

COLLOIDAL SYNTHESIS AND OPTICAL PROPERTIES OF HETEROSTRUCTURED QUANTUM WELLS

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By

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

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ABSTRACT

COLLOIDAL SYNTHESIS AND OPTICAL PROPERTIES OF HETEROSTRUCTURED QUANTUM WELLS

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Colloidal quantum wells (CQWs) have emerged as auspicious gain materials for next-generation colloidal nanolasers owing to their exceptional optoelectronic properties including intrinsically suppressed Auger recombination, large absorption cross-section, low cost of production, and the ability to precisely tailor their attributes. However, the realization of their photonic devices faces fundamental challenges inherent to semiconductor nanocrystals in general, which can be tackled via the design and engineering of their advanced heterostructures. In this thesis, we proposed multiple design strategies to address scientific obstacles associated with using such CQWs as gain materials and developed a variety of their rational heterostructure designs by implementing advanced synthesis techniques, allowing us to systematically study the structure-property relationship. We investigated the optical gain performance of these CQW heterostructures through spectral and temporal spectroscopy techniques to elucidate the underlying mechanisms, which guided us to improve the associated structural aspects of CQWs. This approach culminated in the development of superior CQW heterostructures possessing low optical gain thresholds, giant material gain coefficients, and long gain lifetimes, addressing all main specifications quantifying the quality of a gain material. We also presented proof-of-concept device demonstrations showcasing the advancement in the gain aspect of these CQW heterostructures, such as high-performance amplified spontaneous emission in solution and whispering gallery mode lasing with ultra-low thresholds. The findings of this thesis indicate highly engineered CQW heterostructures offer excellent gain media.

Keywords: Colloidal semiconductor nanocrystals, colloidal quantum dots, colloidal quantum wells, nanoplatelets, optical gain, amplified spontaneous emission, lasing.

ÖZET

KUANTUM KUYULARININ HETEROYAPILARININ KOLOİDAL SENTEZİ VE OPTİK ÖZELLİKLERİ

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Koloidal kuantum kuyuları (KKK'ler) kendinden baskılanmış Auger rekombinasyonu, büyük optik soğurma kesitleri, düşük üretim maliyeti ve optoelektronik özelliklerinin hassas ayarlanabilirliği gibi olağanüstü özellikleri sayesinde, yeni nesil koloidal nanolazerler için umut verici kazanç malzemeleri olarak ortaya çıkmıştır. Ancak, bunların fotonik cihazlarının hayata geçirilmesi, yarıiletken nanokristallere özgü, gelişmiş heteroyapılarının tasarım ve mühendisliğiyle aşılabilecek temel zorluklarla karşı karşıyadır. Bu tezde, KKK'lerin kazanç malzemeleri olarak kullanılmasıyla ilgili bilimsel engelleri aşmak için çeşitli rasyonel heteroyapı tasarım stratejileri önerdik ve yapı-özellik ilişkisini sistematik olarak incelememizi sağlayan ileri sentez tekniklerini uygulayarak KKK heteroyapıları geliştirdik. Bu heteroyapıların optik kazanç performanslarını, altta yatan mekanizmaları aydınlatmak için spektral ve zamansal spektroskopi teknikleri ile inceledik; bu, KKK'lerin ilgili yapısal yönlerini iyileştirmemize rehberlik etti. Bu yaklaşım, düşük optik kazanç eşiklerine, yüksek malzeme kazanç katsayılarına ve uzun kazanç ömürlerine sahip KKK heteroyapılarının geliştirilmesiyle sonuçlandı ki sayılan bu faktörler bir kazanç malzemesinin kalitesini belirleyen ana etkenler arasındadır. Ayrıca kavram kanıtı gösterimi olarak çözeltide yüksek performanslı güçlendirilmiş kendiliğinden ışıma ve ultra düşük eşikli fısıltı galerisi modu lazer gibi KKK heteroyapılarının kazanç yönündeki ilerlemelerini sergiledik. Bu tezdeki bulgular, yüksek düzeyde tasarlanmış KKK heteroyapılarının mükemmel kazanç ortamı sunduğunu göstermektedir.

