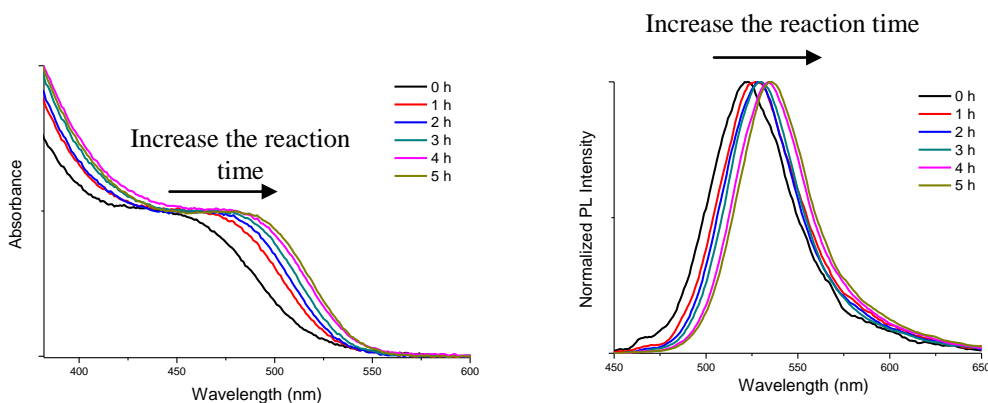


Figure 3.3. Normalized (a) Absorption and (b) PL spectra of Gd doped CdTe nanocrystals (Cd:Gd = 3.12 : 0.03). Both absorption and PL spectra shifted to red with time. Reaction time is 5 hours.

Taken optical spectra for Gd doped CdTe nanocrystals with initial Cd:Gd mole ratio as 3.12 : 0.03 is shown in Figure 3.3 that both absorption and emission spectra shifted to red in spectrum with time because more cadmium or gadolinium ions were added to surface of formed Gd doped CdTe nanocrystal during the reaction time. In the beginning of the reaction, when the reaction temperature reached 90°C, nanocrystals absorbed the light at 445 nm and emitted at 520 nm. Reaction stopped by cooling after 5 hours reaction time. Growth nanocrystals had absorption maximum at 485 nm and PL maximum at 535 nm. Nanocrystals were excited at 400 nm in fluorescence spectrum.

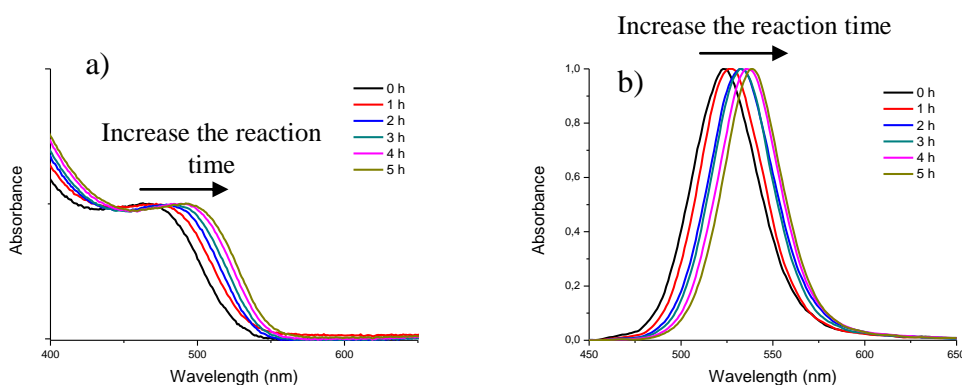


Figure 3.4. Normalized (a) Absorption and (b) PL spectra of Gd doped CdTe nanocrystals contains CdS shell (Cd:Gd = 3.12 : 0.03). Both absorption and PL spectra shifted to red with time. Reaction time is 5 hours.

Gd doped CdTe/CdS core/shell nanocrystals also showed the same trend with Gd doped CdTe nanocrystals without CdS shell. Both absorption and fluorescence spectra shifted to higher wavelengths as nanocrystals grow up. Normalized absorption and fluorescence spectra of nanocrystals were shown in Figure 3.4. The first sampling (0 hours) represents the time after 30 minutes than injection of thiourea to Gd doped CdTe nanocrystals. The fabricated Gd doped CdTe ncore/shell nanocrystals absorbed the light at 465 nm and 490 nm and emitted at 525 nm and 540 nm for the first sampling (0 hours) and five hours reaction time, respectively.

Photoluminescence Quantum Yield of Gd doped CdTe nanocrystals were measured as mention in Section 1.3.1.

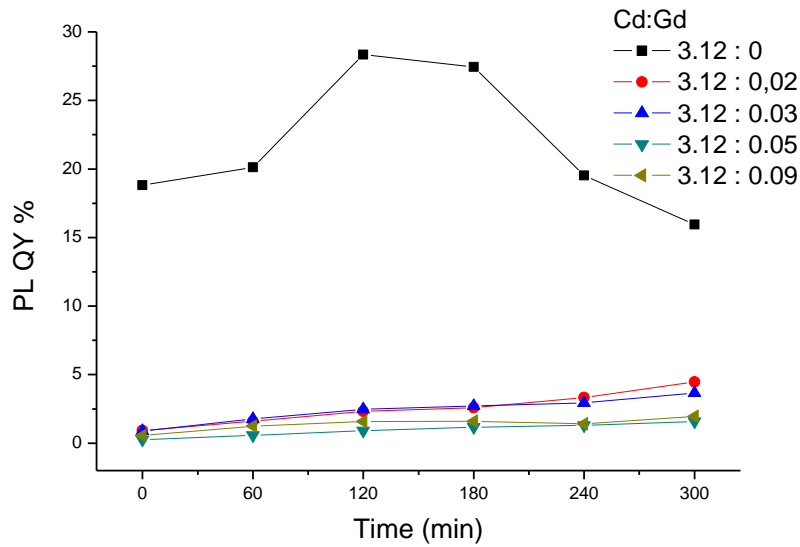


Figure 3.5. Photoluminescence Quantum Yield of Gd doped CdTe nanocrystals with different initial Cd:Gd mole ratio. Nanocrystals contain Gd, had lower PL QY % than CdTe nanocrystals.

