

COLLOIDAL DOPING OF THICK NANOPATELETS

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COLLOIDAL DOPING OF THICK NANOPATELETS

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December 2022

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

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Semiconductor nanoplatelets (NPLs) make an interesting group of nanocrystals with unique optical properties as a result of their quasi 2-dimensional (2D) electronic structure. Such emerging fascinating optical features of NPLs include high absorption cross-section, narrow emission linewidths, and reduced Auger recombination, making them a superior choice compared to conventional semiconductor nanocrystals for optoelectronic applications. Doping of these materials with transition metals, such as silver and copper, provides great opportunities to modify and tune the electronic structure of these NPLs for various devices including light-emitting diodes and luminescent solar concentrators. Such doping with transition metals allows for manipulation of the photoluminescence from these NPLs, control of the recombination processes of the photogenerated carriers in these NPLs, and observation of the giant Zeeman effect as a result of exchange interactions between the dopants and carriers in these NPLs. Previously, CdSe NPLs have been doped with copper and silver only up to vertical thickness of 5 monolayers (ML). However, doping of thicker NPLs has not been possible to date. In this thesis work, we successfully doped thick CdSe NPLs having 7 ML in thickness with silver and copper using partial cation exchange to obtain large Stokes-shifted emission in the near-infrared (NIR) region. Here, the effect of precursor ratio and reaction temperature were systematically studied to tune the resulting emission. For both copper and silver dopants, we successfully quenched fully the band-edge emission, and purely dopant-induced emission was obtained. We also co-doped these NPLs with silver and copper, and we successfully obtained both copper- and silver-induced emissions from these NPLs. We further grew the CdZnS shell on 7 ML CdSe core by hot injection method and doped the resulting

CdSe/CdZnS core/shell NPLs with silver and copper to push their emission further towards longer wavelengths in the NIR region. These thick doped-NPLs with large Stokes shift and emission in the NIR region present a promising platform for light-emitting and -harvesting applications.



Keywords: Colloidal nanoplatelets, doping, Stokes-shifted emission, partial cation exchange, thick nanoplatelets.

ÖZET

KALIN NANOLEVHALARIN KOLLOİDAL KATKILANMASI

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Yarı iletken nanolevhalar, yarı 2 boyutlu elektronik yapılarının bir sonucu olarak benzersiz optik özellikler sergileyen ilginç bir nanokristal grubudur. Nanolevhaların yüksek soğurma kesiti, dar ışıma bant genişlikleri ve azaltılmış Auger rekombinasyonu gibi dikkat çeken optik özellikleri, onları optoelektronik uygulamalar için klasik yarıiletken nanokristallere kıyasla üstün seçenek haline getirir. Bu nanolevhaların gümüş ve bakır gibi geçiş metalleriyle katkılanması, elektronik yapılarının değiştirilmesine ve ayarlanabilmesine imkân tanıyarak ışık yayan diyotlar ve ışıyan güneş yoğunlaştırıcıları gibi farklı uygulamalar için büyük avantaj oluştururlar. Geçiş metalleri ile böyle bir katkılama; bu nanolevhalarından fotoluminesansın ayarlanmasına, bu nanolevhalarla soğurma sonrası oluşan yük taşıyıcıların rekombinasyon süreçlerinin değiştirilebilmesine ve bu nanolevhalarla katkı maddeleri ile taşıyıcılar arasındaki etkileşimlerin bir sonucu olarak artan Zeeman etkisinin gözlemlenmesine yol açar. Dikey kalınlığı beş tek katman (5 TK) olan CdSe nanolevhaların bakır ve gümüş ile katkılanması çalışılarak rapor edilmiştir. Ancak, bu iki geçiş metali ile bundan kalın nanolevhaların katkılanması bu çalışmaya kadar mümkün olmamıştır. Bu tez çalışmasında, yakın kızılötesi (YKÖ) bölgede ışıma büyük Stokes kayması elde etmek için kısmi katyon değişimini kullanarak 7 TK kalınlığındaki CdSe nanolevhalar gümüş ve bakırla başarıyla katkılanmıştır. Burada, ışımayı ayarlamak için öncül reaktif oranı ve reaksiyon sıcaklığının etkisi sistematik olarak incelenmiştir. Hem bakır hem de gümüş metalleri ile ayrı ayrı katkılanarak bu nanolevhaların bant kenarı ışıması başarıyla sönmülmüş ve tamamen katkılanma kaynaklı yeni ışıma elde edilmiştir. Ayrıca bu nanolevhaların gümüş ve bakır ile beraber katkılanması sağlanmış ve bu katkılanmış nanolevhalarla hem bakır hem de gümüş kaynaklı ışımlar başarıyla elde edilmiştir. 7 TK CdSe nanolevha çekirdek olarak kullanılarak sıcak enjeksiyon yöntemiyle etrafında CdZnS kabuk büyümesi sağlanmış ve elde edilen bu çekirdek/kabuk yapılı CdSe/CdZnS nanolevhalar gümüş ve bakır ile katkılanarak YKÖ

bölgedeki ışımanın daha uzun dalgaboylarına kayması sağlanmıştır. Geniş Stokes kayması ve YKÖ bölgesinde ışıması olan bu geçiş metali katkılı kalın nanolevhalar, ışık üretme ve hasat etme uygulamaları için umut vaadeden bir platform sunar.



Anahtar Kelimeler: Kolloidal nanoplateletler, katkılama, Stokes kayması, kısmi katyon değişimi, kalın nanoplateletler.

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Chapter 1

Introduction

Colloidal quantum wells (CQWs), aptly named nanoplatelets (NPLs), are quasi-2-dimensional semiconductor nanocrystals (NCs) that are of great interest because of their unique optoelectronic properties [1] and their cost-effective synthesis [2]. NPL's vertical thickness can be controlled atomically, which allows for narrow fluorescence with a full-width-at-half-maximum (FWHM) of less than 30 nm. Moreover, NPLs have giant oscillator strength and high absorption cross-section. These properties make them an excellent choice for optoelectronic applications including light-emitting diodes (LEDs) [3-7], lasers [8-12], and luminescent solar concentrators (LSCs) [13].

Although nanoplatelets have the edge over other nanocrystals because of their properties, they also have limitations in photoluminescence (PL) spectral tuning because their thickness can be modified in a discrete number of monolayers or atomic planes, resulting in discrete shifting of the PL spectrum. For example, CdSe nanoplatelets have their first excitonic peaks at 510, 550, 580, and 601 nm for the vertical thickness of 4 to 7 monolayers (ML), respectively. A tremendous amount of work has been undertaken to obtain a wider spectral shift, including alloying the nanoplatelets [14-15] and making heterostructures [16-20] to control and modify the band structure. An alternative means to tune their properties is by doping these nanoplatelets. Colloidal nanocrystals have been doped in 2 ways: in-situ doping and post-synthesis doping. In the in-situ, nanocrystals are doped with transition metals by using the dopant precursors during the nucleation process. In post-synthesis doping, after synthesizing the nanocrystals, some of the dopant cations from the

solution replace the host cations from the crystal lattice with the help of cation exchange. The cation exchange process for nanocrystals is much faster than in bulk materials because of the high surface-to-volume ratio, and it makes the synthesis in those compositions possible, which is otherwise not easy to synthesize via nucleation and growth [21-23]. Previously, by full cation exchange, Ag₂Se nanocrystals have been synthesized from CdSe NCs, and the same has been reversed back to CdSe with cation exchange [24]. Moreover, heterostructures have been synthesized as well with cation exchange [25-26]; e.g., from PbTe and PbSe nanocrystals, core/shell heterostructures of PbTe/CdTe and PbSe/CdSe were synthesized, respectively, where only the outer thin layer of the Pb host cation was exchanged with the dopant Cd cation. Manganese [27], copper [28-29], and silver doping [30-31] of II-VI semiconductors nanoplatelets have been of great interest. Our group has applied Mn doping to impart the magneto-optical properties to nanoplatelets [27], while copper and silver doping have been used as viable paths for enhancing optical properties. Previously, our group used copper-doped NPLs to make LEDs with dual emission [32]. Our group also used silver-doped nanoplatelets for making LEDs [33]. Introducing a dopant ion in the crystal lattice of nanoplatelets introduces a mid-gap state, which captures the hole from the valence band, and the electron relaxes to the localized hole at the mid-gap energy state, which results in the redshifted emission. One of the objectives for many researchers is to push the emission deep into the near-infrared region (NIR) for making NIR LEDs, which have great potential for biomedical applications. Tuning the thickness of doped nanoplatelets and dopant precursors can help to push the emission further deep into the near-infrared region. Another potential application for doped nanoplatelets is their use in LSCs [13]. Although doped nanocrystals have already been used for LSCs, these LSCs have low quantum efficiency due to low absorption cross-section and reabsorption in doped NCs. For LSCs performance, reduced reabsorption is one of the most critical design factors. Step-like absorption and Stokes-shifted emission make nanoplatelets a better choice for LSCs. Our group achieved record performance in LSCs with copper-doped 4 ML CdSe nanoplatelets [13]. To reduce self-absorption by Stokes-shifted emission and to obtain emission in the NIR region, investigation of doping of thick nanoplatelets is needed.

CdSe nanoplatelets have been doped with copper up to 5 ML [28] thick core and with silver up to 4 ML [30]. In this thesis, we have proposed to dope the 7 ML thick CdSe NPLs with silver and copper. Our aim is to push PL emission deeply into the NIR and increase the Stokes shift to reduce the reabsorption. Also, we synthesized a CdZnS shell on a 7 ML

CdSe core and doped it to further redshift the emission. We used the partial cation exchange method for all kinds of dopings because of the control over doping levels it allows with varying precursors and temperatures during the post-synthesis doping process. We used optical characterization for absorption, photoluminescence, quantum efficiency, and emission kinetics investigation, and we also used transmission electron microscopy and x-ray diffraction for structural characterization. Finally, we used inductively coupled plasma mass spectroscopy to confirm the incorporation of dopant ions in the crystal lattice of NPLs.



Chapter 2

Background Information

This thesis consists of synthesizing thick CdSe colloidal nanoplatelets, doping these thick nanoplatelets with silver and copper, and then co-doping of these NPLs with silver and copper at the same time. We also investigated the doped heterostructure for such thick nanoplatelets. For a better understanding of our findings, here we explain the basics of colloidal nanoplatelets, their heterostructures, and the doping of nanoplatelets in this chapter.

2.1 Semiconductor Nanocrystals

Crystalline materials with one or more dimensions smaller than 100 nm are known as nanocrystals. Nanocrystals having only a few hundred to thousands of atoms of semiconductor materials are semiconductor nanocrystals. As the crystal size decreases from bulk crystalline materials, electrons are confined to a limited space, which leads to discretized energy levels like atoms instead of continuous conduction and valence energy bands in bulk semiconductors. In bulk semiconductors, the energy bandgap is constant for any specific bulk semiconductor material, but it varies in nanocrystals and can be tuned by size modification via the quantum confinement effect. Changing the nanocrystal size, the band gap is tuned. As the nanocrystal size is increased, the energy band gap is decreased and vice versa. Figure 2.1 illustrates this effect.

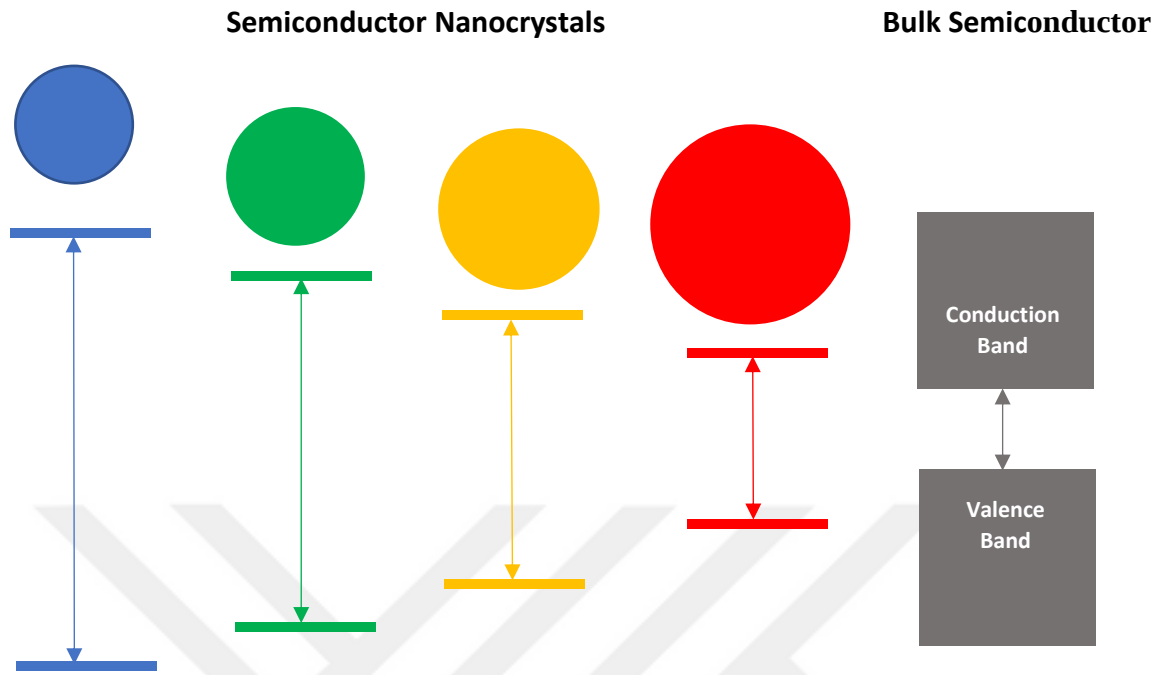


Figure 2.1: Schematic representation of quantum size effect on band diagram for bulk and nanocrystal semiconductors.

As nanocrystals include only a few hundred atoms, electrons and holes are confined together to a limited space, being bound to each other, known as an exciton. These electron-hole pairs move together in a crystal with a constant separation from each other known as Bohr's radius [34]. The quantum confinement effect is effective only in those nanocrystals that have at least one dimension comparable to Bohr's radius, which is typically shorter than 10 nm. Nanocrystals with all dimensions comparable to Bohr's radius are zero-dimensional (0-D) materials, while nanocrystals with 2 and 1 dimensions comparable to Bohr's radius are 1-D and 2-D, respectively. Because of their size ranges, the zero-dimensional NCs feel a confinement effect in all dimensions, while the 1-D NCs feel a confinement effect in 2 dimensions and the 2D NCs are confined only in 1 dimension.

Among the different classes of nanocrystals, quantum dots are examples of quasi-zero dimensional NCs, nanowires, nanotubes, and nanorods are examples of 1-D NCs, and nanoplatelets are examples of 2-D NCs.

2.2 Colloidal Nanocrystals

The quantum confinement effect in colloidal NCs was observed in 1981 [35]. Since then, obtaining monodisperse nanocrystals has been one of the major challenges. This goal of synthesizing monodisperse nanocrystals was first achieved by Bawendi *et al.* [36]. Through colloidal synthesis, the authors obtained monodisperse nanocrystals with less than 5% size variation [36]. A colloidal synthesis requires three constituents: solvent, precursors, and ligands. Usually, a noncoordinating solvent such as octadecene is used to provide a synthesis environment. Molecular precursors are the source of monomers that are used for nucleation and growth. Ligands are used for the stability and uniformity of the nanocrystals. La Mer's [37] nucleation and growth model described that, to achieve monodisperse nanocrystals, nucleation and growth stages should be strictly separated from each other. As the precursors are injected at higher temperatures, they decompose into monomers. For homogeneous nucleation to occur, a high monomer concentration is required. After the decomposition of the precursor, the concentration of the monomers is above this critical concentration, which is required for the nucleation. Small crystallites are formed as a result of the nucleation.