Anahtar Kelimeler: Koloidal yarıiletken nanokristaller, kuantum noktacıkları, koloidal kuantum kuyuları, nanolevhalar, optik kazanç, güçlendirilmiş kendiliğinden ışıma, lazer.

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Chapter 1

Introduction

The discovery of quantum confinement effects in colloidal systems by the groundbreaking research of Alexei Ekimov [1] and Louis Brus [2] in the late 1970's and early 1980's launched the field of colloidal semiconductor nanocrystals (CSNCs). These studies paved the way for the development of nanocrystal semiconductors with tunable electronic and optical properties, revolutionizing the field of colloidal applications. Apart from their distinct optoelectronic characteristics, the low manufacturing costs of CSNCs and simplicity of their integration into diverse host matrices present numerous prospects for technological progress in a wide variety of fields like light-emitting diodes (LEDs), photodetectors, lasers, luminescent solar concentrators (LSCs), solar cells, and display technologies.

CSNCs offer diverse means to tailor their optical, electronic, and chemical properties, such as control over size, composition, ligands, and shape. The shape of CSNCs bears irreplaceable importance in defining the optoelectronic behavior of these material systems. Colloidal quantum wells (CQWs), which are the most recently discovered sub-family of CSNCs having quasi-2D geometry with 1D confinement, have attracted great attention owing to their remarkable excitonic properties. One fascinating feature of these colloidal quantum wells is the ability to control their thickness, which is along the direction of confinement, with atomic precision. This precision results in very narrow emission spectra, typically with a full-width-at-half-maximum (FWHM) of less than 10 nm if the critical thickness is well controlled and/or magic size. In contrast, standard colloidal quantum dots (CQDs) typically have an FWHM of around 30 nm due to unavoidable size distribution. CQWs also exhibit exceptionally large absorption cross-sections, surpassing those of CQDs, due to their large lateral dimensions and giant oscillator strength owing to quasi-2D geometry. Their two-dimensional geometry further enhances the penetration of the optical field, contributing to their absorption cross-section. Another remarkable advantage of CQWs over CQDs is the intrinsic suppression of Auger recombination processes, attributed to their large volume and anisotropic shape, with the photogenerated charges being free to move across the lateral plane. Additionally, advancements in synthetic methods have enabled engineering the depth and profile of the confinement barrier of these quantum objects via the synthesis of heterostructures with various elemental compositions. This capability, combined with effective surface passivation by the shell, further mitigates Auger recombination. These perks of CQWs enabled the demonstrations of

promising performance levels in various optoelectronic applications including LEDs with high external quantum efficiencies exceeding the outcoupling limit of CQD-LEDs [3] owing to their directional emission, highly performing luminescent solar concentrators owing to the Stoke's shift engineering via doping [4], and sensitive remote temperature sensors thanks to their efficient Förster energy transfer [5]. Moreover, demonstrations of ultra-low amplified spontaneous emission (ASE) and lasing thresholds [6], high modal gain coefficients [7], and substantial gain cross-sections using CdSe CQWs and their heterostructures highlight the superiority of CQWs for lasing applications. Yet, for the realization of next-generation colloidal electrically-driven lasers, three main characteristic gain properties of CQWs should be improved: gain threshold, gain coefficient, and gain lifetime.

In this thesis, we have focused on the development of CQW heterostructures to improve these abovementioned requirements. As the bottleneck for the gain applications in the confined systems is fast nonradiative Auger processes, our main strategy was to generate heterostructures with suppressed Auger recombination. Two well-established approaches to address this issue are based on smoothening the confinement barrier and increasing the overall size of particles. Additionally, we have developed novel weakly confined cubic-shaped quantum shell heterostructures to minimize Auger recombination, which would benefit from the partial recovery of momentum conservation under weak confinement, "volume scaling law" due to large size and aforementioned superiorities of CQWs owing to 1D confinement. Throughout the thesis, we implemented advanced synthesis methods to control size, shape, and composition with unprecedented control so that the role of each parameter can be systematically studied.