As it given in Figure 3.5 photoluminescence quantum yield of nanocrystals showed a significant difference when Gd content added to CdTe nanocrystals. PL QY % of CdTe nanocrystals increased up to 28 % after two hours of Te injection, then decreased to 15 % during the reaction. This is also expectable that when the reaction time increases, size of nanocrystals also increase and some defect states started to form which causes the decrease in quantum yield of nanocrystals. Synthesized CdTe nanocrystals had an maximum quantum yield at 528 nm as shown in Figure 3.6.

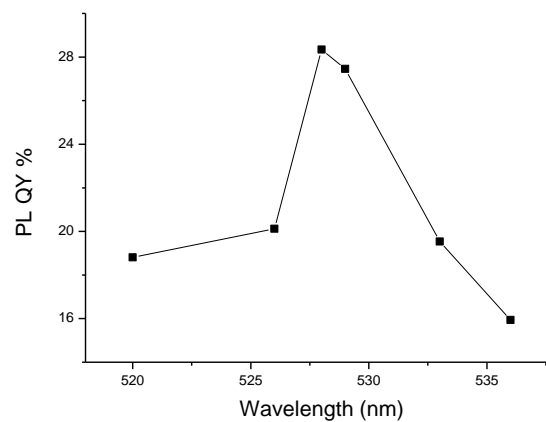


Figure 3.6. Photoluminescence Quantum Yield versus wavelength of CdTe nanocrystals.

In the other hand Gd doped CdTe nanocrystals had lower quantum yield than CdTe nanocrystals as shown in Figure 3.5. Gd doped nanocrystals had PL QE % up to 4%. This significant decrease in quantum yield occurred because of the additional metal ion to CdTe nanocrystal.

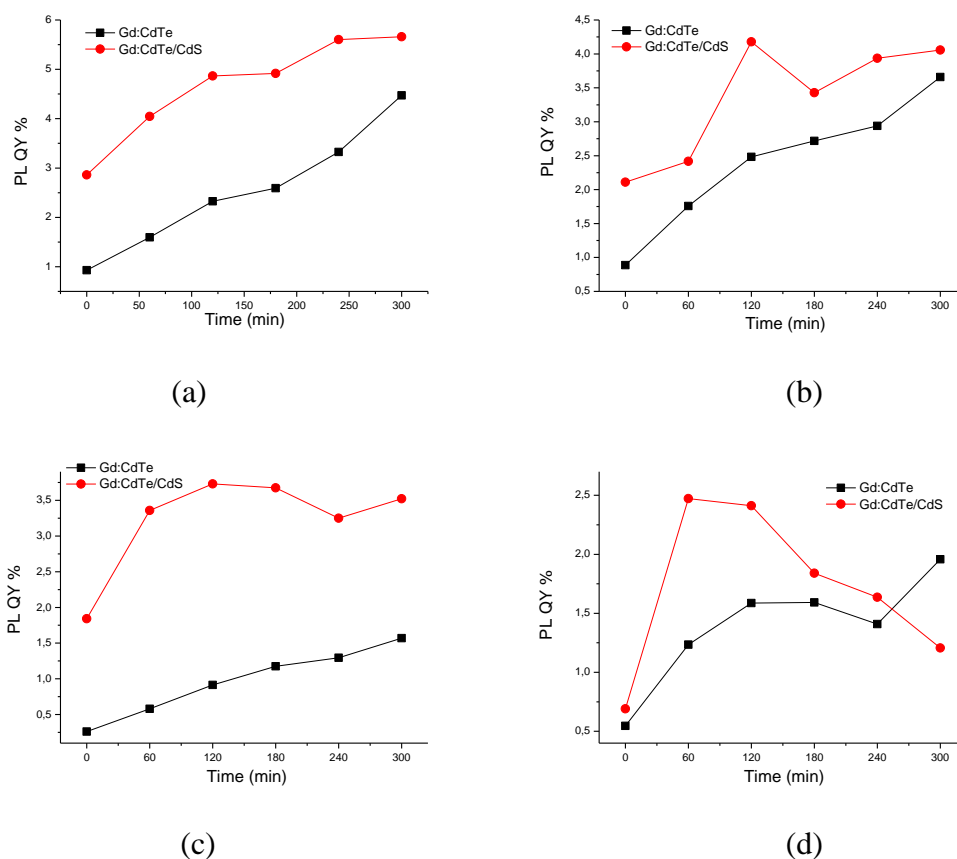
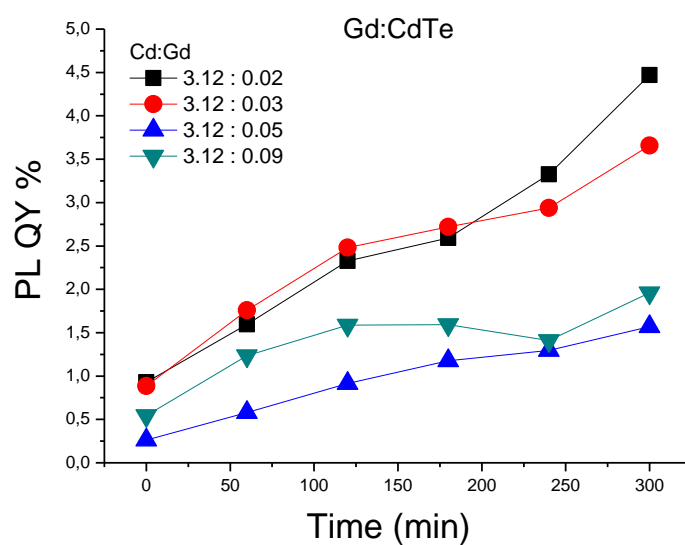
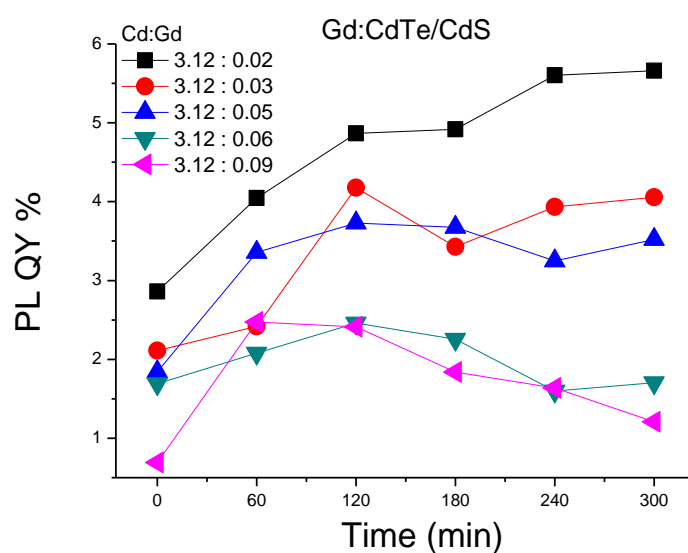