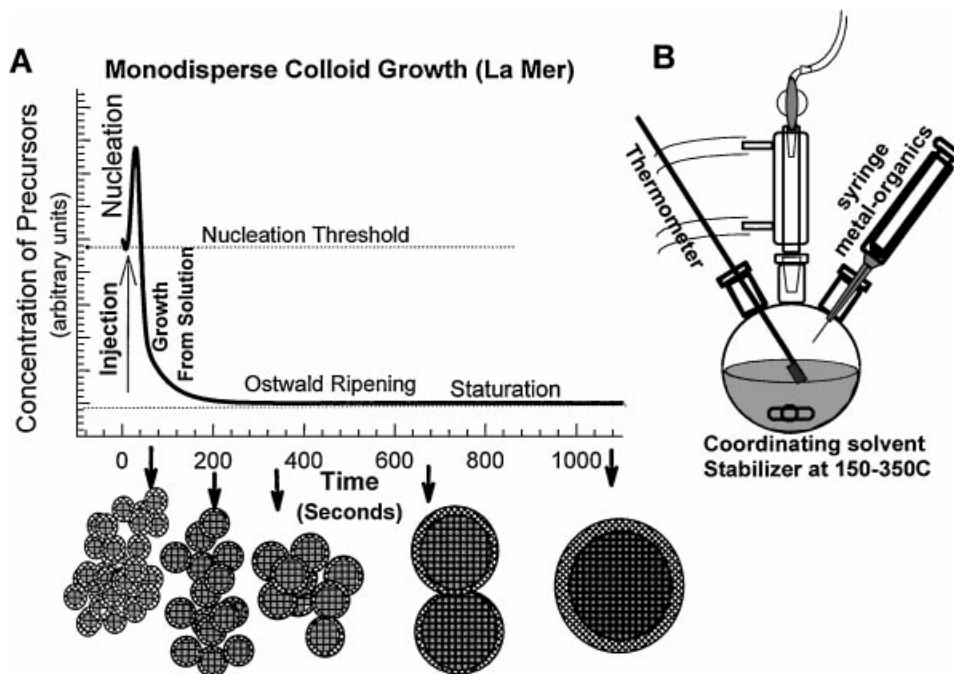


Figure 2.2: Nucleation and growth stages representation for obtaining monodisperse NCs [38].

As shown in Figure 2.2, As the nucleation occurs, the concentration of the monomers declines below the critical limit, which is required for the nucleation. Hence, the nucleation of new crystals is ruled out due to the availability of fewer monomers; after that, the rest of the monomers are used in the growth of the newly formed nanocrystals. In this way, by separating the growth and nucleation stages, monodisperse nanocrystals can be synthesized. During the growth stage, initially smaller crystals grow faster compared to the bigger crystals due to high monomer concentration, which causes a decline in size distribution. Later, when the monomer's concentration decreases, Ostwald ripening occurs, where small nanocrystals start to dissolve while larger ones continue growing, which results in an increase in the size distribution. One of the critical tasks in the colloidal synthesis approach is to control Ostwald ripening. Obtaining monodispersity in nanocrystals is not achievable without controlling Ostwald ripening.

2.3 Colloidal Semiconductor Nanoplatelets

An immense amount of research on colloidal quantum dots has been undertaken, but the search for narrow emitters has not been fully met and this has been a strong motivation for many groups to focus on nanoplatelets for the previous decade, as this sub-family of nanocrystals in the core architecture having magic size does not possess inhomogeneous broadening. Nanoplatelets are a comparatively new class of nanocrystals and were first reported in 2008 [2]. They are also named nanosheets or colloidal quantum wells. Nanoplatelets are typically considered superior to other classes of nanocrystals because they are vertically atomic scale-thick and their thickness can be controlled precisely. Quantum wells have been widely prepared by molecular beam epitaxy (MBE) [39] [40]. The colloidal approach was used for the first time for the synthesis of quantum wells by Ithuria *et al.* [2], and because these nanocrystals have similar optical properties to the quantum wells synthesized by MBE, the term colloidal quantum wells was coined for these types of nanocrystals. These NPLs have lateral dimensions in the range of larger than 10 nm, and vertical thickness is less than Bohr's radius, and their thickness depends on the number of monolayers of the nanoplatelet. 4 monolayer (ML) CdSe NPLs are 1.2 nm thick, and the thickness of 7 ML CdSe NPLs is 2.1 nm. A 7-monolayer thick CdSe colloidal quantum well has 7 layers of selenium and 8 layers of cadmium. They are arranged in

alternating layers of cadmium and selenium atoms, and cadmium layers form both facets. Ithuria *et al.* developed the recipe for the synthesis of anisotropic 2-D semiconductor nanocrystals [2]. In a noncoordinating solvent, long chain Cd precursor and Se powder are heated. Synthesis of the 2-D CdSe nanocrystal is achieved by adding a short-chain Cd precursor in the reaction from 180 °C to 220 °C. Short-chain precursor addition reduces the solubility limit of the precursor, resulting in phase separation [41]. The difference in activation energy between thinner and thicker facets is the driving force of anisotropic growth [41]. The low activation energy for one facet compared to the other ensures faster growth at that facet. Thinner facets grow faster due to low activation energy. Later the reaction is maintained at 240 °C for 5 to 20 min for lateral growth. Lateral growth can be tuned by changing this growth time. Figure 2.3 shows the absorbance of 4 ML NPLs. The first peak (~ 510 nm) is due to electron transition from the heavy hole (e-hh), and the second peak is from the light hole to the conduction band (e-lh). From Figure 2.4, it can be seen that NPLs have a very sharp peak with low full-width-at-half-maximum (FWHM). The figure shows a FWHM of ~10 nm suggesting inhomogeneous broadening suppression.

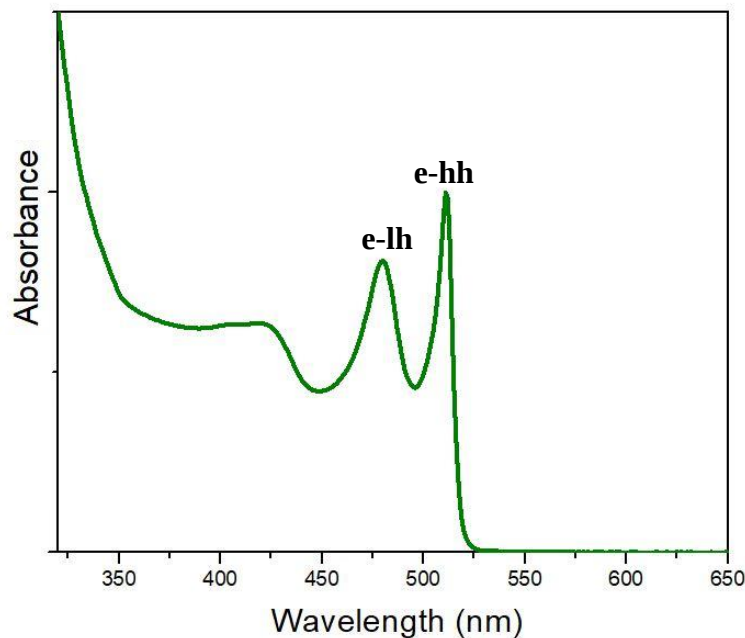


Figure 2.3: 4 ML CdSe NPLs absorbance.

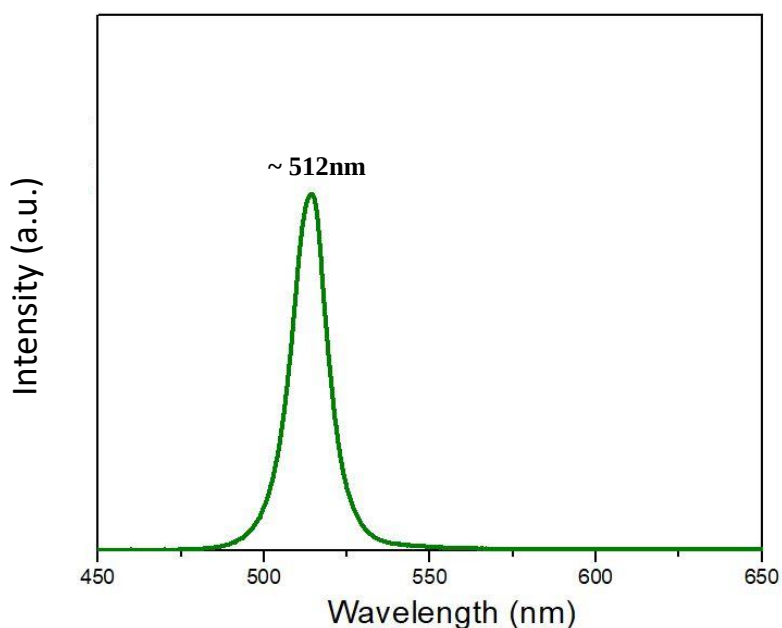


Figure 2.4: Photoluminescence of 4 ML thick CdSe NPLs.

By varying the short-chain precursor injection temperature and growth temperature, we can synthesize 3, 4, and 5 ML NPLs [41].

The activation energy required for growing the 6th monolayer is much higher than the energy required for growth on a thinner facet, i.e., lateral growth. To achieve this goal of synthesizing thicker NPLs, a chloride precursor is added, which lowers the activation energy barrier required for the growth of the 6th and thicker layers [42]. As a result, we can synthesize thicker CdSe nanoplatelets. To achieve the synthesis of thick NPLs, first, 4 ML CdSe core is synthesized, and then the reaction is continued by raising the temperature to 310 °C. By optimizing the chloride precursor injection temperature and lateral growth time and temperature, 6, 7, and 8 ML thick NPLs can be synthesized [42]. Absorbance and PL of 4 to 8 ML thick NPLs are shown in Figure 2.5. With the addition of each layer, the PL and absorption peaks are red-shifted.

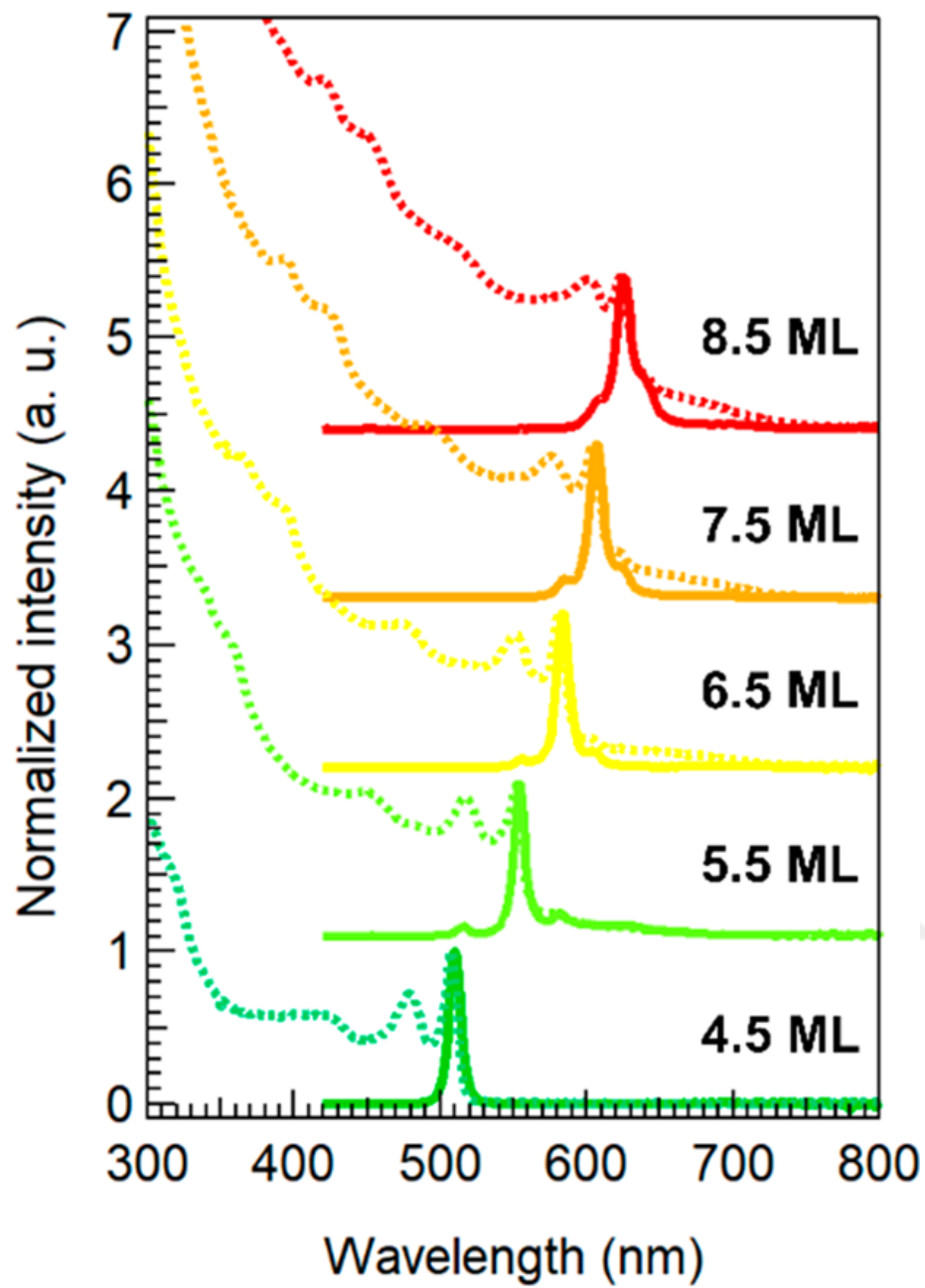


Figure 2.5: Change in absorption and PL peaks position with change in the thickness of NPLs [42].

2.4 Heterostructures of Colloidal Nanoplatelets

A simple CdSe nanoplatelet consisting of only alternating cadmium and selenium atoms is called a core. CdSe cores have a low photoluminescence quantum yield (PLQY) because of surface atoms dangling bonds and surface traps. Layers can be grown on a core forming various distinct heterostructures. Region grown anisotropically on the lateral side is known as the crown, and coating grown isotropically is known as the shell.

These heterostructures are synthesized to enhance quantum yield as they passivate the surface. Another reason for heterostructure synthesis is to modify the band structure. Depending on the material of the shell or crown, these heterostructures might be of type I, type II, or quasi-type II. Core/shell NPLs can be synthesized by the hot injection method [43] as well as the colloidal atomic layer deposition method [44]. In this thesis work, we synthesized core/shell NPLs to enhance the PLQY as well as to obtain redshift in the PL emission.

2.5 Colloidal Doping of Nanoplatelets

Colloidal nanocrystals can be doped in 2 ways: in-situ doping and post-synthesis doping [29-31] [45-46]. In the first method, doping is achieved by adding the dopant precursor during the synthesis of nanocrystals, i.e., during nucleation. In the 2nd method, first, the required nanocrystals are synthesized, and later they are doped by cation exchange. In-situ doping is very tough and it is challenging to control the doping levels, and it can result in the synthesis of some unwanted population of by-products or nanocrystals, while in partial cation exchange, we have control over the doping levels. Because of this control, we preferred partial cation exchange for the doping procedure in this thesis.

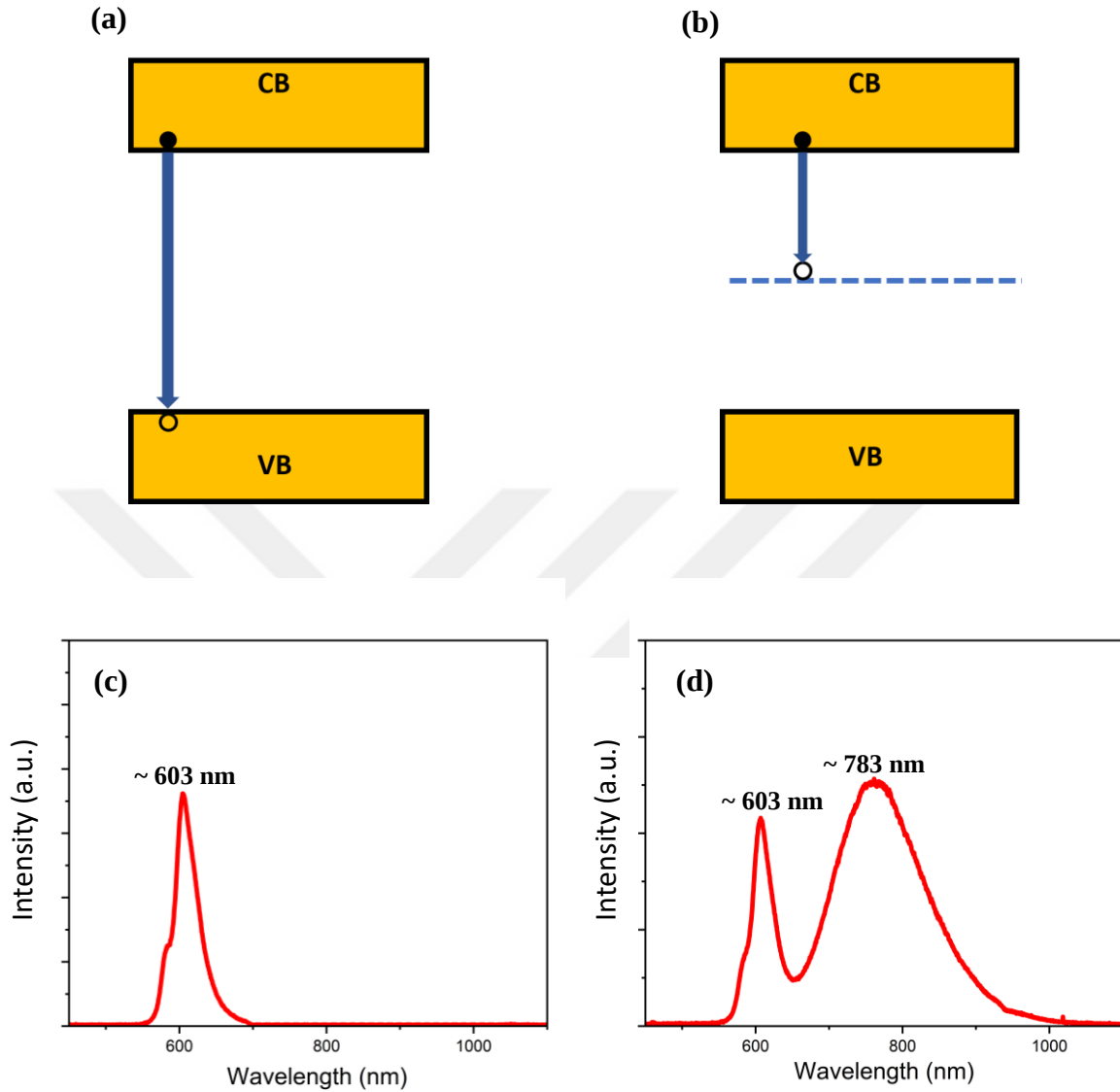


Figure 2.6: Schematic of the electron-hole recombination in (a) undoped and (b) doped NPLs and corresponding PL of (c) undoped NPLs and (d) doped NPLs.