1.1 Organization of the Thesis

In Chapter 2, we provided brief information about CSNCs, including their overall composition, quantum confinement effect, heterostructures of CSNCs, their electronic structure, and optical properties. Moreover, we discussed the colloidal quantum wells, their synthesis, and heterostructures. Finally, we presented an overview of the optical gain mechanism of CSNCs, amplified spontaneous emission, and lasing.

In Chapter 3, we demonstrated light amplification from CQW heterostructures dispersed in water, which was challenging due to the low concentration of emitters in a low refractive index medium. These sources of losses were compensated by the high gain capability of well-

designed CQW heterostructures with suppressed Auger recombination owing to a smooth confinement barrier, large absorption cross-section, and long gain lifetime.

In Chapter 4, we presented unprecedently high material gain obtained from “giant” CQW heterostructures with thick cores having large lateral areas. The high gain performance of these materials was mainly attributed to the suppressed Auger recombination processes and the high number of states per energy in this system owing to the large volume of the CQWs so that higher energy states could contribute to the optical gain.

In Chapter 5, we investigated the role of shell composition and thickness on the optical gain performance of CQW heterostructures with thick cores. The shell growth performed via colloidal atomic layer deposition allowed us to control the thickness of the shell with atomic precision and elemental composition at each monolayer of the shell.

In Chapter 6, we developed a synthesis protocol to obtain weakly confined cubic quantum shell structures with various shell thicknesses. The motivation of this work was to synthesize cubic quantum shells that do not suffer from the variation of facets throughout the structure, which is unavoidable in spherical systems. Additionally, the corners of these cubes might have unique energy states that can be utilized in optical gain. Their large size reaching a weakly confined regime will help to obtain bulk-like gain where the Auger recombination process is a bottleneck.

In Chapter 7, we conclude with the final remarks on the thesis and give an overview of some of the ongoing studies along with future research directions.

Chapter 2

Scientific Background

The scope of this thesis includes the synthesis of novel colloidal quantum well heterostructures, their characterization, and the assessment of their optical performances, particularly for optical gain applications. This chapter aims to provide essential background information about colloidal semiconductors, including principles of their synthesis, characterization, and related optical phenomena, to help the reader understand the principles of this thesis study presented in the following chapters.

2.1 Colloidal Semiconductor Nanocrystals (CSNCs)

The term “colloid” refers to particles with sizes larger than molecules dispersed in a matrix. The growth of colloidal nanocrystals dispersed in a glass matrix, which was used to obtain stained glasses, has a thousand-year old history. However, the systematic study of colloidal semiconductor nanocrystals embedded in glass matrix was initiated by Alexey Ekimov in 1979 at the S. I. Vavilov State Optical Institute, Russia [1, 8]. Colloids dispersed in liquids (liquid colloids), on the other hand, do not share the long history of the former. Luis Brus at Bell Labs, USA, reported the first study on the synthesis of colloidal semiconductor nanocrystals in liquid in 1982 [9], without being aware of Ekimov’s work. Today, the term “colloidal semiconductor nanocrystals” is used to describe the particles that are capped with organic molecules (ligands) dispersed in liquids rather than glass matrix, and that is the adopted terminology in this thesis (see Figure 2.1a).