Figure 3.7. Comparison of photoluminescence quantum yield of Gd: CdTe and Gd: CdTe/CdS with initial Cd:Gd mole ratio as (a) 3.12 : 0.02 , (b) 3.12 : 0.03 , (c) 3.12 : 0.05 and (d) 3.12 : 0.09. Reaction time is 5 hours.

Gd doped CdTe nanocrystals with CdS shell had also lower quantum yield than CdTe nanocrystals but higher than doped nanocrystals without CdS shell. Figure 3.7 shows the comparison of Gd doped CdTe and Gd doped CdTe / CdS nanocrystals in terms of photoluminescence quantum yield. Nanocrystals with CdS shell showed higher quantum yield than nanocrystals which do not have CdS shell. It is also shown that quantum yield of both core and core/shell type Gd doped CdTe nanocrystals increased during the reaction time. The only exception of this trend is seen for the fifth hour sample of Gd doped CdTe nanocrystals when the initial Cd:Gd mole ratio is 3.12 : 0.09.



(a)



(b)

Figure 3.8. Comparison of photoluminescence quantum yield of (a) Gd:CdTe and (b) Gd:CdTe/CdS nanocrystals with respect to time and different initial Cd:Gd mole ratios.

Comparison of quantum yields with respect to different initial Cd:Gd mole ratios for Gd doped CdTe and Gd doped CdTe/CdS nanocrystals are shown in Figure 3.8. Both core and core/shell type nanocrystals showed the same trend that increasing the Gd content in the total metal concentration in the reaction medium resulted decrease in quantum yield of nanocrystals.

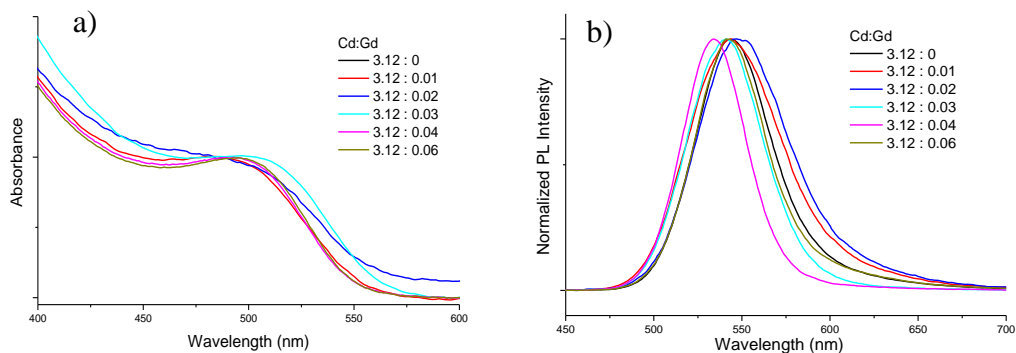


Figure 3.9. (a) Absorption and (b) Normalized PL Spectra of Gd doped CdTe nanocrystals with different initial Cd:Gd mole ratio. Both absorption and PL spectra changed with different Gd content. Reaction time is 4 hours.

Different amount of Gadolinium, changed both size and the optical spectrum of the nanocrystals. Figure 3.9 shows the absorption and normalized PL emission spectra for nanocrystals with different initial Cd:Gd mole ratio. Reaction time was chosen as 4 hours after the injection of Te precursor. Peak maximum changed in both absorption and emission spectra. The reason of this indirect shift in spectra according to the initial Cd:Gd mole ratio is the different reaction rates of Cd and Gd ions when different initial Cd:Gd mole ratio exist in the reaction medium.