During the partial cation exchange, some of the cadmium atoms are replaced with the dopant (silver or copper) atoms. The dopant atoms make a sub-band energy level between the valence and conduction bands, the hole from the valence band is captured at this level, and electrons relax to this sub-gap level. This gives red-shifted emission with high Stoke's shift. Figure 2.6 illustrates that in undoped 7 ML thick CdSe nanoplatelets, electrons relax to the valence band, generating band-edge emission, and in doped nanoplatelets the hole is localized and electron relaxes to the sub-bandgap energy level, giving rise to red-shifted emission.

Chapter 3

Characterization Methods for Colloidal Nanoplatelets

In this chapter, different characterization techniques used to investigate doped and undoped colloidal nanocrystals have been discussed. In this thesis work, we carried out optical, structural, and compositional characterizations.

3.1 Optical Characterization for Colloidal Nanoplatelets

Optical characterization of doped and undoped NPLs was carried out to understand the effect of doping on the excitonic properties of nanoplatelets. Optical characterization helps to determine the monodispersity and electronic structure of the nanocrystals.

3.1.1 Steady-State Absorption Spectroscopy

As colloidal quantum wells have specific excitonic peaks at specific wavelengths depending upon the thickness of the quantum structure, steady-state absorption spectroscopy becomes one of the most important tools to confirm the synthesis of colloidal quantum wells. From the absorption spectra, we obtain information regarding the size, shape, and purity of the produced nanocrystals.

We used Carry 100 model UV-Vis spectrometer for these measurements. To measure the absorption spectra, the synthesized NPLs were cleaned and dispersed in hexane. Then, these samples were excited with photons ranging from ultraviolet to NIR wavelengths (i.e., 200 to 800 nm). Photons that are greater in energy than the bandgap of the NPLs are

absorbed, and photons with smaller energy are transmitted. The absorption spectrum is obtained by collecting the transmitted photons from the sample.

As NPLs have specific excitonic absorption peaks, absorption spectra can also be used to determine the thickness of NPLs. As the thickness of nanoplatelets increases, due to the decrease in quantum confinement, the excitonic peaks are shifted to lower energies. The absorbance of 7 ML NPLs, shown in Figure 3.1, presents the red shift in peaks compared to 4 ML NPLs shown in Figure 2.3 . 7 ML CdSe NPLs have the first excitonic peak at 601 nm compared to 510 nm for 4 ML CdSe NPLs.

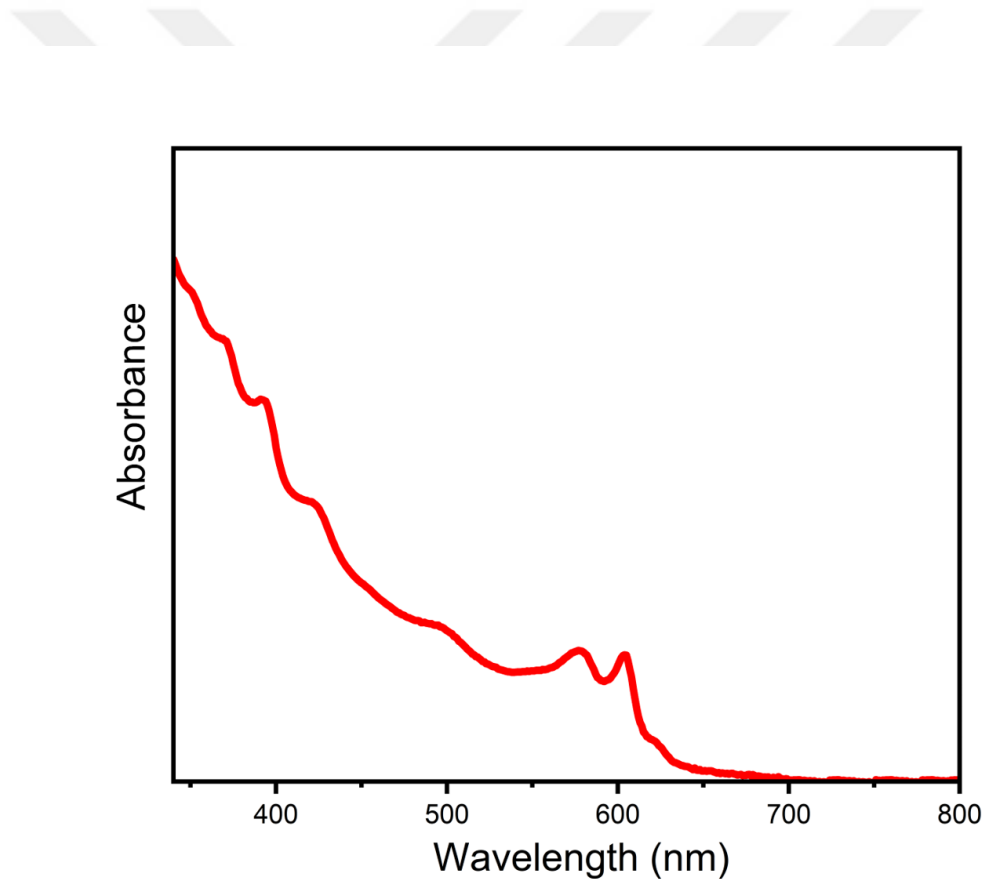


Figure 3.1: Absorption spectrum of 7 ML CdSe nanoplatelets.

The formation of heterostructures was also verified by steady-state absorption spectroscopy. We have used absorption spectroscopy to verify that doped NPLs have the

same excitonic features as undoped NPLs and that no new species were synthesized during the post-synthesized doping by cation exchange. Figure 3.2 shows that the absorption spectrum of Ag-doped thick nanoplatelets is similar to that of the undoped NPLs with a minor difference of small tail, which arises due to metal-to-ligand charge transfer.

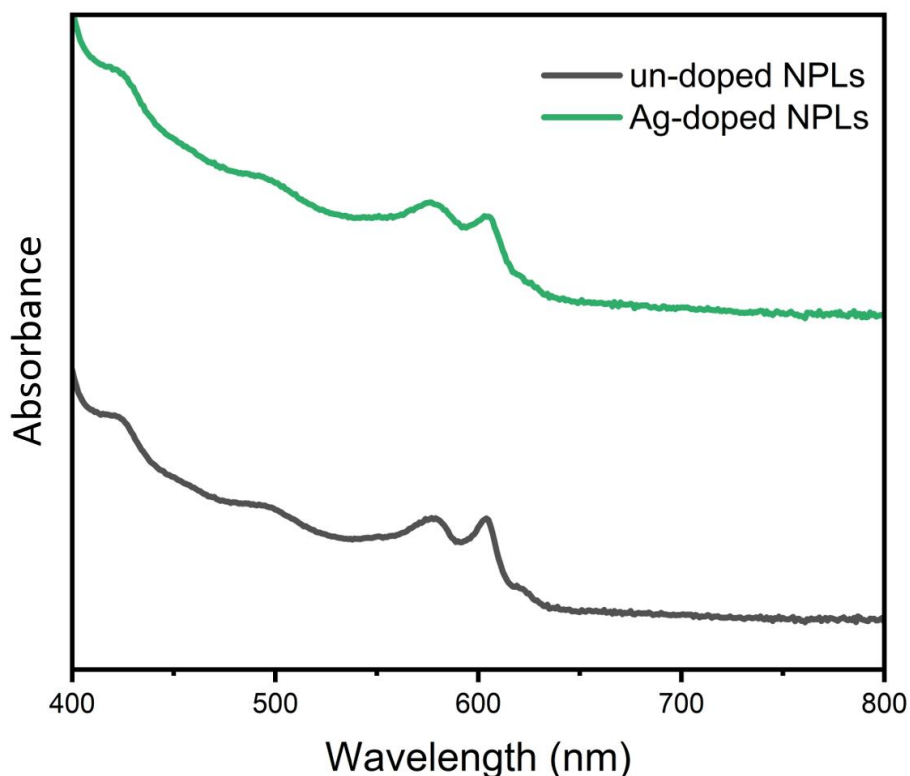


Figure 3.2: Absorption spectra of Ag-doped and undoped CdSe NPLs.

3.1.2 Photoluminescence Spectroscopy

To measure the photoluminescence of nanoplatelets, NPLs dispersed in hexane are excited with photons, higher in energy than their bandgap. Upon excitation, excitons are generated, and later electrons and holes recombine, which results in the photoluminescence. Figure 3.3 show the PL of 4 and 7 ML NPLs.

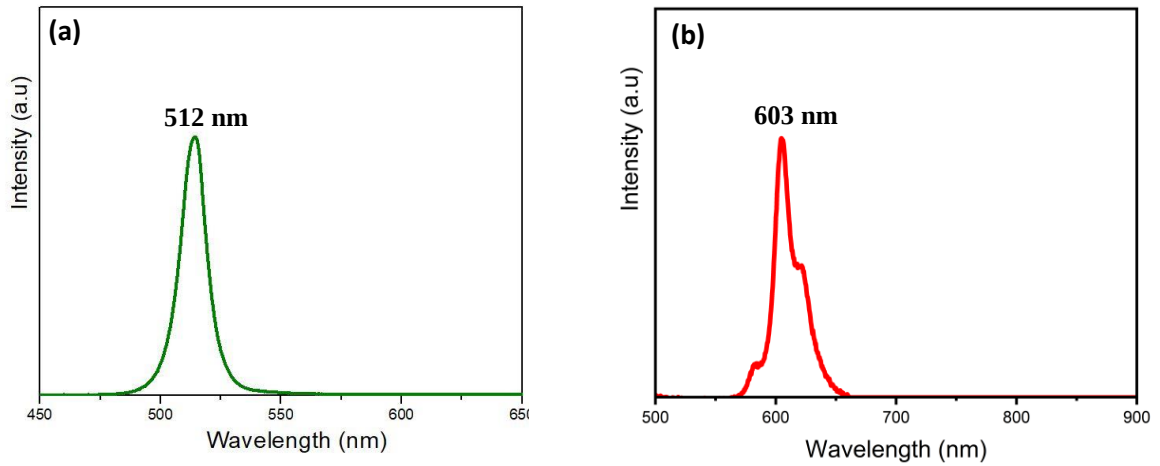


Figure 3.3: PL of (a) 4 ML and (b) 7 ML CdSe NPLs.

4 ML NPLs have a FWHM of 10 nm, and this narrow peak is the result of inhomogeneous broadening suppression. As it is easy to separate 4 ML NPLs from other populations by selective size separation, we can obtain the pure population of 4 ML NPLs, which is evident from the PL of 4 ML NPLs shown in the figure. For thick NPLs, it is difficult to separate 7 ML NPLs from 6 and 8 ML NPLs by selective size separation. Even after the separation, small populations from 6 and 8 ML NPLs exist in the ensemble. Hence we observe a sharp PL emission from 7 ML NPLs along with small tails emitted from 6 ML NPLs at shorter wavelengths and 8 ML NPLs at longer wavelengths.

3.1.3 Photoluminescence Quantum Efficiency

The quantum efficiency is ratio of the emitted to absorbed photons. It is also known as PL quantum yield (PL-QY). PL-QY is important when choosing a material for optoelectronic applications (e.g., LEDs and LSCs). PL-QY can be measured by 2 methods: absolute and relative measurements. In this work, we have used the absolute measurement method to find the PL-QY. In this method, an integrating sphere having a highly reflective inner surface was used. The NPL sample dispersed in hexane was filled in a cuvette, which was then placed in this sphere. First, the blank spectrum was taken when no sample was inside the sphere. Then dark measurement was taken, when there was no light incident, and the sample was inside the sphere. Third, the sample spectrum was collected when the sample was excited by direct light. Fourth, scattered light spectrum was collected by exciting the

sample with the scattered light. By using de Mallo method [47], PL-QY was calculated from these four collected spectra.

3.1.4 Time-Resolved Photoluminescence

To study the emission kinetics of fluorescent nanocrystals, for this thesis work, we used time-resolved photoluminescence (TRPL). TRF reveals information about the average lifetime of nanoplatelets as well as information about the recombination rates. In this thesis, a pulsed laser at a wavelength of 375 nm was used to excite the nanoplatelets, while a single time-correlated single photon counting unit (TCSPC) was used for photons detection. Pico harp 200 was used as a TCSPC. TCSPC starts counting the time from the excitation of NPLs and stops the time when a photon is detected by the detector. As a single photon is not powerful enough to create a signal, a photon multiplier tube (PMT) is used to multiply and generate a large number of photons from a single detected photon. The electrical signal is proportional to the intensity of the photon. These photon counts are placed in small time bins to generate a decay curve in the form of photons count vs time. Figure 3.4 shows the decay curve of 7 ML thick CdSe NPLs.

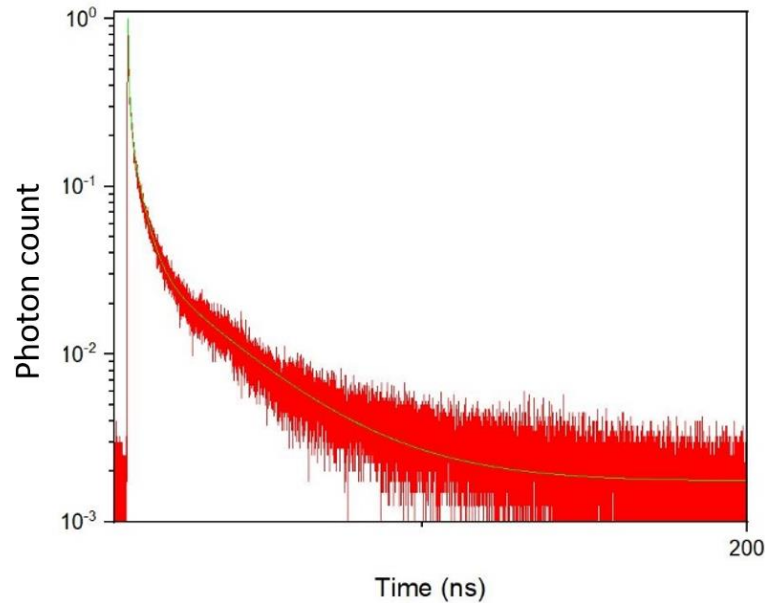


Figure 3.4: TRPL decay curve of 7 ML CdSe NPLs.

3.2 Structural and Elemental Analyses for Colloidal Nanoplatelets

The quality of a nanocrystal depends on its crystal structure, size, and shape. We have used structure characterization to analyze the effect of post-synthesis doping on the size, shape, size distribution, and crystal structure of the colloidal quantum wells. In this study, we have used transmission electron microscopy (TEM), X-ray diffraction spectroscopy (XRD), and scanning electron microscopy (SEM) for structural analysis.

3.2.1 Electron Microscopy

TEM is a piece of equipment for nanocrystal analysis. TEM is useful to image and resolve the nanocrystal material image down to 0.2 nm. In our work, TEM was used mainly for size and shape analyses of the doped and undoped NPLs.

For TEM analysis, sample preparation is a tricky task. To obtain images of nanoplatelets with a better contrast and resolution, samples are needed to be prepared in a proper manner. Both doped and undoped NPLs are suspended in a nonpolar solvent hexane. These NPLs are capped with ligands. First of all, ligands are removed from NPLs by cleaning them three times. After cleaning, these NPLs are diluted. Dilution needs to be performed carefully, as too little concentration will result in a low number of NPLs in the image, while a higher concentration will end up in agglomerated NPLs, resulting in unclear images. Later, these diluted NPLs were dropped on a copper grid. The copper grid mesh was put in a vacuum for evaporation before using these samples for TEM analysis.