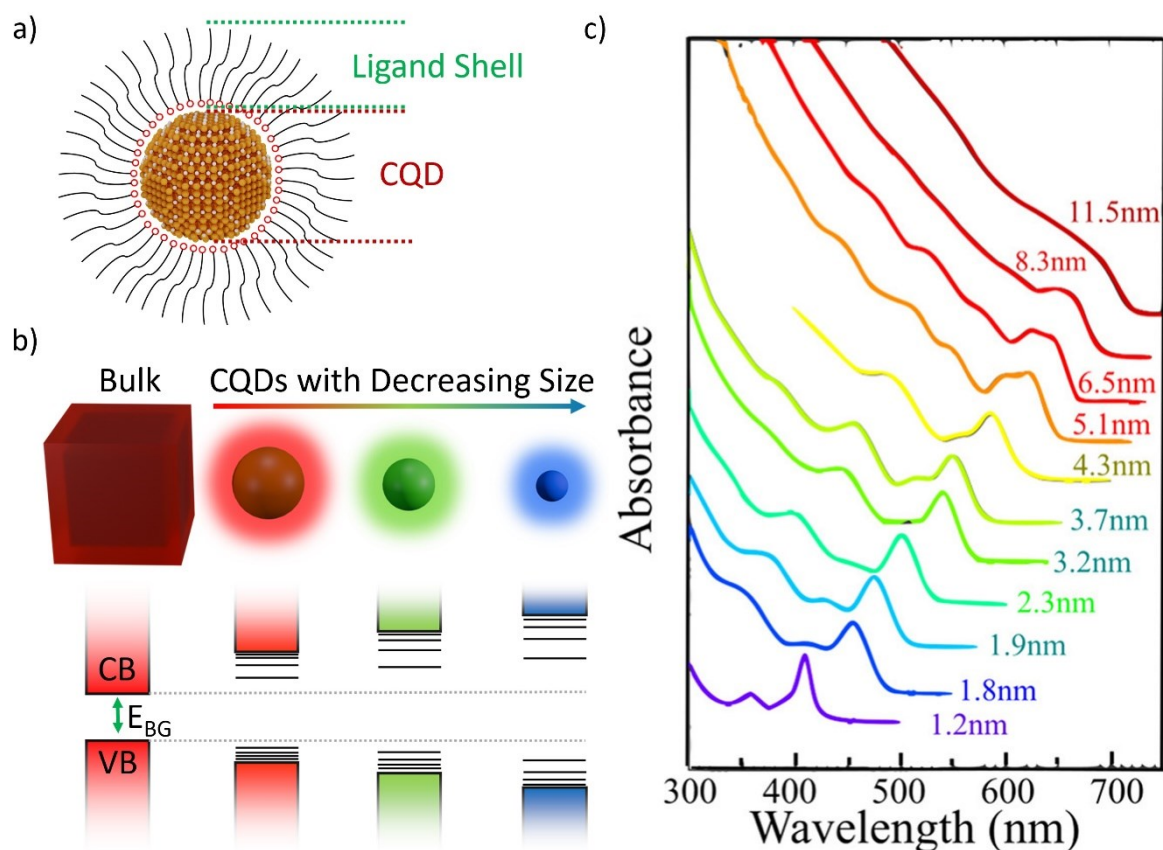


Figure 2.1. a) A model of a spherical colloidal semiconductor nanocrystal, a colloidal quantum dot (CQD), with an inorganic core capped with organic ligands, b) a schematic illustrating quantum confinement effect, and c) absorbance spectra of CdSe CSNCs of various sizes. Adapted with permission from [8]. Copyright 2024 American Chemical Society.

CSNCs are tiny semiconductor particles with dimensions comparable to the bulk exciton Bohr radius (or de Broglie wavelength of an electron in the structure). These dimensions typically fall into the range of 2-20 nm, corresponding to hundreds to thousands of atoms in the whole structure. As the electron is excited to the conduction band (CB) with an external stimulus, it experiences strong Coulomb attraction and spin-exchange coupling with the remaining hole in the valence band (VB), resulting in a confined electron-hole pair called an exciton. The charge carriers confined in small space enhance many-body phenomena that alter electronic and optoelectronic properties. The low number of constituting atoms leads to the discretization of energy levels. In bulk semiconductors, the interaction (bonding) of an infinite number of atoms in the crystal results in the formation of continuous bands, the valence and conduction bands, which are separated by a fixed bandgap energy (E_{BG}). The bandgap energy depends on the elemental composition and the semiconductor crystal structure. However, the finite number of atoms in semiconductor nanocrystals limits the number of interactions, which hinders the

formation of continuous bands, where they have discretized atomic-like energy levels, as depicted in Figure 2.1b. This is the reason why they are also called artificial atoms.