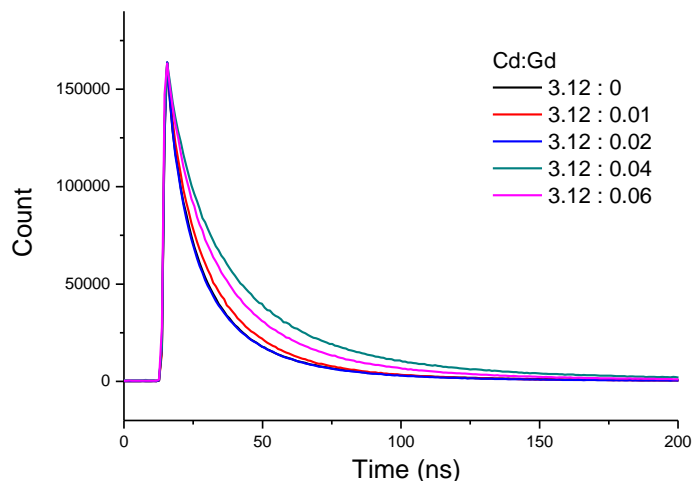


Figure 3.10. Fluorescence decay traces for CdTe and Gd doped CdTe nanocrystals. Lifetime values of Gd doped CdTe nanocrystals were changed with different Gd content.

Fluorescence decay traces were taken for CdTe and Gd doped CdTe nanocrystals in order to obtain photodynamic information. Three or four exponential fitting procedure was applied to reach the best χ^2 value as close to 1. The lifetime results with each component are shown in Table 3.1. According results, only CdTe and sample Gd:CdTe-3 (Cd : Gd = 3.12 : 0.02) had four components, other nanocrystals had three components. Similar results obtained that, fast and slow processes have approximately same lifetime values. Average lifetime values were calculated by relative percents of each components and shown in Table 3.1. Average lifetime values showed that, if Gadolinium percentage is less than 1 % (CdTe, Sample Gd:CdTe-1 and Gd:CdTe-3) lifetime values does not show significant difference that lifetime values are between 25 ns and 29 ns. When Gd content increase to % 1.3 and 2, lifetime values of nanocrystals increase to 41.58 ns and 34.16 ns, respectively.

Table 3.1. Fluorescence lifetime values for CdTe and Gd doped CdTe nanocrystals. χ^2 values are between 1,000 and 1,268.

Sample	Initial Cd:Gd mole ratio	τ_1 (ns)	Rel %	τ_2 (ns)	Rel %	τ_3 (ns)	Rel %	τ_4 (ns)	Rel %	$\tau_{average}$ (ns)
CdTe	3.12 : 0	3,44	3,96	11,29	38,29	26,13	44,54	93,21	13,21	28,41
Gd:CdTe-1	3.12 : 0.01	6,80	14,98	20,85	79,32	64,41	14,70	---	---	25,15
Gd:CdTe-3	3.12 : 0.02	4,15	7,86	13,12	42,43	29,56	41,38	101,08	8,32	26,53
Gd:CdTe-4	3.12 : 0.04	9,02	11,33	29,28	63,20	86,60	25,47	---	---	41,58
Gd:CdTe-5	3.12 : 0.06	9,21	16,52	26,67	65,67	84,86	17,81	---	---	34,16

3.3.2. Structural Characterization

Structural characterization of Gd doped CdTe nanocrystals was done by Dynamic Light Scattering (DLS) instrument, X-Ray diffraction (XRD) analysis and Scanning Electron Microscopy – Energy Dispersive X-Ray Spectroscopy (SEM-EDS), Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

DLS measurements were taken in order to obtain size of Gd doped CdTe nanocrystals. During the reaction size of the nanocrystals were control in order to obtain the increase in size of Gd doped CdTe nanocrystals. Size of the nanocrystals were increase from 21 nm to 32 nm for the sampling times 60 min and 180 min respectively for Gd doped CdTe nanocrystals in which initial Cd:Gd mole ratio was 3.12:0.02. Figure 3.11 shows the increase in size of Gd doped CdTe nanocrystals with time.

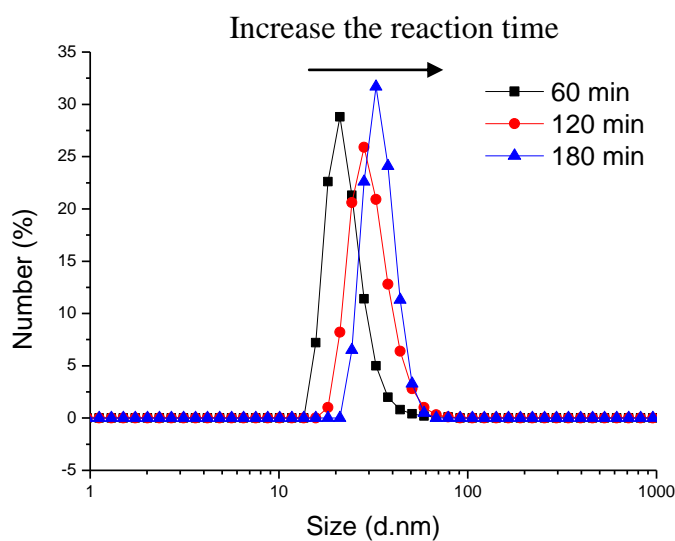


Figure 3.11. DLS Results for Gd doped CdTe nanocrystals. Size of Gd doped CdTe nanocrystals increased during the reaction. (Cd:Gd = 3.12 : 0.02)

Figure 3.12 shows Gd doped CdTe nanocrystals which contains CdS shell that increasing Gd content in the beginning of the reaction, resulted bigger nanocrystals. Resulted Gd doped CdTe/CdS nanocrystals have hydrodynamic diameter as 9 nm, 15 nm, 24 nm, 28 nm and 38 nm for initial Cd:Gd mole ratio 3.12 : 0.02, 3.12 : 0.03, 3.12 : 0.05, 3.12 : 0.06 and 3.12 : 0.09 respectively. According to the results, Gd doped CdTe nanocrystals which contains CdS shell were smaller than nanocrystals without CdS

shell. CdS shell made Gd doped CdTe nanocrystals more compact and stable which is understood in comparison of quantum yield of core and core/shell type Gd doped CdTe nanocrystals. It is also seen that nanocrystals which do not have CdS shell, started to accumulate when Gd content in total metal concentration is increased to 2 and 3 %. When CdS shell was added to the Gd doped CdTe nanocrystals with the same Cd:Gd mole ratio, accumulation was not observed. It is also seen in the size distribution of Gd doped CdTe/CdS nanocrystals in Figure 3.12. Quantum Yield of Gd doped CdTe/CdS nanocrystals were decrease with increase the initial Gd content and increase the size of nanocrystals.