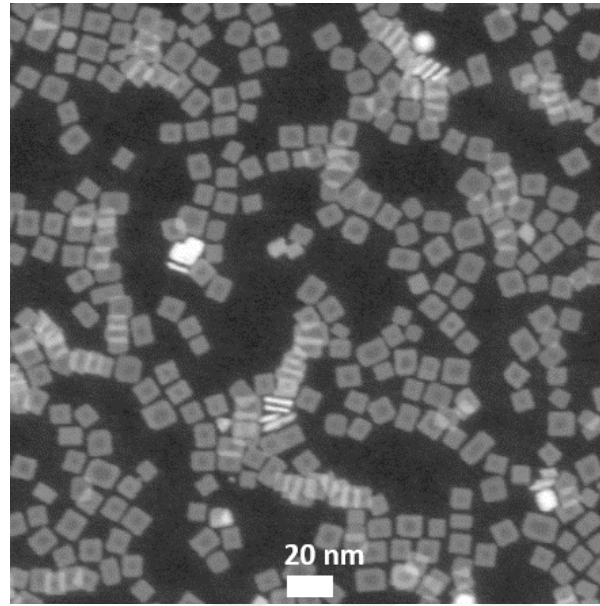


Figure 3.5: 7 ML thick CdSe square nanoplatelet's TEM image.

Figure 3.5 presents TEM images of 7 ML thick CdSe NPLs. TEM image reveals that the synthesized nanoplatelets are square-shaped with lateral dimensions of $\sim 15 \text{ nm} \times 15 \text{ nm}$. Also, the nanoplatelets are monodisperse. It can be estimated that they are around 2 nm thick, which is equivalent to the thickness ($\sim 2.1 \text{ nm}$) of 7 ML thick CdSe nanoplatelets.

3.2.2 X-Ray Diffraction Spectroscopy

X-ray diffraction (XRD) is useful in determining the crystal structure of a material. The crystal structure of the nanocrystals determines the final shape as well as optical properties. In x-ray diffraction, x-rays bombard the material, and then diffracted x-rays are collected from the sample. X-rays are generated from a cathode tube. The tube generates characteristic and white radiations. Characteristic radiation wavelength depends on the cathode material. In our lab, we used a copper x-ray tube that has a characteristic wavelength of 1.54 Angstrom. A monochromator is used to filter out characteristic x-rays, which are incident on the sample. According to Bragg's law,

$$2d \sin \theta = n\lambda \quad (3.1)$$

Here d is interplanar spacing and λ is the wavelength of the x-rays. When X-rays hit the nanocrystals, some of the X-rays diffract from the planes while others penetrate into the sample and diffract from the crystal planes. So, X-rays diffracting from different crystal planes cover different distances. If the rays diffracting from inner planes cover an extra

distance which is a multiple of λ , i.e., $n\lambda$ ($n=1, 2, 3, 4\dots$). Only then, after diffraction, the diffracted x-rays will be in phase, and constructive interference will occur; else, destructive interference will happen. As the incident angle is changed, the relative distance traveled by x-rays, which are diffracted from different planes, changes. So we receive a diffraction pattern in which we obtain peaks at only those angles at which the constructive interference occurs.

3.2.3 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

ICP-MS is a useful method for analyzing the trace elements, isotope ratio, and cations ratio. In this thesis, ICP-MS was used to confirm doping and determine dopant ratios in CdSe NPLs. ICP-MS is powerful enough to determine the dopant cations up to parts per billion in the NPLs ensemble. An ICP-MS instrument consists of various components, including a sampling interface, nebulizer, plasma torch, mass separation device, ion focusing system, and vacuum chamber. For analysis by ICP-MS, standards are also required to be prepared along with samples. For standard preparation, first, a 2-3% nitric acid solution is needed. A flask is filled with 50 mL of this diluted nitric acid solution. Then, depending upon the trace element, we desire to measure a specific amount of cation that is added to this nitric acid solution. For copper and silver measurements, 100 μL of their respective solutions is added each. This solution contains around 1000 ppb. Then, they are diluted to 5 standards with 100, 500, 250, 125, and 62.5 ppb concentrations, which are used as standards. For sample preparation, doped nanoplatelets are washed and cleaned with acetone. The doped NPLs dispersed in hexane have some unreacted dopant precursors in them. If less cleaning is applied, then these precursors might be present in the samples prepared for ICP-MS and would give a high amount of dopants compared to their actual amount present in the NPLs ensemble. On the other hand, too much cleaning adversely affects the samples, as it might lead to self-purification. After cleaning, 100 μL of doped samples is collected in a 10 mL centrifuge vial. The samples are dried in a vacuum for 1 h. Later 160 μL of nitric acid is added to each vial, and after waiting for 15 min, NPLs are dispersed in nitric acid. Afterwards, distilled water is added in each vial to make a total of 8 mL solution for each sample.

These prepared samples are used for analysis. During the analysis, the liquid sample is converted into a spray with a nebulizer. Bismuth is used as an internal standard and is

mixed with the sample before pumping into the nebulizer. Different size droplets are formed, and small droplets are turned into ions in the plasma torch while the rest of the droplets are filtered out. Later 4 quadrupole mass spectrometer separates these ions on the basis of the mass-to-charge ratio. The detector detects ions and generates electrical signals.



Chapter 4

Colloidal Doping of Thick Nanoplatelets

4.1 Experimental

4.1.1 Chemicals

For the synthesis of doped thick NPLs, the chemicals we used consist of cadmium oxide, cadmium acetate dihydrate $[\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}]$ ($\geq 98\%$), cadmium acetate anhydrous $[\text{Cd}(\text{Ac})_2]$, cadmium chloride, elemental selenium (Se) (99:998% trace metals basis), cadmium nitrate tetrahydrate $[\text{Cd}((\text{NO}_3)_2) \cdot 4\text{H}_2\text{O}]$ (99:999% trace metals basis), zinc acetate dihydrate (98%), 1-octane thiol ($\geq 98.50\%$), silver nitrate, copper iodide, sodium myristic acid ($> 99\%$), 1-octadecene (technical-grade) (ODE), oleyl amine, hexane, acetone, trioctylphosphine (TOP), ethanol, and toluene.

4.1.2 Precursors Preparation

Cadmium Myristate

We prepared cadmium myristate in our lab using methanol, sodium myristate, and cadmium nitrate based on an existing recipe [20]. 3.13 g of sodium myristate in 250 ml methanol and 1.23 g of cadmium nitrate in 40 mL of methanol were dissolved in two separate reagent bottles by continuous stirring. After continuous stirring for 2 h, they were dissolved. After dissolution, we mixed them into one reagent bottle and continued stirring for two more h. Then methanol was drained using a filter, and the cadmium myristate

precipitate was washed with methanol three times. Later, this precipitate was kept in vacuum for 24 h to dry it.

Preparation of Chloride Precursor

Chloride precursor is needed to lower the activation energy barrier to facilitate the growth of CdSe nanoplatelets thicker than 5 ML [42].

To prepare chloride precursor, 320 mg of cadmium oxide and 80 mg of cadmium chloride were added to a 3-neck 100 mL flask in 40 mL of oleic acid. First, the reaction was put under vacuum for 30 min at 95 °C, after that system was switched to Argon flow and the temperature of the system was raised to 200°C. At 200°C, the color of the solution changed from orange to transparent. After 15 min, the reaction was cooled down below 40°C. The precursor was collected in vials and stored in the fridge for further use.

Preparation of Silver Precursor

The silver precursor was prepared to use for the partial cation exchange reaction. To prepare the precursor, 51 mg of silver nitrate was dissolved in 18 mL of 1-octadecene, and in a vial in the glove box, 150 µL of TOP was added to the solution. The mixture was put in the glove box under stirring for 24 h till complete dissolution.

Preparation of Copper Precursor

The copper precursor was also prepared in the glove box, where 70 mg of copper iodide was added to 7 mL of octadecene and 200 µL of TOP in a vial in the glove box and was put for 2 h of stirring till complete dissolution.

4.1.3 Synthesis of CdSe Nanoplatelets

To synthesize 7 ML CdSe NPLs, we modified the previously used recipe [42]. 255 mg of cadmium myristate, 40 mg of cadmium nitrate tetrahydrate, 40 mg of elemental selenium, and 22 mL of ODE were loaded in a 3-neck 100 mL flask. A magnetic stirrer was loaded in a flask to keep the solution stirring throughout the synthesis process. First, the solution was put under vacuum at room temperature for 30 min, and then the temperature was slowly raised to 95 °C, where it was kept under vacuum again for 1 h to degas and remove the unwanted solvent. Then the solution was switched from vacuum to Argon flow, and the temperature was raised to 240 °C. During temperature rise, the color of the solution was monitored closely, and when the color changed to yellowish orange, generally between

190 and 195 °C, cadmium acetate anhydrous or cadmium acetate dihydrate was added to the mixture swiftly. Depending on the required lateral dimensions, cadmium acetate dihydrate or anhydrous was added. 140 mg of cadmium acetate anhydrous was added to obtain square-shaped NPLs, which are shown in Figure 3.6, and 160 mg of cadmium acetate dihydrate was added to prepare rectangular-shaped NPLs. Subsequently, at 240 °C, the mixture was kept for 20 min for lateral growth. With a needle, a small amount of the mixture was taken out, and the absorption spectrum was taken to confirm the synthesis of 4 ML CdSe NPLs at this point. After that, the temperature was raised to 310 °C, and at 280 °C, 1.5 mL of chloride precursor was added quickly. At 310 °C, the absorption and PL data were taken after 15 min each to observe the growth of 4 ML NPLs into 5, 6, and then 7 ML thick NPLs. Normally it takes around 60 to 90 min at 310 °C to reach the desired NPLs thickness. Then the solution was air-quenched to room temperature, and during the temperature reduction, at 240 °C, 2 mL of oleic acid was injected into the mixture. Below 40 °C, the synthesized NPLs were collected in a 50 mL falcon tube. After adding 20 mL of hexane, the mixture was centrifuged at 6,000 rpm for 6 min to separate thick NPLs from unreacted products and quantum dots. After the first centrifuge, thick NPLs precipitate out on the side walls of the falcon tube while remaining unreacted products and QDs remain in the supernatant. After checking the absorption spectra of the supernatant, the supernatant is discarded if little to no amount of thick NPLs are found in the supernatant, else the supernatant is centrifuged again to separate out the rest of the thick NPLs. The NPLs precipitated on falcon tube walls, are dispersed again in 15 mL of hexane and again centrifuged using the same parameters. Now, this results in the precipitation of thick NPLs (8 ML) and QDs to be separated out and the supernatant containing an ensemble of mostly 7 ML thick nanoplates and small portions of 6 and 8 ML NPLs. These NPLs are stored in vials and later used for the synthesis of core/shell NPLs and post-synthesized doping procedures.

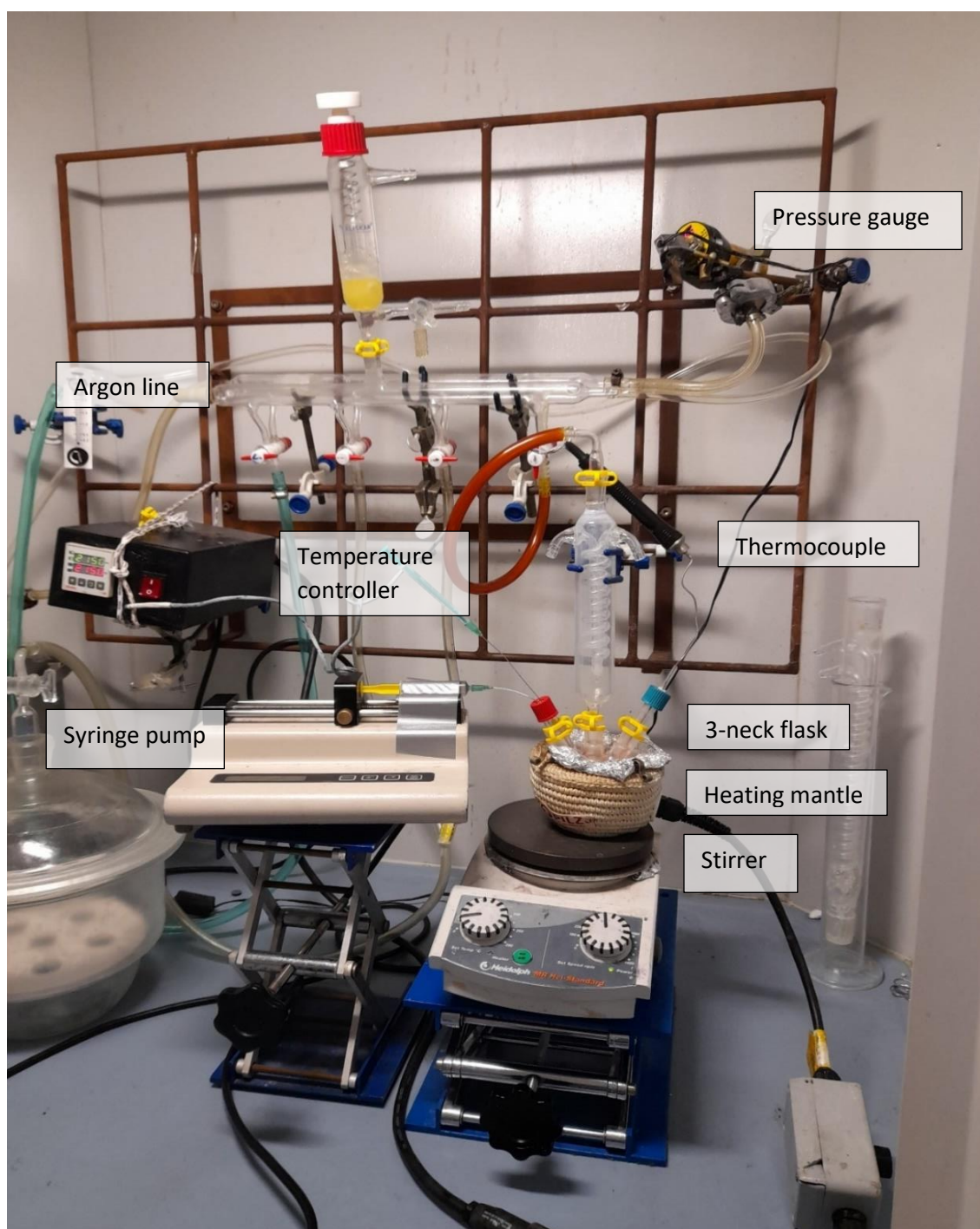


Figure 4.1: Schlenk line setup used for the colloidal synthesis in our lab.

4.1.4 Synthesis of CdSe/CdZnS Core/Shell Nanoplatelets

The 7 ML CdSe core nanoplatelets have a low quantum yield of around 10% [42], and their PL peak wavelength is around 605 nm. We coated 7 ML CdSe core NPLs with an alloyed CdZnS shell to enhance the PL-QY and redshift the emission wavelength by increasing the thickness of NPLs and relaxing the wavefunction.

We grew the CdZnS shell on 7 ML CdSe cores by using the hot injection method [48]. For the synthesis of CdSe/CdZnS core/shells, 7 ML CdSe NPLs dispersed in 1 mL of hexane, 22 mg of cadmium acetate, 72 mg of zinc acetate, 7 mL of ODE, and 1 mL of oleic acid were added to a 50 mL flask. The reaction was put under vacuum to evaporate hexane. The temperature was raised to 85 °C. At high temperature, Zn acetate and oleic acid form zinc oleate and produce water. The system was kept under vacuum at this temperature for 30 min again to evaporate the water. The mixture was switched to Argon gas flow before injecting 1 mL of OLA at the same temperature. The reaction temperature was set to 300 °C, and at the temperature of around 160 °C, the first drop of octan thiol solution was injected into the mixture. The octane-thiol solution was prepared by adding 280 μ L of octan thiol in 16 mL of ODE. This is the source of sulfur in the CdZnS shell. The octane-thiol solution was injected using a syringe pump at the rate of 10 mL/hour. This rate was chosen to initially start the reaction for shell synthesis smoothly, and when the temperature reached 240 °C, the injection rate was lowered to 4 mL/hour to ensure uniform shell synthesis. At 300 °C, the mixture was kept for growth. During growth time, the samples were collected using a long needle syringe to check the PL, and once we reached our required emission wavelength, we stopped the reaction and quenched it. And before storing these NPLs, they were cleaned using the standard procedure.