As the size is comparable to the exciton Bohr radius, the bandgap also becomes a function of the size. For instance, as shown in Figure 2.1c, just by changing the size of CdSe CSNCs, one can cover the whole visible spectrum. This phenomenon, where the optical properties change as the size approaches the exciton Bohr radius, is called the quantum confinement effect. The bandgap of CSNCs can be estimated by the so-called Brus equation [2],

$$E_{BG,NC} = E_{BG,bulk} + \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{\epsilon_{NC}R} + \frac{e^2}{R} \sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R} \right)^{2n} \quad (2.1)$$

having

$$\alpha_n = \frac{(\epsilon - 1)(n + 1)}{\epsilon_{NC}(\epsilon n + n + 1)} \quad (2.2)$$

and

$$\epsilon = \frac{\epsilon_{NC}}{\epsilon_{surrounding}} \quad (2.3)$$

where the first term in Equation (2.1), $E_{BG, bulk}$, is the bulk bandgap of the semiconductor. The second term in the equation is the confinement energy (quantization energy, a kinetic energy), where $\hbar$ is the Planck's constant divided by 2π , R is the radius of the CSNC, and m_e^* and m_h^* are reduced mass of the electron and hole. The third term is the Coulomb energy (exciton binding energy, a potential energy, where ϵ_{NC} is the dielectric permittivity of the nanocrystal, the effect of which is demonstrated in Figure 2.2. The last term, which is generally omitted due to the small contribution, is charge solvation energy loss, where the bar implies that the value is averaged, and S is the distance of the carrier from the center of the particle.

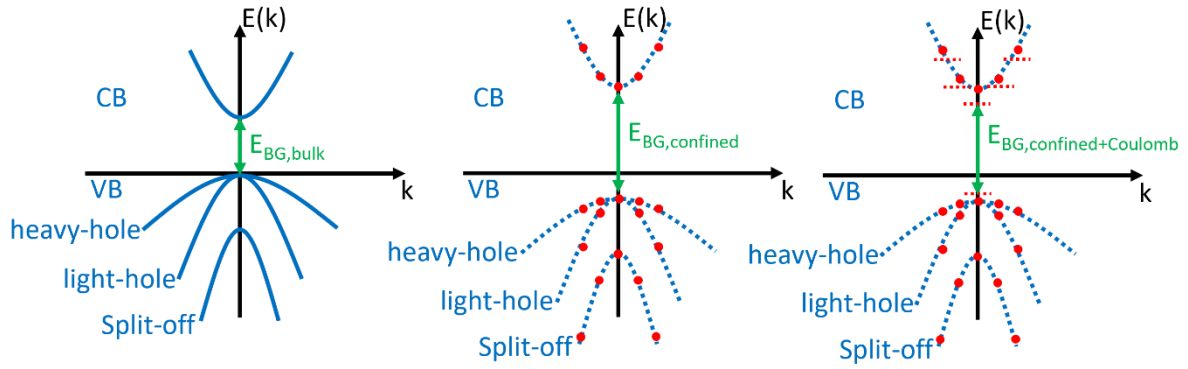


Figure 2.2. E-k diagram of a bulk semiconductor, quantum confined semiconductor, and quantum confined semiconductor also considering Coulomb's interaction.