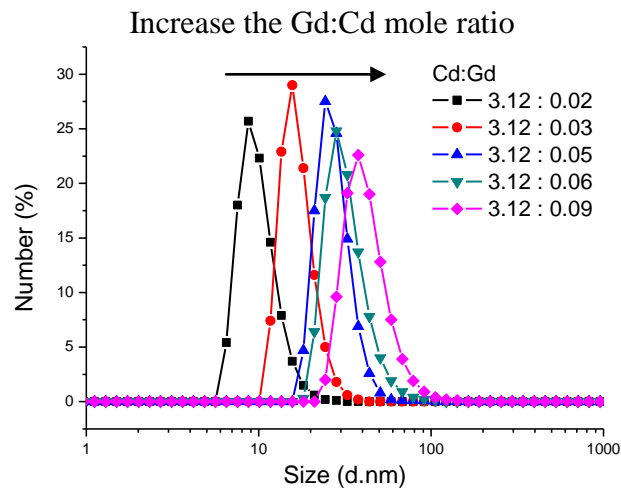


Figure 3.12. DLS Results for Gd doped CdTe/CdS nanocrystals. Size of Gd doped CdTe/CdS nanocrystals increased with increasing initial Gd:Cd mole ratio. Reaction time is 5 hours.

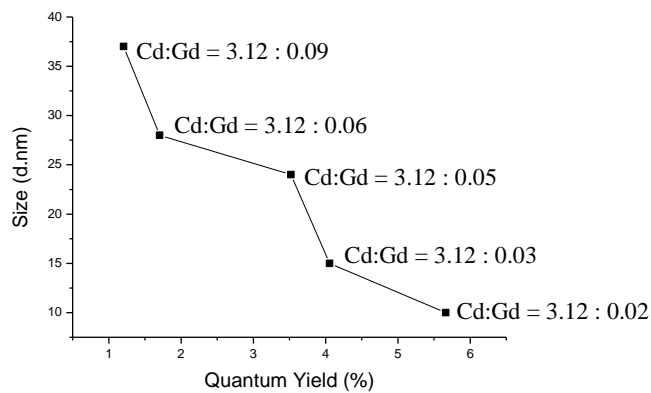


Figure 3.13. Photoluminescence Quantum Yield vs. Size of Gd doped CdTe/CdS nanocrystals. Increase the size, decrease the quantum yield. Reaction time is 5 hours.

Gd doped CdTe nanocrystals with different initial Cd:Gd mole ratio were purified with isopropanol and centrifugation as mention in Section 2.2.4. ICP-MS and SEM-EDS analysis were carried out for these purified nanocrystals in order to obtain compositional information. Both ICP-MS and SEM-EDS analysis showed that, Gd content in purified nanocrystals increase with increasing the initial Gd:Cd mole ratio. Table 3.2 shows the numerical values for results of ICP-MS and SEM-EDS analysis with the initial Cd:Gd mole ratio. Proportionality of increase of Gd content in composition with the increase of initial Gd content is shown in Figure 3.14.

Table 3.2. ICP-MS and SEM-EDS results of Gd doped CdTe nanocrystals. Gd content in the composition obtained from ICP-MS and SEM-EDS increased with the increase in initial Gd:Cd mole ratio. Reaction time is 4 hours.

Sample	Initial Cd:Gd	ICP-MS* Results (Cd:Gd)	SEM-EDS* Results (Cd:Gd)
Gd:CdTe-1	3.12 : 0.01	100:0.26	100:9
Gd:CdTe-2	3.12 : 0.015	100:0.58	100:10
Gd:CdTe-3	3.12 : 0.02	100:0.61	100:11.9
Gd:CdTe-4	3.12 : 0.04	100:0.77	100:14.6
Gd:CdTe-5	3.12 : 0.05	100:1.53	100:17.9

*These values are not real initial amounts, they resemble only the mole ratios.

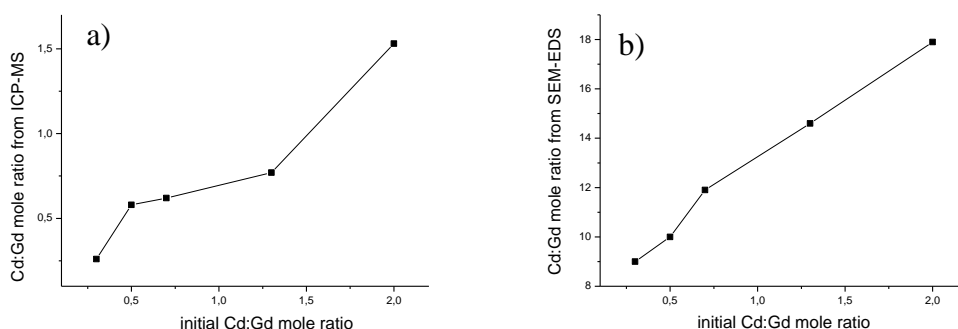


Figure 3.14. (a) ICP-MS and (b) SEM-EDS results of Gd doped CdTe nanocrystals. Gd content in composition of nanocrystals increase proportionally with initial Gd content. Reaction time is 4 hours.