4.1.5 Synthesis of Doped Nanoplatelets

Synthesis of Ag-doped Thick CdSe Nanoplatelets

Silver doping of 7 ML thick CdSe core NPLs was carried out by post-synthesis using partial cation exchange. 4 mL of octadecene and 7 ML CdSe NPLs were loaded in a 50 mL flask. The mixture was kept in vacuum for 60 min at room temperature to remove unwanted solvents. After switching to Argon flow, the mixture was heated to 160 °C. At 160 °C, the silver precursor was injected with the syringe pump at the rate of 2.5 mL/hour. After the start of the precursor injection, a small amount of the NPLs mixture was collected for optical characterization after a regular interval. A quick analysis was performed with the

help of PL observation of the collected NPLs mixture. When the band-edge emission was quenched completely, the reaction was stopped. In an alternative approach, a fixed amount of precursor was injected, and the temperature was raised slowly. Again the reaction was stopped at the temperature where the band-edge emission was quenched. Then the mixture was water-quenched and collected after cleaning.

Synthesis of Cu-doped Thick CdSe Nanoplatelets

To synthesize copper-doped thick nanoplatelets, thick NPLs, after cleaning, were loaded in a 50 mL flask and were subjected to vacuum at room temperature and 40 °C for 60 min. Then, the mixture was switched to Argon flow, and the temperature was raised to 210 °C. At 210 °C, the copper precursor was injected at a rate of 2 mL/hour with a syringe pump. After 100 µL precursor injection, band-edge emission was quenched, and the reaction was stopped. After using the standard procedure of cleaning, Cu-doped thick NPLs were dispersed in hexane and stored in a vial.

Synthesis of Ag-Cu Co-doped Thick CdSe Nanoplatelets

Thick nanoplatelets were co-doped with silver and copper by partial cation exchange method. In a 3-neck flask, 4 mL of octadecene and thick NPLs were put under vacuum and stirred for 60 min. Later, the temperature was raised to 160 °C after switching the reaction to Argon flow. At 160 °C, 1 mL of Ag precursor was added at an injection rate of 2.5 mL/hour, and the temperature was raised to 210 °C. At 210 °C, the copper precursor was added at a rate of 1 mL/hour. The amount of precursor affected the dopant emission, and different amounts of the copper precursor were added depending upon the choice of PL emission we targeted. By adding 0.05 mL of copper precursor, no band-edge emission and no emission from the silver sub-band level were observed.

Synthesis of Doped Core/Shell Nanoplatelets

CdSe/CdZnS core/shell NPLs were also doped with silver and copper to push the PL further deep into the NIR region. CdSe/CdZnS core/shell NPLs were doped with silver and copper using the same procedures explained before.

4.2 Results and Discussion

4.2.1 CdSe Nanoplatelets

After the synthesis and cleaning of thick nanoplatelets, optical characterization was performed. Figure 4.2 (a) presents the absorbance of thick nanoplatelets.

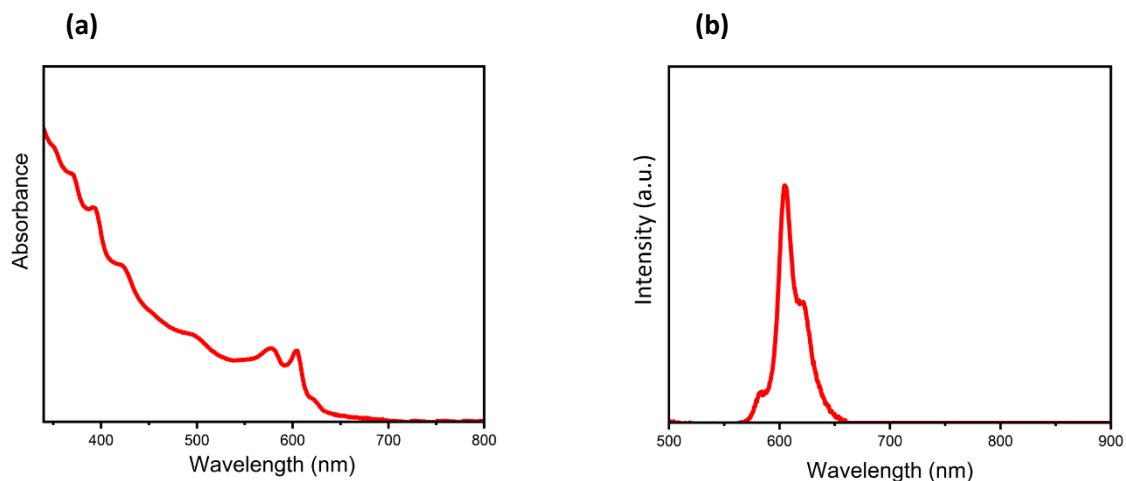


Figure 4.2: (a) Absorbance and (b) the PL of 7 ML thick CdSe NPLs.

From the photoluminescence of the thick nanoplatelets shown in Figure 4.2(b), it can be seen that the PL peak is centered at 605 nm and its FWHM is around 14 nm. Also, the PL shows satellite peaks on both sides. The peak on the shorter wavelength side centered at 583 nm is from a small population of 6 ML NPLs present in the ensemble and the peak centered at 623 nm is from a population of 8 ML NPLs in the NPLs ensemble.

Following the optical characterization of thick NPLs, structural characterization was undertaken with TEM and XRD. Figure 4.3 shows TEM images of 7 ML thick CdSe NPLs. Figure 4.3(a) depicts square NPLs that were synthesized using cadmium acetate dihydrate. From the image, the lateral dimensions can be estimated. These square synthesized NPLs have lateral dimensions of around 15 nm $\times$ 15 nm. Also, from the stacked-up NPLs, shown in the TEM image, the estimated vertical thickness is $\sim$ 2.1 nm. Thus, from these TEM images, the synthesis of monodisperse 7 ML thick nanoplatelets was confirmed. Figure 4.3(b) shows rectangular NPLs synthesized with cadmium acetate anhydrous. The lateral dimensions are in the range of 10 nm $\times$ 40 nm. In both these NPLs, the lateral dimensions

are larger than the exciton Bohr's radius; therefore, NPLs do not feel the quantum confinement effect in lateral directions.

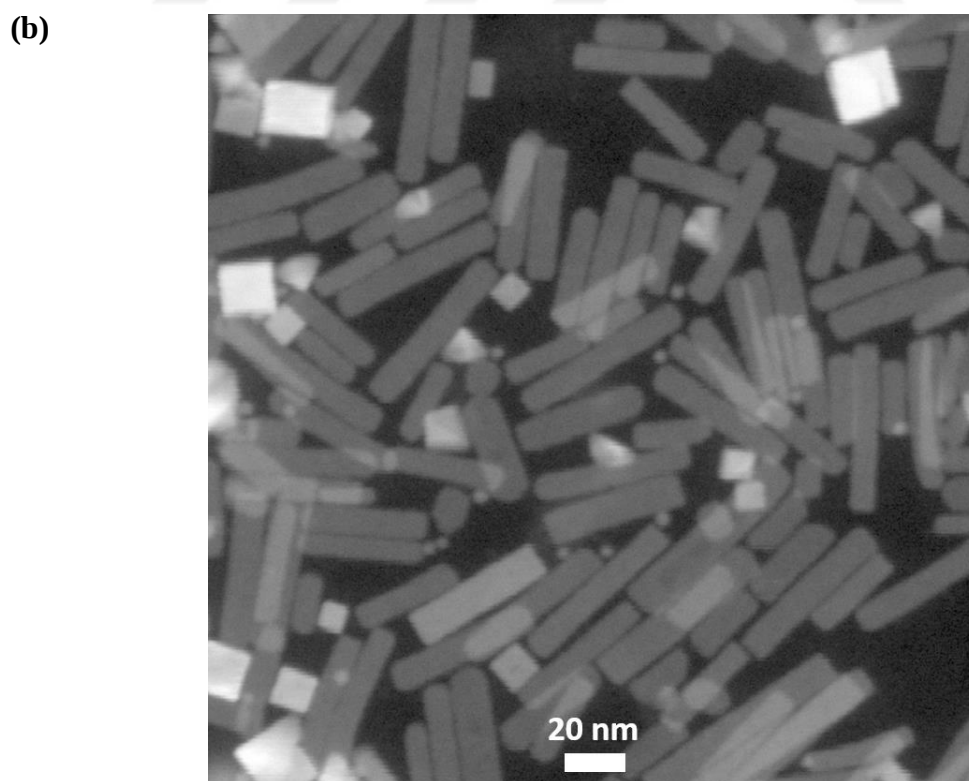
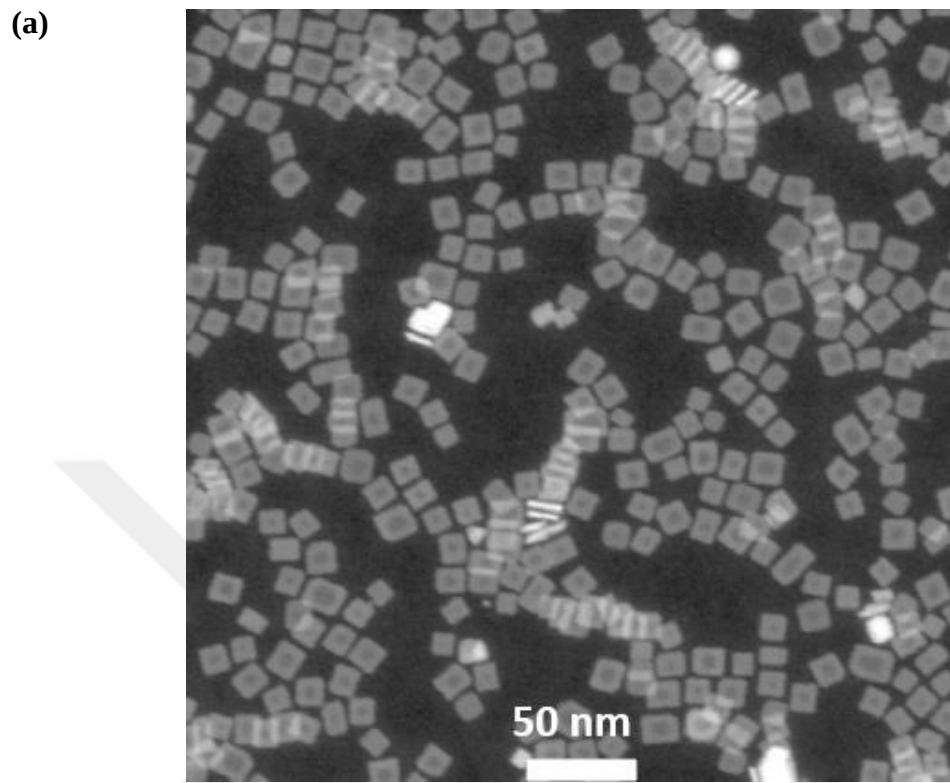


Figure 4.3: TEM images of (a) square NPLs and (b) rectangular NPLs.

With the help of XRD, it was confirmed that these thick CdSe NPLs had a zinc blende crystal structure. In Figure 4.4, the stick lines show the standard diffraction pattern lines for a CdSe bulk material, and NPLs diffraction peak match with these stick lines confirming the zinc blende crystal structure.

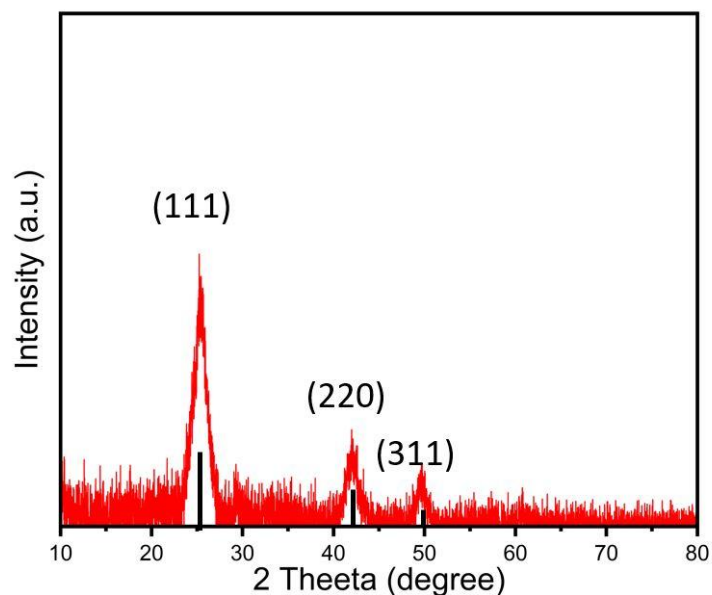


Figure 4.4: XRD diffraction pattern of 7 ML CdSe NPLs.

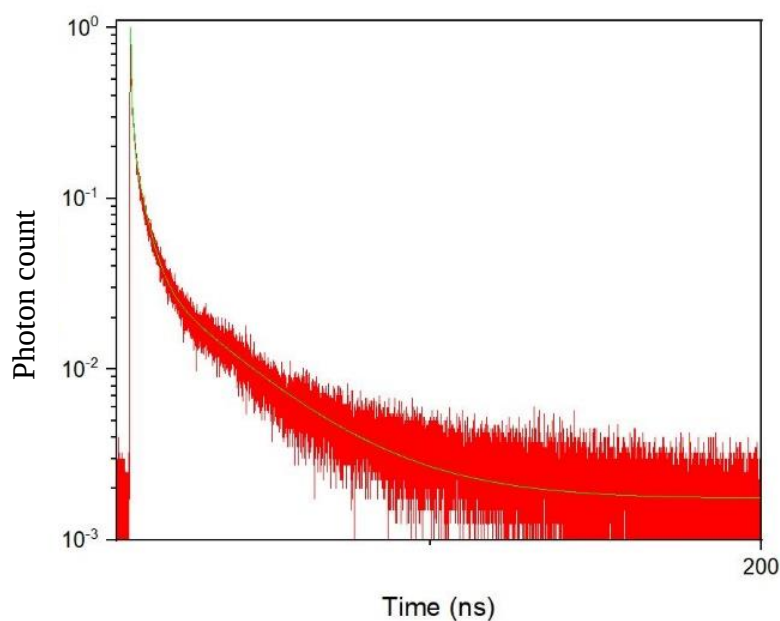


Figure 4.5: TRPL decay curve of 7 ML thick CdSe nanoplatelets.

The average photoluminescence decay lifetime of 7 ML thick nanoplatelets was measured by TRPL. The average lifetime for 7 ML CdSe NPLs was 13.3 ns. In the literature, the average lifetime for 7 ML NPLs is 10.5 ns [42]. The decay curve of 7 ML fitted with 3 exponentials is shown in Figure 4.5.

4.2.2 CdSe/CdZnS Core/Shell Nanoplatelets

First, thick CdSe NPLs cores were synthesized, and then we used these thick core NPLs for preparing CdSe/CdZnS core/shell structure. Optical characterization was carried out to examine the optical features. Figure 4.6 shows the absorption and PL spectra of the resulting CdSe/CdZnS core/shell NPLs.

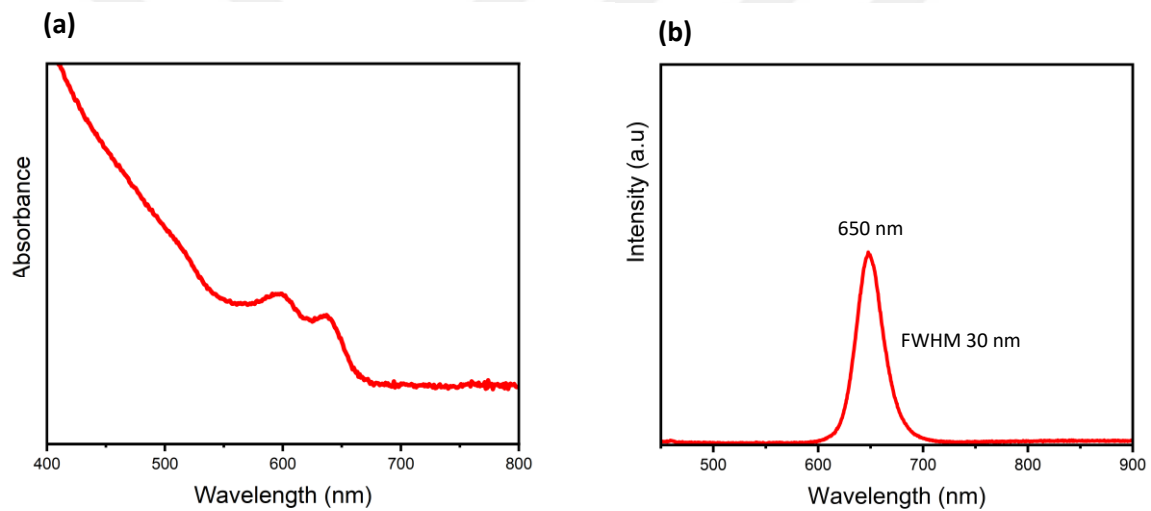


Figure 4.6: (a) Absorbance and (b) PL spectra of CdSe/CdZnS core/shell NPLs.