Owing to the quantum confinement effect, including the dielectric confinement effect and the low number of constituting atoms, CSNCs fall into a material class between the bulk semiconductors and the molecules. Hence, they have their unique properties, which have more degree of freedom than these aforementioned material classes to be tailored for a specific application. For instance, the low effective dielectric permittivity of CSNCs results in higher electron-hole Coulomb interaction (exciton binding energy), which is screened in the bulk case [2, 10-12]. This results in higher oscillator strength than their bulk counterparts and dye molecules, enhancing their absorbance [13]. Electron-phonon coupling in CSNCs, compared to dye molecules, is lower, resulting in narrower and brighter emissions. This suppressed electron-vibration coupling combined with discretized energy levels due to the quantum confinement effect results in narrower emission linewidths [8, 14]. Additionally, the radiative lifetimes of CSNCs reach thousands of nanoseconds owing to the existence of dark and bright states as a result of their excitonic fine structure, whereas the radiative lifetimes of only tens of nanoseconds are achievable with the dye molecules [15-17]. The ability to tune the discretized energy levels and electronic structure gives access to control over electronic transport. Due to their large surface-to-volume ratio, their physical and chemical properties are also prone to be adjusted via surface modifications.

CSNCs are obtained via cost-effective synthesis protocols and can be easily implemented on a wide range of material matrices, which is not possible with current semiconductor technologies relying on epitaxial growth on a suitable substrate. These superior properties make CSNCs a promising material for next-generation optoelectronic applications (Figure 2.3) [14]. For instance, the bright and pure color emission, tunable across the visible and near-infrared spectrum, is promising to achieve efficient, bright and color-accurate displays [18]. Tailoring energy states and charge interactions via compositional and structural modifications enable the

optical gain and lasers, practical for optical communication, holography, and 3D display applications [19]. Their long radiative lifetimes, bright emissions, and the ability to tune surface chemistry, for example, attaching proteins and antibodies, make it possible to employ CSNCs in theragnostics [20]. For electronic/optoelectronic devices such as transistors and photodetectors, the surface chemistry manipulations to facilitate their close-packed assembly with increased conductivity without requiring high-temperature and vacuum conditions (as in the case of epitaxially grown quantum dots or thin films) plays an important role [21-22].