The same reactions repeated with the initial Cd and Gd mole ratios given in Table 3.3. Compositional analysis was carried out with ICP-AES and results obtained. The same trend was observed with that Gd content in composition obtained from ICP-AES is directly proportional with initial Gd content in metal concentration in the reaction flask.

Table 3.3. ICP-AES results of Gd doped CdTe nanocrystals. Gd content in the composition obtained from ICP-AES increased with the increase in initial Gd:Cd mole ratio. Reaction time is 5 hours

Sample	Initial		ICP-AES* Results (Cd:Gd)
	<u>CdCl₂</u> (mmol)	<u>Gd(NO)₃</u> (mmol)	
Gd:CdTe-1	3.12	0.016	100:2.1
Gd:CdTe-2	3.12	0.031	100:2.0
Gd:CdTe-3	3.12	0.047	100:2.9
Gd:CdTe-4	3.12	0.062	100:5.6
Gd:CdTe-5	3.12	0.094	100:8.0

* These values are not real initial amounts, they resemble only the mole ratios.

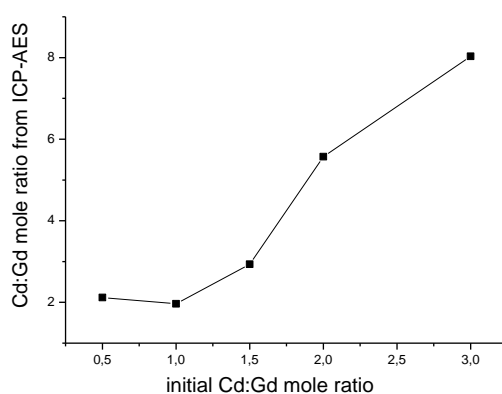


Figure 3.15. ICP-AES results of Gd doped CdTe nanocrystals. Gd content in composition of nanocrystals increase proportionally with initial Gd content. Reaction time is 5 hours.

Figure 3.15 shows the direct proportionality between initial Cd:Gd mole ratio and Gd content obtained from ICP-AES in the final composition. Results from SEM-EDS, ICP-MS and ICP-AES, showed the same trend for Gd doped CdTe nanocrystals that nanocrystals were growing homogeneously.

XRD analysis was carried out in order to understand the structure of the nanocrystals. XRD pattern of Gd doped CdTe nanocrystals with 3.12 : 0.06 initial Cd:Gd mole ratio is shown in Figure 3.16. Cubic zinc blende structure of CdTe nanocrystals did not have any change after Gadolinium doping that Gd doped CdTe nanocrystals also cubic and have zinc blende structure. The reason of this could be both the small amount of Gd content and well-dispersed gadolinium in the nanocrystals (Liu et al. 2011).

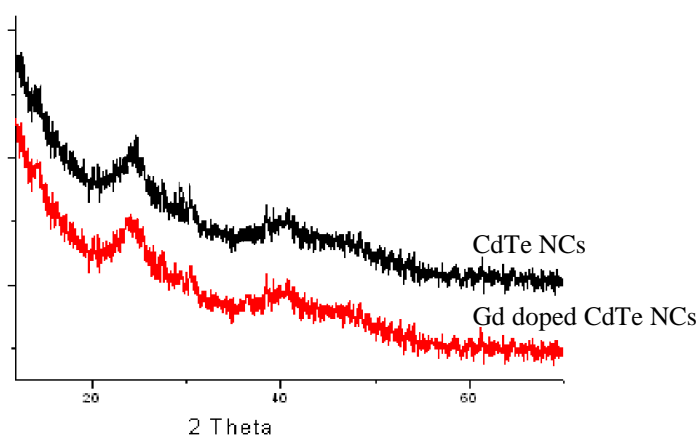


Figure 3.16. XRD pattern of Gd doped CdTe nanocrystals (Cd:Gd = 3.12 : 0.06). Both CdTe and Gd doped CdTe nanocrystals are cubic and have zinc blende structure.

3.4. Conclusion

One pot aqueous synthesis method was used to synthesize thioglycolic acid capped Gd doped CdTe nanocrystals. Initial Cd:Gd mole ratio was changed from 3.12:0.01 to 3.12:0.09. Absorption and photoluminescence spectra was obtained for optical characterization. Also lifetime measurements were performed that lifetime of Gd doped CdTe nanocrystals showed similar properties around 25 ns with CdTe nanocrystals when Gd content was less than 1%. Increasing Gd content in the

composition results higher lifetimes as 35 – 40 ns. Size of Gd doped CdTe nanocrystals also obtained from DLS technique which showed that increasing Gd content resulted increase in the size of nanocrystals up to 38 nm when CdS shell was covered to Gd doped CdTe nanocrystals. Nanocrystals with CdS shell were more compact and stable that quantum yield of core/shell type nanocrystals were higher. ICP-MS, ICP-AES and SEM-EDS results proved the Gd content in nanocrystals and showed that nanocrystals were growing homogeneously. According to results Gd content in final composition was directly proportional with the initial Gd content in total metal concentration. XRD was performed to obtain structural information about nanocrystals that Gd doped CdTe nanocrystals are cubic have zinc blende structure.

CHAPTER 4

CONCLUSION

In this study we synthesized HgCdTe and Gd doped CdTe nanocrystals by cation exchange reaction and one pot aqueous synthesis method respectively.