The 7 ML CdSe core NPLs used for synthesizing the core/shell structure emitted at around 605 nm. Figure 4.6(a) shows two excitonic peaks in the core/shell NPLs. Figure 4.6(b) presents the PL emission at 650 nm with a FWHM of 30 nm.

4.2.3 Ag: Doped CdSe Nanoplatelets

After synthesizing the Ag-doped thick nanoplatelets, we characterized those nanoplatelets using all the techniques presented in Chapter 3. As our main aim was to achieve the Stokes-shifted and dopant-induced PL, we started the characterization of our doped NPLs with optical characterization. Later, we analyzed our doped nanoplatelets with TEM, XRD, ICPMS, and TRPL as well. Figure 4.7 presents the absorbance and PL of undoped and doped thick NPLs with an increasing amount of precursor injected.

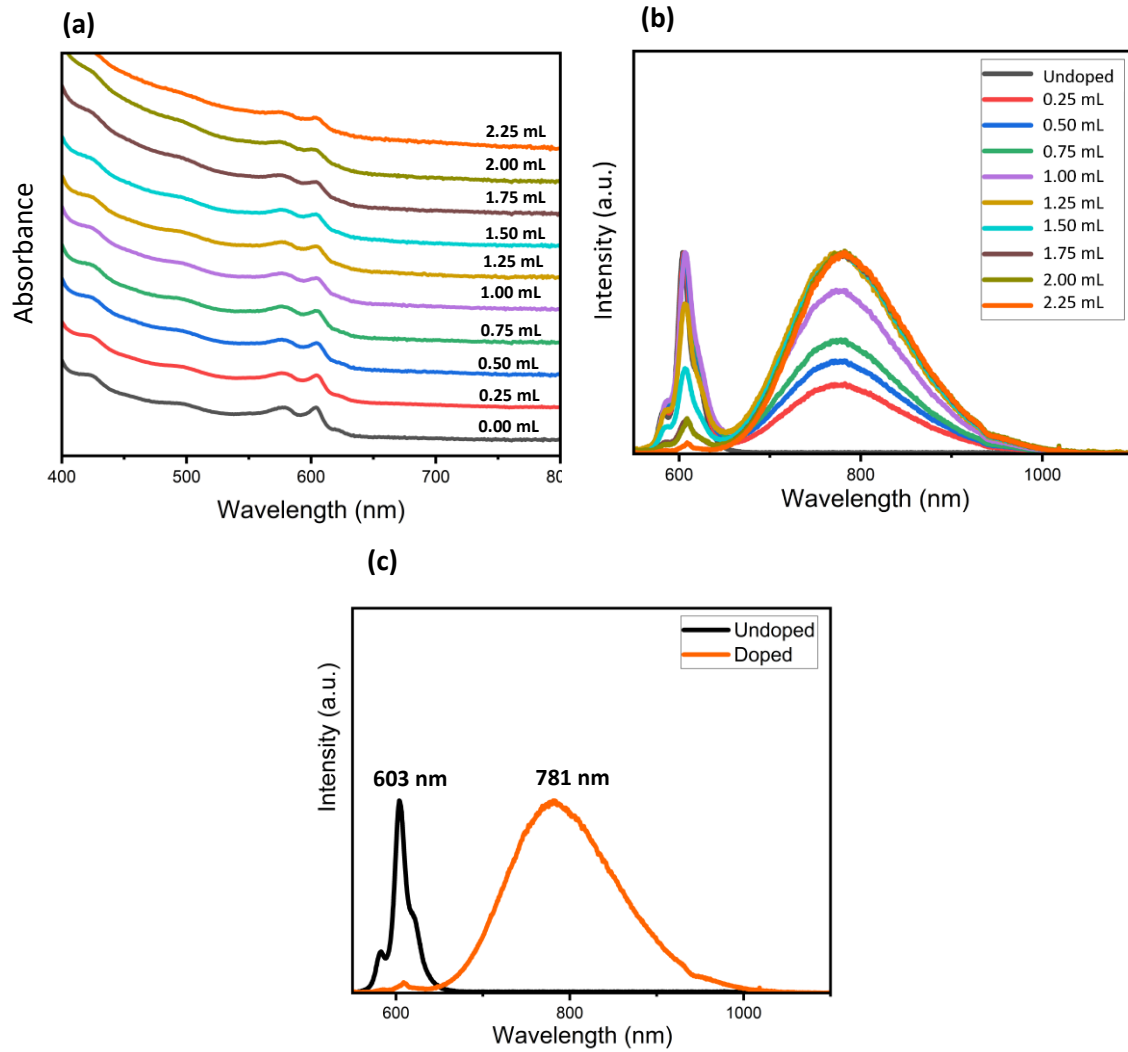


Figure 4.7: (a) Absorbance and (b) PL of Ag-doped thick NPLs with increasing Ag precursor amount and (c) PL of Ag-doped and undoped NPLs.

From the PL emission, we can observe that with an injection of 0.25 mL of precursor, a new PL peak appeared, which had the Stokes-shift of 178 nm. This new emission peak is

associated with dopant-induced emission. Figure 4.8 illustrates the phenomenon of dopant-mediated emission. Upon doping the NPLs with silver, a mid-gap energy level is introduced between the conduction and valence bands. Upon excitation, electron and hole pairs are created in the NPLs. First, the electrons from nanoplatelets are excited to the conduction band. In the second step, the hole left behind in the valence band is captured and relaxes to the silver mid-gap energy level, resulting in the oxidation of Ag^+ to Ag^{2+} . Then in the 3rd step, electron from the conduction band relaxes to the mid-gap energy level and brings Ag^{2+} to the Ag^{1+} state again [31].

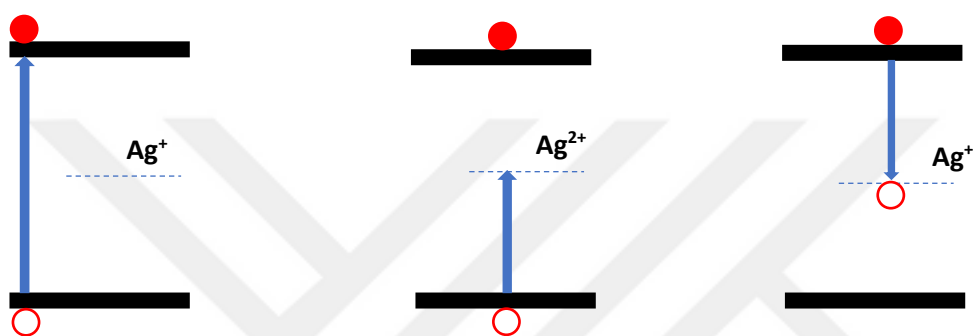


Figure 4.8: Schematics of dopant-mediated emission in Ag-doped NPLs.

The absorption spectra, shown in Figure 4.7(a), show that the doped NPLs have absorption spectra similar to those of the undoped NPLs, with the only difference of a small tail appearing at the longer wavelength of the first excitonic peak. This tail appears because of direct absorption by electrons at the Ag mid-gap energy level and is known as metal-to-ligand charge transfer. The band-edge and dopant-induced peaks remain fixed at 603 and 781 nm, respectively. These Ag-doped NPLs have a Stoke shift of 178 nm. With the injection of 2.25 mL of precursor, the band-edge peak was quenched, and only emission from the dopant mid-gap level was present. The dopant-induced emission is broad because of electron-phonon coupling [31].

TEM images were recorded and analyzed to check whether any size and shape changes occurred during the doping procedure carried out at high temperatures. TEM images revealed that no change in size and shape was observed after silver doping by partial cation exchange.

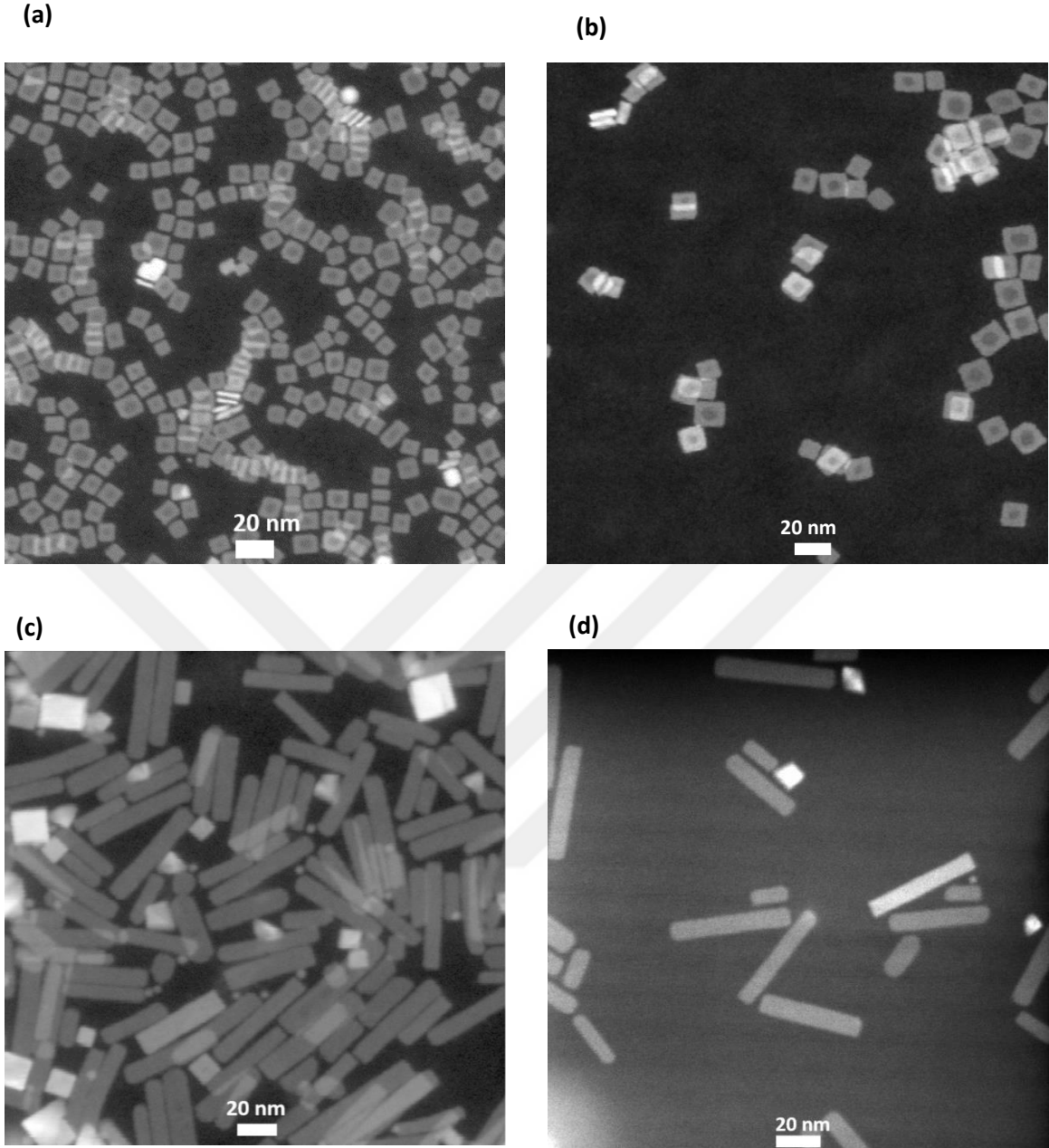


Figure 4.9: TEM images of (a) undoped 7 ML thick CdSe square NPLs, (b) Ag-doped 7 ML thick CdSe square NPLs, (c) undoped 7 ML thick CdSe rectangular NPLs, and (d) Ag-doped 7 ML thick CdSe rectangular NPLs.

The square NPLs have lateral dimensions of around $15\text{ nm} \times 15\text{ nm}$ before and after doping, while rectangular NPLs have lateral dimensions of $10\text{ nm} \times 40\text{ nm}$ before and after doping. Hence their size and shape were conserved after the doping procedure.

XRD analysis revealed that Ag-doped NPLs do not change their structure, and after doping, they still have the same zinc blend crystalline structure as undoped 7 ML thick CdSe nanoplatelets. No change in phase or crystal structure (from zinc blend to wurtzite) was observed. Also as the doped NPLs diffraction pattern is similar to the undoped NPLs pattern, such as no new peak originated after the doping, which confirms that no new species such as Ag_2Se was synthesized during doping.

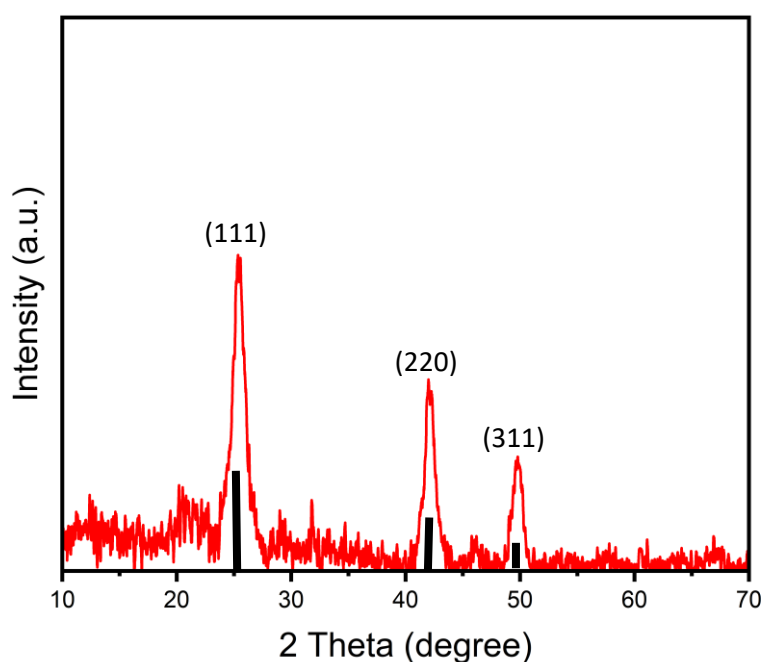


Figure 4.10: XRD pattern of Ag-doped 7 ML thick CdSe NPLs.

The incorporation of silver ions in NPLs was confirmed by ICP-MS. Figure 4.11 shows the ICPMS data.

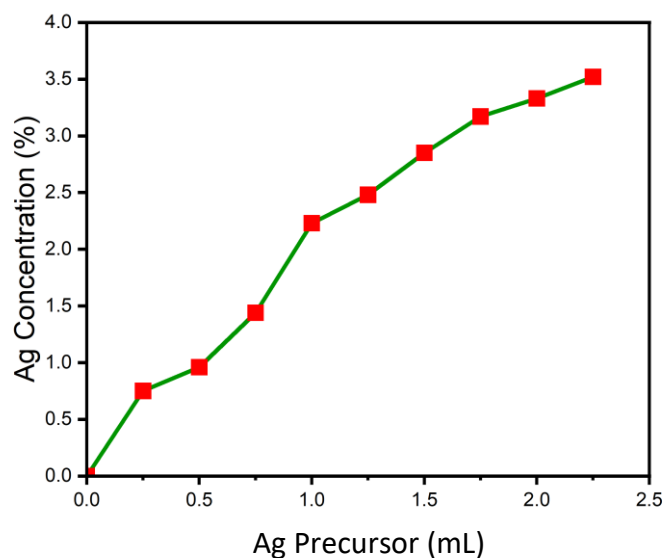


Figure 4.11: ICP-MS analysis for Ag concentration in NPLs.

Using ICP-MS, we analyzed the ratios of cations (silver and cadmium) present in Ag-doped 7 ML CdSe nanoplatelets. The data reveals that at injecting 0.25 mL of silver precursor, 0.73% of cadmium ions were replaced by silver via partial cation exchange. As we increased the precursor amount, the ratio of silver cations doped into the NPLs also increased, resulting in an increase in the dopant-induced emission and a decline in the band-edge emission. During the start of the doping procedure, all of the NPLs in the ensemble did not incorporate silver in them. Those NPLs where silver was incorporated emitted in the NIR region, while NPLs that were not doped with silver had band-edge emission. Finally, at 2.25 mL of silver precursor injection at 160°C temperature, in almost all of the NPLs, silver was incorporated, and the band-edge emission was quenched. At this precursor injection, the NPLs ensemble had around 3.6% silver inside the CdSe NPLs.