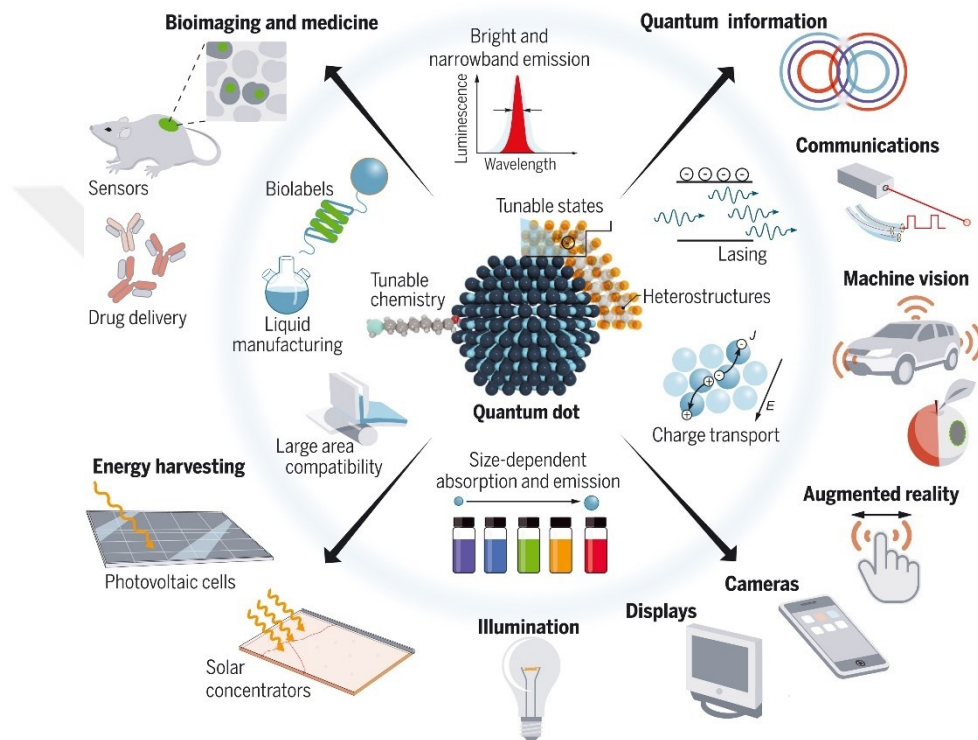


Figure 2.3. Application fields of CSNCs. From [14]. Reprinted with permission from AAAS.

2.1.1 Heterostructures of Colloidal Semiconductor Nanocrystals

The increased surface-to-volume ratio with decreasing particle size makes surface atoms to take an important role in the optical and electronic properties of the CSNCs, which become sensitive to the particle environment. Firstly, the surface atoms of CSNCs are undercoordinated, where the nonbonding molecular orbitals -called surface dangling bonds- of the surface atoms remain in the bandgap. Since the carrier wavefunctions leak to the surface, these energy states trap the carriers, and the performance of CSNCs is affected adversely. Ligands (some molecules with functional groups, e.g., oleic acid, oleyl amine, etc.) bonded to surface, passivate these surface dangling bonds while providing colloidal stability at the same time. Yet, mostly due to steric hindrance of these molecules, not each and every atom is

saturated. Additionally, the surface of CSNCs contains various crystallographic planes with different ratios of atoms (cations and anions). For the case of II-VI CSNCs, the facets with chalcogenides are difficult to saturate since there are no molecules with a strong affinity towards them. At this point, the growth of a secondary structure with a different elemental composition, namely a shell, around the core is the most effective pathway to passivate the undercoordinated surface atoms [23]. The core@shell CSNCs have ligands on the outer surface of the whole structure to sustain colloidal stability in the dispersion. In addition to the passivation of surface trap sites, shell structures have a crucial role in the optoelectronic properties of the CSNCs depending on their composition and thickness. Generally, the shell material's bandgap encompasses the core's valence and conduction band edges so that both the electron and hole wavefunctions are confined mainly in the core, do not leak to the outer surface, and do not feel the surface trap sites. The electronic structure of such core@shell CSNCs with both carriers confined in the core is called type I heterostructures. If the conduction band offset of the shell is slightly higher than that of the core and the valence band offset of the shell is relatively lower than that of the core, the structure is called quasi-type II heterostructure, where the electron wavefunction spatially exceeds the core, but the hole wavefunction remains in the core. If the valence and conduction band offsets of the shell material are significantly higher or lower than those of the core material, the electrons and holes are spatially separated, with one residing in the core and the other in the shell. This electronic structure is called a type II heterostructure (Figure 2.4).

Each electronic structure has its own merits for certain applications. Auger recombination processes, where an excited electron recombines with a hole nonradiatively by giving its energy to a third resident charge carrier, is a bottleneck for CSNC-based device performances. Optical gain and LEDs work on a multicarrier generation process, possibly triggering Auger recombination. In LEDs, this causes external quantum efficiency (EQE) droop -a decrease in efficiency with the current increase- and excess heating, creating problems even at brightness levels around 500-1,000 cd/m² [14]. To tackle this problem, implementing compositionally graded multishell CSNC heterostructures having a type I electronic structure leads to the achievement of droop-free EQEs with high brightness level of 100,000 cd/m² [24-25]. The smooth confinement barrier, instead of an abrupt potential profile, is shown to suppress Auger recombination [26]. Later, by combining this CSNC structure and a charge-balancing LED architecture, a brightness level reaching 400,000 is achieved [27]. So far, with these spherical CSNCs, the colloidal quantum dots, EQE levels of ~20% for red and green and ~18% for blue

emission have been achieved, reaching the limits of theoretical light extraction efficiency [28-30] from high-index semiconductor medium. Suppression of Auger recombination with “giant” CdSe@CdS CQDs having alloyed interface-hence a smooth potential barrier combined with the extension of the electronic wave function- resulting in a quasi-type II electronic structure led to the achievement of ultra-low optical gain thresholds [31]. Type II electronic heterostructures are handy for applications that rely on efficient carrier separation upon excitation, such as solar cells and photosensors [32-33].