In the synthesise of thioglycolic acid capped HgCdTe nanocrystals synthesized seed CdTe nanocrystals used and Hg precursor added to form HgCdTe nanocrystals by cation exchange reaction. Size of HgCdTe nanocrystals varied from 8 nm to 44 nm. Desired size of nanocrystals were obtained by adjusting initial CdTe nanocrystals. Starting with smaller CdTe nanocrystals forms smaller HgCdTe nanocrystals. If bigger HgCdTe nanocrystals are desired, bigger CdTe nanocrystals are used as seed. Increasing the amount of Hg precursor in the total metal concentration yielded red shifts in both absorption and fluorescence spectra to near infrared region of electromagnetic spectrum. Aging process showed higher shift to NIR region in absorption and fluorescence spectra for HgCdTe nanocrystals. Lifetime measurements performed for both CdTe and HgCdTe nanocrystals. Results showed a significant difference in lifetime values of CdTe and HgCdTe nanocrystals, HgCdTe nanocrystals have longer lifetime values than CdTe nanocrystals. However, comparison in HgCdTe nanocrystals with different Hg content showed that increasing Hg content caused the decrease in lifetime of nanocrystals. XRD results showed that both CdTe and HgCdTe nanocrystals are cubic and have zinblende structure. Compositional information could not obtained from XRD analysis because of identical lattice parameters of CdTe and HgTe nanocrystals. SEM-EDS and XRF measurements were performed to obtain compositional information.

We synthesized thioglycolic acid capped Gd doped CdTe nanocrystals by one pot aqueous synthesis method. We changed the initial Cd:Gd mole ratio from 3.12:0.01 to 3.12:0.09. Lifetime values, absorption and photoluminescence spectra was obtained for optical characterization. Lifetime measurements showed that lifetime of Gd doped CdTe nanocrystals showed similar properties around 25 ns with CdTe nanocrystals when Gd content was less then 1%. Increasing Gd content in the composition results higher lifetimes as 35 – 40 ns. DLS technique was used to obtain size of Gd doped

CdTe nanocrystals. Results showed that increasing Gd content resulted increase in the size of nanocrystals up to 38 nm when CdS shell was covered to Gd doped CdTe nanocrystals. Nanocrystals with CdS shell were more compact and stable that quantum yield of core/shell type nanocrystals were higher. ICP-MS, ICP-AES and SEM-EDS results proved the Gd content in nanocrystals. According to these analysis Gd content in final composition was directly proportional with the initial Gd content in total metal concentration which showed that nanocrystals were growing homogeneously. XRD was performed to obtain structural information about nanocrystals that Gd doped CdTe nanocrystals are cubic have zinc blende structure.

We concluded that CdTe nanocrystals can be used to synthesize doped nanocrystals by chemical doping. We demonstrated that optical and structural properties of Hg and Gd doped CdTe can be rendered by chemical doping.

REFERENCES

- Brust, M., M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman. 1994. "Synthesis of Thiol-Derivatized Gold Nanoparticles in a 2-Phase Liquid-Liquid System." *Journal of the Chemical Society-Chemical Communications* (7):801-802.
- Deng, L., Y. Shan, J. J. Xu, and H. Y. Chen. 2012. "Electrochemiluminescence behaviors of Eu^{3+} -doped CdS nanocrystals film in aqueous solution." *Nanoscale* no. 4 (3):831-836.
- Drbohlavova, J., V. Adam, R. Kizek, and J. Hubalek. 2009. "Quantum Dots - Characterization, Preparation and Usage in Biological Systems." *International Journal of Molecular Sciences* no. 10 (2):656-673.
- Fang, Z., P. Wu, X. H. Zhong, and Y. J. Yang. 2010. "Synthesis of highly luminescent Mn:ZnSe/ZnS nanocrystals in aqueous media." *Nanotechnology* no. 21 (30).
- Fery-Forgues, Suzanne, and Dominique Lavabre. 1999. "Are Fluorescence Quantum Yields So Tricky to Measure? A Demonstration Using Familiar Stationery Products." *Journal of Chemical Education* no. 76 (9):1260.
- Feynman, Richard. P. 1960. "There is a plenty room at the bottom." *Journal of Microelectromechanical Systems* (1992) no. 1:60-66.
- Hughes, Micheal Pycaft. 2000. "AC electrikinetics: applicatiins for nanotechnology." *Nanotechnology* no. 11:124-132.
- Jiang, L., and Y. J. Zhu. 2010. "A General Solvothermal Route to the Synthesis of CoTe, Ag₂Te/Ag, and CdTe Nanostructures with Varied Morphologies." *European Journal of Inorganic Chemistry* (8):1238-1243.
- Jiang, L., Y. J. Zhu, and J. B. Cui. 2010. "Nanostructures of Metal Tellurides (PbTe, CdTe, CoTe₂, Bi₂Te₃, and Cu₇Te₄) with Various Morphologies: A General Solvothermal Synthesis and Optical Properties." *European Journal of Inorganic Chemistry* (19):3005-3011.
- Khatei, Jayakrishna, Naresh Babu Pendyala, and K. S. R. K. Rao. 2011. "Solvothermal synthesis of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ nanostructures—Their structural and optical properties." *Journal of Alloys and Compounds* no. 509 (13):4632-4635.
- Kobayashi, Y., J. Imai, D. Nagao, M. Takeda, N. Ohuchi, A. Kasuya, and M. Konno. 2007. "Preparation of multilayered silica-Gd-silica core-shell particles and their magnetic resonance images." *Colloids and Surfaces a-Physicochemical and Engineering Aspects* no. 308 (1-3):14-19.