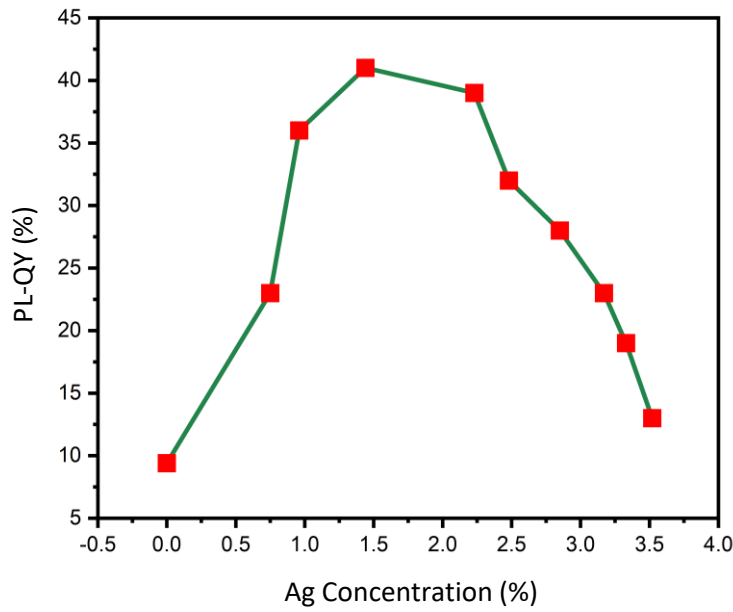


Figure 4.12: Variation in PLQY with the increasing silver doping levels.

Nanocrystals with very low doping were first reported by Norris *et al.* when they observed a PLQY surge of CdSe QDs with just a few atoms of silver doped per QD. In our thick silver-doped NPLs, we observed similar behavior. Our thick CdSe core NPLs had a PL-QY of 10%, and their PL-QY increased with increasing the doping level. At around 1.5% of silver incorporation in NPLs, we observed a maximum of 41% efficiency, and after, it started to decline to the same level of the initial PL-QY of the undoped core. The reason for the QY increase can be explained in terms of surface passivation. We assume that by adding the precursor, the TOP in the precursor passivates the surface by attaching to the surface atoms, which leads to an increase in PL-QY [45]. After a certain limited level of TOP passivating the surface, TOP has no further effect on PL-QY, and after this level, PL-QY decreases because of an increase in the ratio of silver ions adsorbed at the surface, which acts as surface traps and causes the electrons to recombining nonradiatively. Also, during partial cation exchange, some of the cadmium ions coming out of the crystal lattice also acts as nonradiative recombination sites after getting attached at the surface.

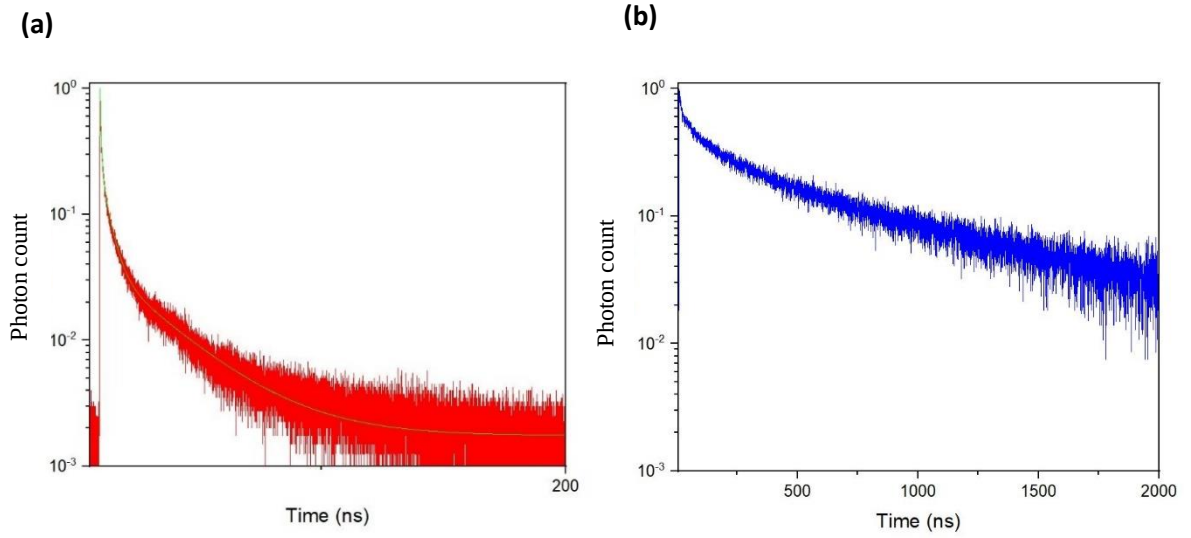


Figure 4.13: TRPL decay curve of (a) undoped NPLs at the band-edge and (b) doped NPLs at dopant-induced emission.

The TRPL decay curves were fitted with a 3-exponentials decay function for both doped and undoped NPLs. The TRPL analysis revealed that 7 ML thick CdSe NPLs had an average lifetime of 13.3 ns whereas Ag-doped NPLs had an average lifetime of 386 ns. Both of these values match with the literature [31]. As shown in Table 4.1, both doped and undoped have 3 decaying channels. The fastest decaying channel for the undoped NPLs is 0.36 ns, followed by slower channels of 3.3 ns, and similarly, the fastest channel for the doped NPLs is 7.1 ns, followed by 74.4 and 639.9 ns channels. Because of the hole localization in the doped NPLs, the average lifetime for the doped NPLs is higher than that of the undoped NPLs.

Table 4.1: TRPL decay time components for undoped NPLs.

A_1	τ_1	A_2	τ_2	A_3	τ_3
145.19	24.758	826.5	3.30	2908	0.3641

Table 4.2: TRPL decay time components for Ag-doped NPLs.

A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)
21142	639.9	115130	74.5	271700	7.16

4.2.4 Cu: Doped CdSe Nanoplatelets

Optical and structural characterization was carried out on copper-doped thick-core NPLs. The absorbance and PL spectra are shown in Figure 4.14.

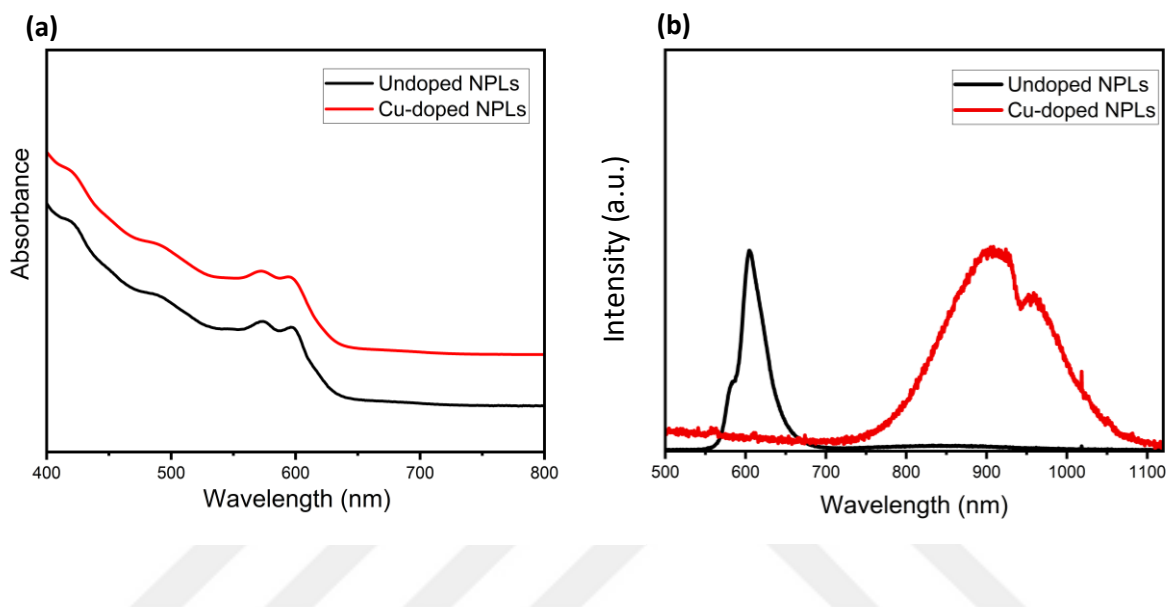


Figure 4.14: (a) Absorbance and (b) PL spectra of Cu-doped 7 ML thick nanoplatelets.

The copper-doped thick NPLs after doping had a Stokes' shift of 300 nm, and the dopant-induced peak was centered at 910 nm. In Cu-doped NPLs, the copper dopant also creates a mid-gap energy state which localizes the hole after capturing from the valence band, and the delocalized electron is relaxed to the copper mid-gap state resulting in Stoke's-shifted PL.

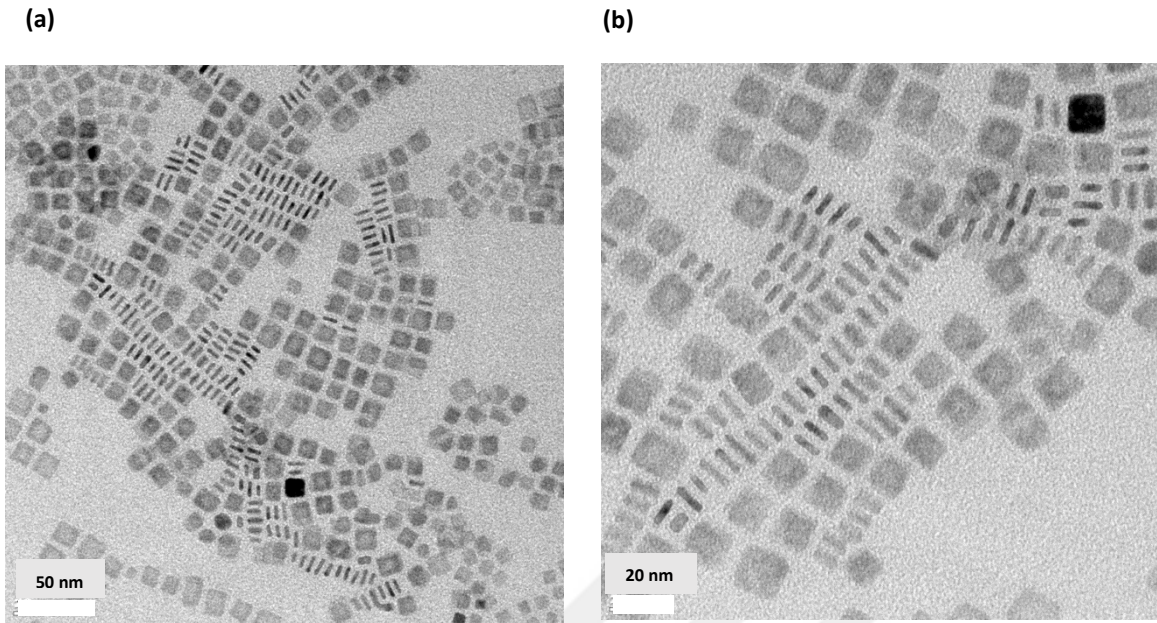


Figure 4.15: TEM images of (a) (b) Cu-doped NPLs.

Through structural characterization, the effect of doping on shape and crystal structure was investigated. Figure 4.15 presents TEM images of Cu-doped NPLs, The NPLs are square-shaped, and they did not get etched because of doping. Also, the Figure shows the XRD pattern, and it reveals that the crystal structure is intact as well, because the peaks all the relevant peaks are at their position.

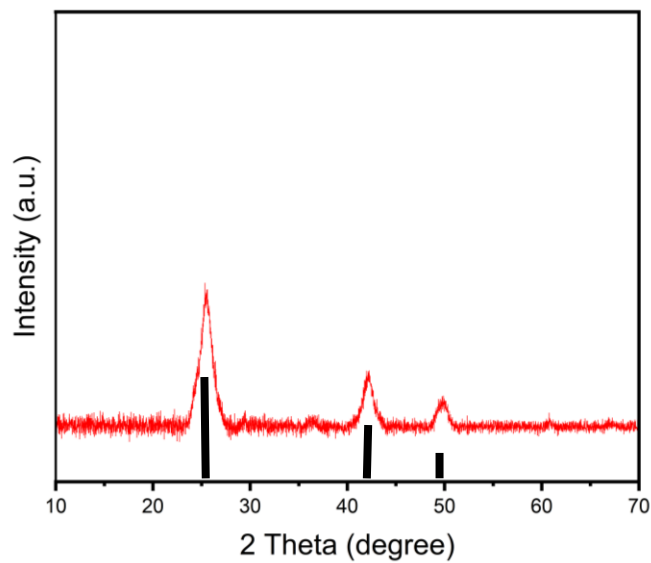


Figure 4.16: XRD pattern of Cu-doped 7 ML thick CdSe NPLs.

4.2.5 Ag-Cu: Doped CdSe Nanoplatelets

For the co-doping of 7 ML thick CdSe core nanoplatelets, first the 7 ML core NPLs were synthesized, followed by the co-doping of 7 ML cores with silver and copper using the procedure explained earlier in this chapter. Then optical and structural characterizations were carried out on these co-doped thick CdSe nanoplatelets.

The photoluminescence peak of the 7 ML CdSe core was centered at 593 nm. Upon doping these thick cores with silver, the band-edge PL peak was quenched and the dopant-induced emission peak appeared at 772 nm. This peak emerged because of silver sub-energy level and hole localization. Then, as we injected the copper precursor into these Ag-doped thick NPLs, copper was also incorporated into the nanoplatelets. A sub-gap energy level was introduced from copper. The ionization energy for silver is higher than that for copper. Thus copper is easier to oxidize than silver. The holes are captured in the copper sub-gap energy level. The excited electrons relax to this level. This results in further redshifted PL emission compared to silver dopant-mediated emission. Figure 4.17 presents the absorbance and the PL of these co-doped NPLs.

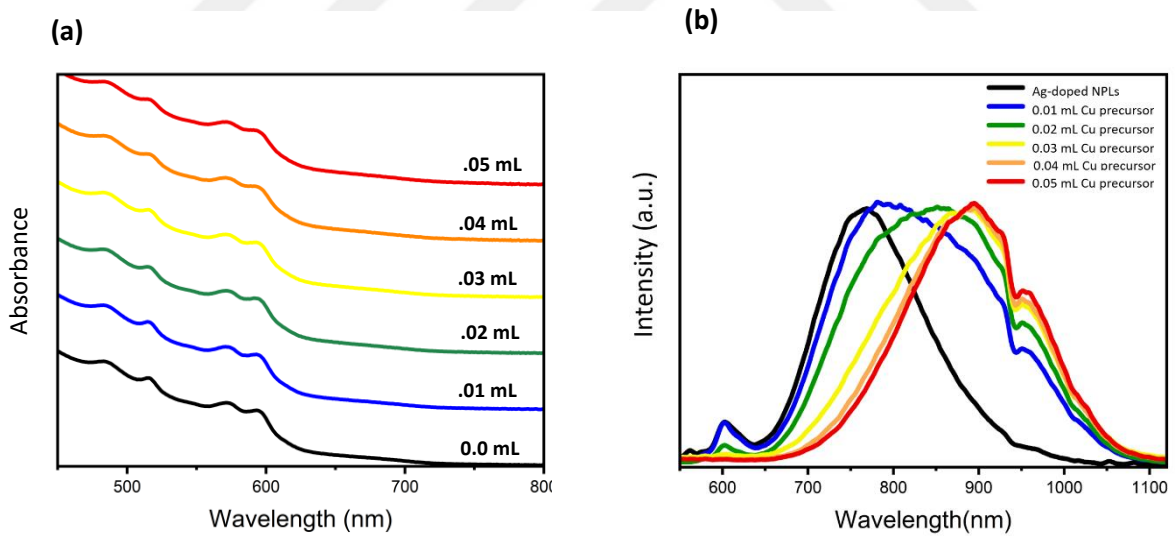


Figure 4.17: (a) Absorbance and (b) PL of Ag-Cu co-doped NPLs with increasing Cu precursor.

Figure 4.17(b) presents the evolution of peak emission shift as we increase the copper precursor injection amount in already silver-doped NPLs. Before copper precursor injection, NPLs are doped with silver with an emission peak at 772 nm and a FWHM of

212 nm, as shown in Figure 4.17. As we start injecting the copper precursor, we observe the evolution of the PL peak. At a very small amount of copper precursor injection, the peak position moves little to 775 nm, but FWHM has increased to 313 nm. The broad peak originates because some of the NPLs are incorporated with copper, resulting in emission at longer wavelengths. Hence we obtain emission from both copper and silver sub-levels, as some electrons relax to silver and some relax to copper sub-gap energy level. As we increase the copper precursor injection from 0.01 to 0.05 mL, the NPLs ratio doped with copper in the ensemble increases, and the ratio of electrons relaxing to copper sub-gap energy level increases leading to a peak shift from 772 to 890 nm. At 0.05 mL of copper precursor injection, the PL spectrum of these co-doped NPLs looked similar to that of just copper-doped thick NPLs. Figure 4.15(b) shows the evolution of spectral peak emission position from that of purely Ag-doped PL spectra with a peak emission position at 771 nm to purely Cu-doped-like spectra with a peak position at 885 nm.