- Lakowicz, Joseph R. 2006. *Principles of Fluorescence Spectroscopy* 3rd ed. Vol. 13. New York: Springer Science+Business Media.
- Lesnyak, Vladimir, Andrey Lutich, Nikolai Gaponik, Markus Grabolle, Alexei Plotnikov, Ute Resch-Genger, and Alexander Eychmuller. 2009. "One-pot aqueous synthesis of high quality near infrared emitting Cd_{1-x}Hg_xTe nanocrystals." *Journal of Materials Chemistry* no. 19 (48):9147-9152.
- Li, I. Fang, and Chen-Sheng Yeh. 2010. "Synthesis of Gd doped CdSe nanoparticles for potential optical and MR imaging applications." *Journal of Materials Chemistry* no. 20 (11):2079-2081.
- Liang, Guo-Xi, Ling-Ling Li, Hong-Yin Liu, Jian-Rong Zhang, Clemens Burda, and Jun-Jie Zhu. 2010. "Fabrication of near-infrared-emitting CdSeTe/ZnS core/shell quantum dots and their electrogenerated chemiluminescence." *Chemical Communications* no. 46 (17):2974-2976.
- Liu, H. J., G. G. Liu, G. H. Xie, M. L. Zhang, Z. H. Hou, and Z. W. He. 2011. "Gd³⁺, N-codoped trititanate nanotubes: Preparation, characterization and photocatalytic activity." *Applied Surface Science* no. 257 (8):3728-3732.
- Love, J. Christopher, Lara A. Estroff, Jennah K. Kriebel, Ralph G. Nuzzo, and George M. Whitesides. 2005. "Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology." *Chemical Reviews* no. 105 (4):1103-1170.
- Michalet, X., F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir, and S. Weiss. 2005. "Quantum Dots for Live Cells, in Vivo Imaging, and Diagnostics." *Science* no. 307 (5709):538-544.
- Murray, C. B., D. J. Norris, and M. G. Bawendi. 1993. "SYNTHESIS AND CHARACTERIZATION OF NEARLY MONODISPERSE CDE (E = S, SE, TE) SEMICONDUCTOR NANOCRYSTALLITES." *Journal of the American Chemical Society* no. 115 (19):8706-8715.
- Nie, S. M., Y. Xing, G. J. Kim, and J. W. Simons. 2007. "Nanotechnology applications in cancer." *Annual Review of Biomedical Engineering* no. 9:257-288.
- Pan, D. C., S. C. Jiang, L. J. An, and B. Z. Jiang. 2004. "Controllable synthesis of highly luminescent and monodisperse CdS nanocrystals by a two-phase approach under mild conditions." *Advanced Materials* no. 16 (12):982-+.
- Pradhan, N., D. Goorskey, J. Thessing, and X. G. Peng. 2005. "An alternative of CdSe nanocrystal emitters: Pure and tunable impurity emissions in ZnSe nanocrystals." *Journal of the American Chemical Society* no. 127 (50):17586-17587.

- Qian, H., C. Dong, J. Peng, X. Qiu, Y. Xu, and J. Ren. 2007. "High-quality and water-soluble near-infrared photoluminescent CdHgTe/CdS quantum dots prepared by adjusting size and composition." *Journal of Physical Chemistry C* no. 111 (45):16852-16857.
- Rogach, A. L., M. T. Harrison, S. V. Kershaw, A. Kornowski, M. G. Burt, A. Eychmüller, and H. Weller. 2001. "Colloidally Prepared CdHgTe and HgTe Quantum Dots with Strong Near-Infrared Luminescence." *physica status solidi (b)* no. 224 (1):153-158.
- Rogach, Andrey L., Thomas Franzl, Thomas A. Klar, Jochen Feldmann, Nikolai Gaponik, Vladimir Lesnyak, Alexey Shavel, Alexander Eychmüller, Yuri P. Rakovich, and John F. Donegan. 2007. "Aqueous Synthesis of Thiol-Capped CdTe Nanocrystals: State-of-the-Art." *The Journal of Physical Chemistry C* no. 111 (40):14628-14637.
- Shao, P. T., Q. H. Zhang, Y. G. Li, and H. Z. Wang. 2011. "Aqueous synthesis of color-tunable and stable Mn²⁺-doped ZnSe quantum dots." *Journal of Materials Chemistry* no. 21 (1):151-156.
- Smith, Andrew M., and Shuming Nie. 2010. "Bright and Compact Alloyed Quantum Dots with Broadly Tunable Near-Infrared Absorption and Fluorescence Spectra through Mercury Cation Exchange." *Journal of the American Chemical Society* no. 133 (1):24-26.
- Steigerwald, M. L., and C. R. Sprinkle. 1987 . " ORGANOMETALLIC SYNTHESIS OF II - VI SEMICONDUCTORS . 1. FORMATION AND DECOMPOSITION OF BIS(ORGANOTELLURO)MERCURY AND BIS(ORGANOTELLURO)CADMIUM COMPOUNDS." *Journal of the American Chemical Society* no. 109 (23):7200-7201.
- Talapin, D. V., S. Haubold, A. L. Rogach, A. Kornowski, M. Haase, and H. Weller. 2001. "A novel organometallic synthesis of highly luminescent CdTe nanocrystals." *Journal of Physical Chemistry B* no. 105 (12):2260-2263.
- Tang, Bo, Fei Yang, Yan Lin, Linhai Zhuo, Jiechao Ge, and Lihua Cao. 2007. "Synthesis and Characterization of Wavelength-Tunable, Water-Soluble, and Near-Infrared-Emitting CdHgTe Nanorods." *Chemistry of Materials* no. 19 (6):1212-1214.
- Zheng, J. J., F. M. Gao, G. D. Wei, and W. Y. Yang. 2012. "Enhanced photoluminescence of water-soluble Mn-doped ZnS quantum dots by thiol ligand exchange." *Chemical Physics Letters* no. 519-20:73-77.