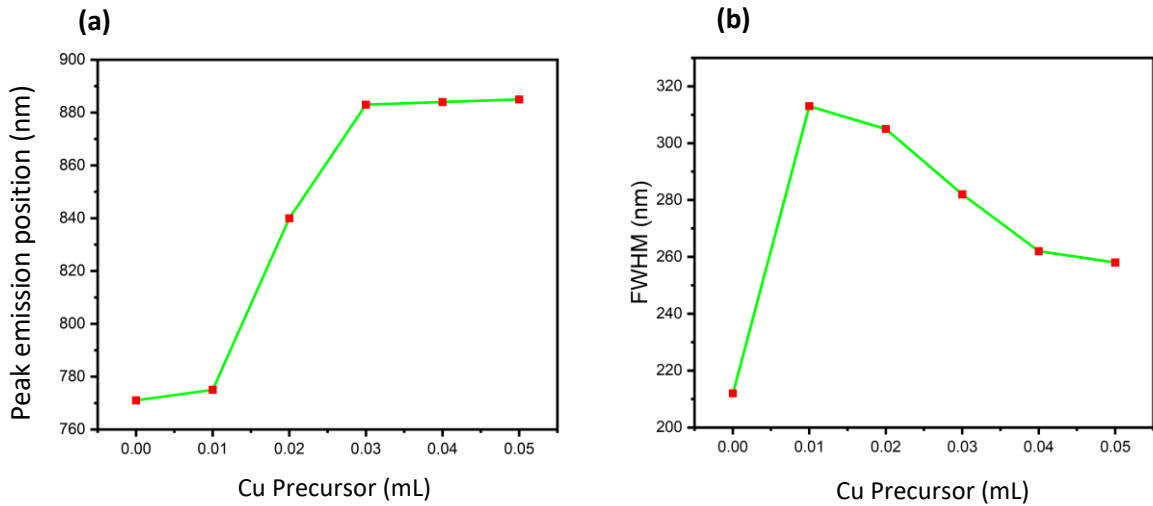


Figure 4.18: (a) Peak emission position shift from Ag-doped to Cu-doped with increasing copper precursor and (b) variation of FWHM of dopant-induced PL with increasing Cu precursor amount.

FWHM was also affected by copper precursor injection. Figure 4.18(b) illustrates this observation. Ag-doped thick NPLs had a FWHM of 212 nm, and with precursor injection, this increased to a maximum of 318 nm, and then with a further increase of Cu precursor injection, FWHM started decreasing, and at 0.05 mL of copper precursor injection, these

co-doped NPLs had FWHM of 258 nm, which is equivalent to the FWHM of purely copper doped thick NPLs.

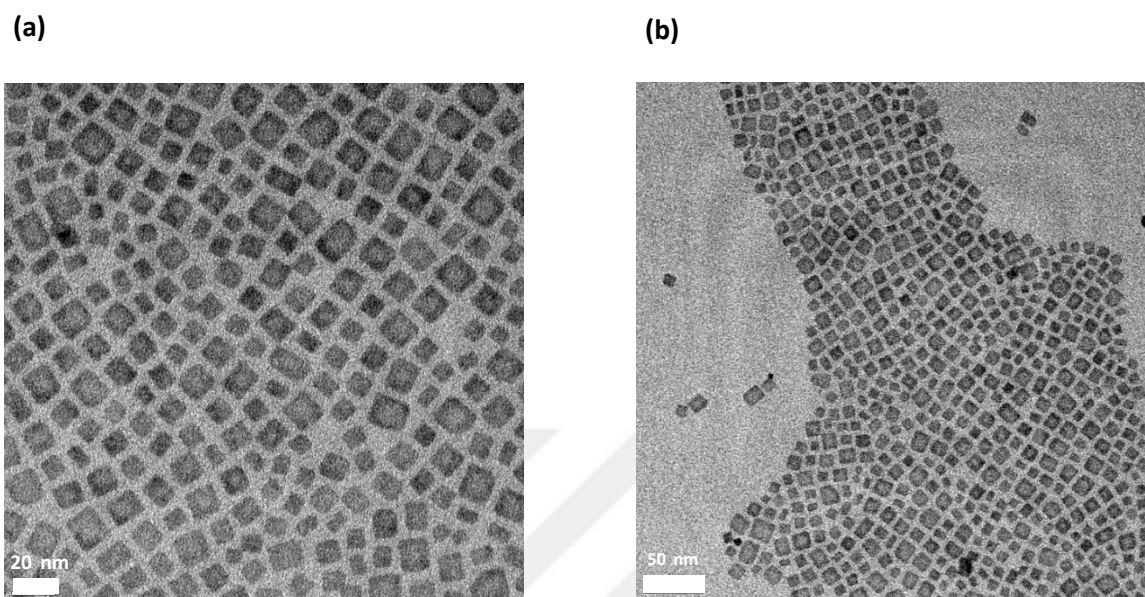


Figure 4.19: (a) (b) TEM images of Ag-Cu co-doped NPLs.

The TEM images of co-doped NPLs reveal that their shape is square and no change occurred in shape.

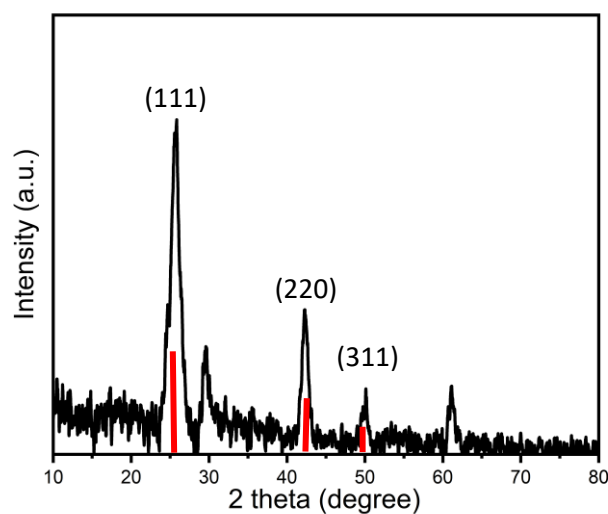


Figure 4.20: XRD pattern of co-doped NPLs.

With the help of X-ray diffraction, we confirmed that these silver and copper co-doped NPLs have diffraction patterns similar to the undoped NPLs, and their zinc blend crystal structure is still intact, and no changes in crystal structure occurred after the co-doping of these thick nanoplatelets.

To check the incorporation of copper in these thick NPLs, we carried out the ICP-MS analysis of these thick co-doped NPLs.

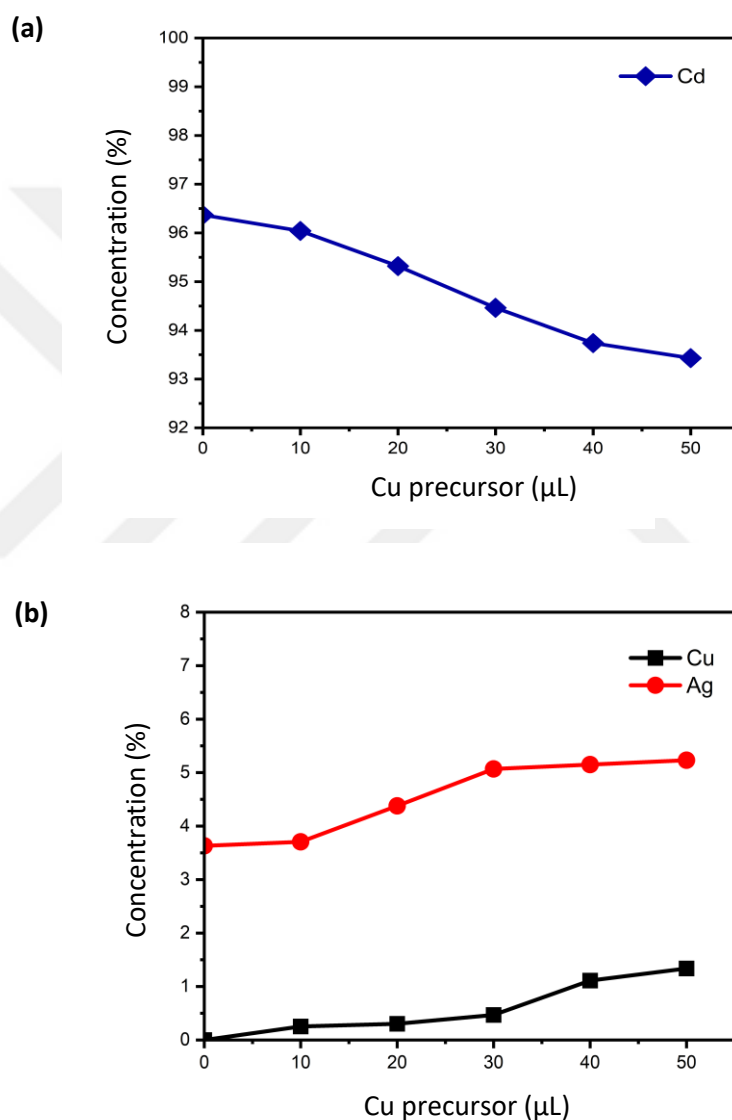


Figure 4.21: Atomic Concentration (%) of (a) cadmium and (b) silver and copper in co-doped NPLs with increasing Cu precursor.

Figure 4.21 shows the cation ratio present in co-doped NPLs as a function of the copper precursor amount injected during the doping procedure. Silver-doped thick NPLs had

3.78% of silver. When we increased the copper precursor in it, not only did the copper ratio increase, but the silver ratio increased as well. The silver ratio increased because of the growth time we allowed. As silver has a higher diffusion coefficient, it continued the cation exchange process with cadmium, even in the presence of copper. and with just 1.13% of copper cations present in the NPLs ensemble, all the NPLs exhibited copper-induced dopant emission. As cadmium ions were being replaced with silver and copper during the doping procedure, cadmium concentration dropped from 96.4% for the case of silver doped to 93.5% for the case of co-doped NPLs. From these findings, we assume that just 1.1% of cation exchange is enough to quench the band edge PL. In the case of silver doping, our NPLs were doped with less than 4% of silver ions to quench the band-edge emission, and in literature [30-31], more than 8% of silver was doped to quench the band-edge PL.

Our findings reveal that 1.1% copper incorporation is enough to obtain completely copper-induced dopant emission. We assume that both in silver and copper, normally, most of the dopant ions are adsorbed at the surface, and a significantly lower ratio of dopant ions is incorporated into the crystal lattice.

4.2.6 Doped Core/Shell Nanoplatelets

The optical characterization of thick CdSe/CdZnS core/shell doped NPLs with silver showed that the band-edge emission was quenched and dopant-induced emission intensity increased as we increased the precursor injection. The Ag-doped core/shell doped NPLs exhibited emission behavior similar to the doped 7 ML NPLs. Their dopant-induced emission was also centered at 810 nm.

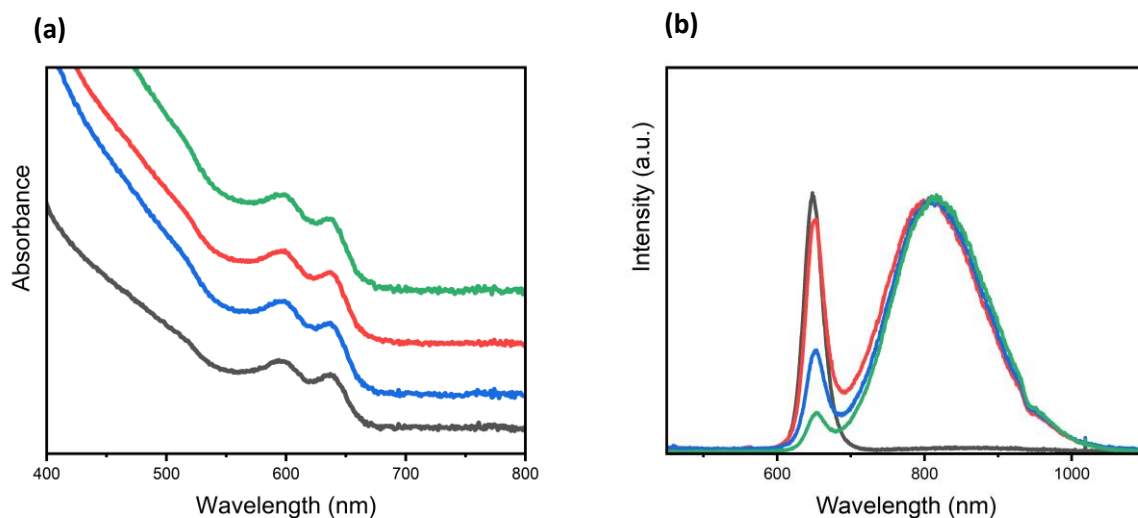


Figure 4.22: (a) Absorbance of Ag-doped CdSe/CdZnS core/shell with increasing precursor ratio and (b) corresponding PL.

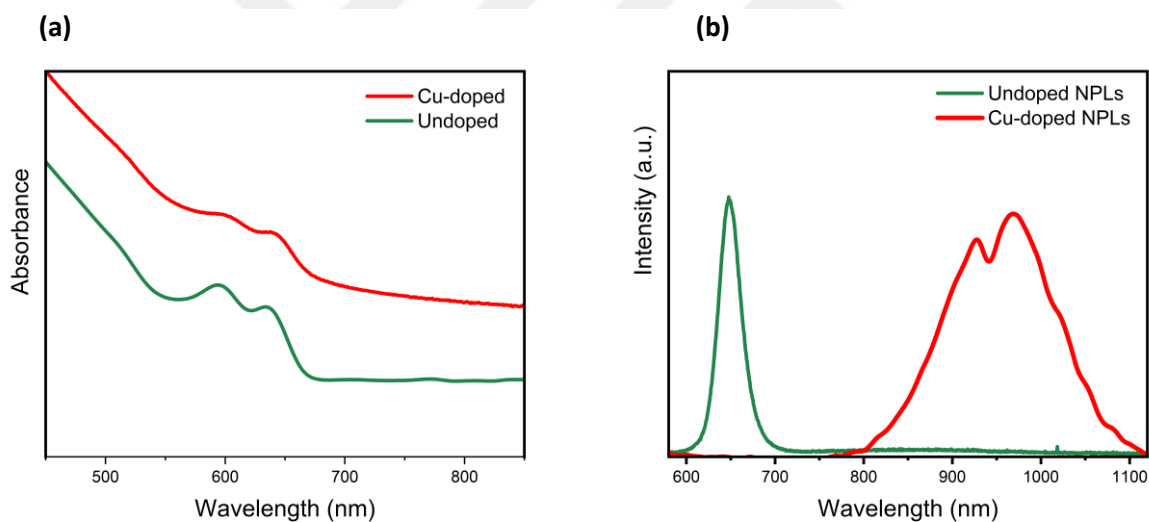


Figure 4.23: (a) Absorbance of and (b) PL of Cu-doped CdSe/CdZnS core/shell NPLs.

The copper-doped CdSe/CdZnS core/shell NPLs had dopant emission peaking at 960 nm.

Chapter 5

Conclusion

Nanoplatelets having unique optical properties offer possibly great potential for applications such as LEDs and LSCs. But their discrete PL and reabsorption limit their potential. We proposed to address these limitations by doping thick NPLs with transition metals. We synthesized square and rectangular 7 ML thick CdSe NPLs with aspect ratios of 1:1 and 1:4. We observed a blue shift in excitonic peaks of the square NPLs because of smaller lateral dimensions and smaller lateral surface area than the rectangular NPLs. Then, we doped thick NPLs for the first time with silver and copper using partial cation exchange and achieved Stoke's-shifted emission in the NIR region. For silver, the Stoke's shift was 178 nm, and for copper doping, a Stoke's shift of 300 nm was observed.

We also observed variation in PL-QY with increasing doping levels. The PL-QY of NPLs increased fourfold in silver-doped NPLs and then later declined to the initial level. We also co-doped NPLs with silver and copper and achieved dopant emission both from the silver and copper. The PL evolved purely from silver-induced emission to copper-induced emission as we increased the copper ratio in the silver-doped NPLs for co-doping. The PL was pushed further deeper into the NIR region by synthesizing the core/shell NPLs and doping the core/shell NPLs with silver and copper. We used ICP-MS to investigate the concentration ratios of dopant cations in the NPLs. Moreover, we used XRD and TEM for structural analysis and observed that the doped NPLs were stable with size, shapes, and crystal structure intact.

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