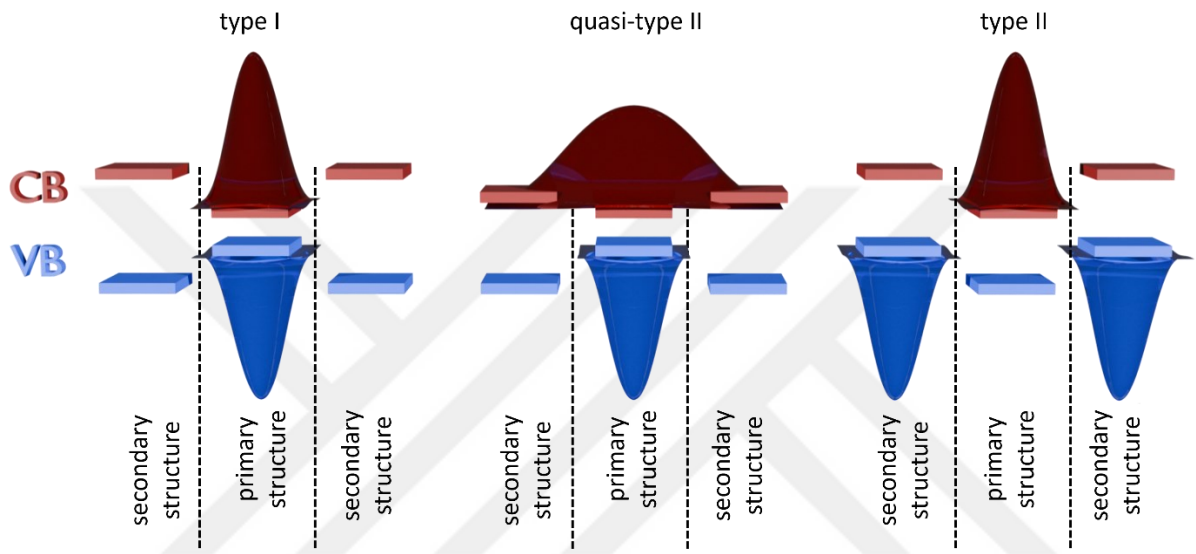


Figure 2.4. Electronic band structures of CSNC heterostructures with type I, quasi-type II, and type II band alignments and respective electron and hole wavefunction distributions.

2.1.2 Colloidal Quantum Wells (CQWs)

The shape is an essential parameter for the optoelectronic properties of CSNCs. Around 20 years after the discovery of CSNCs-particularly CQDs (spherical CSNCs)- by Louis Brus, Xiaolang Peng reported the synthesis of elongated CdSe CSNCs, so-called nanorods, in 2000 [34]. The shape of CSNCs defines quantum confinement, dielectric polarization, and electron correlation. CQDs have unidirectional confinement (3D confinement). Hence, they are considered to be quasi-0D particles. However, nanorods are 1D materials, since the confinement only exists in the directions perpendicular to the long axis of the nanorod (2D confinement). As a result, the binding energy of excitons is larger in nanorods compared to CQDs, and they emit polarized light. The mode of confinement (1D, 2D, or 3D) changes the density of states (DOS) profile as a function of the energy. The bulk semiconductors have a continuous parabolic DOS profile. As depicted in Figure 2.5, in the case of CQDs (3D confinement, quasi-0D material) density of states are discretized delta functions. With nanorods

(2D confinement, 1D material), this profile becomes continuous with intense peaks at certain energies [35].

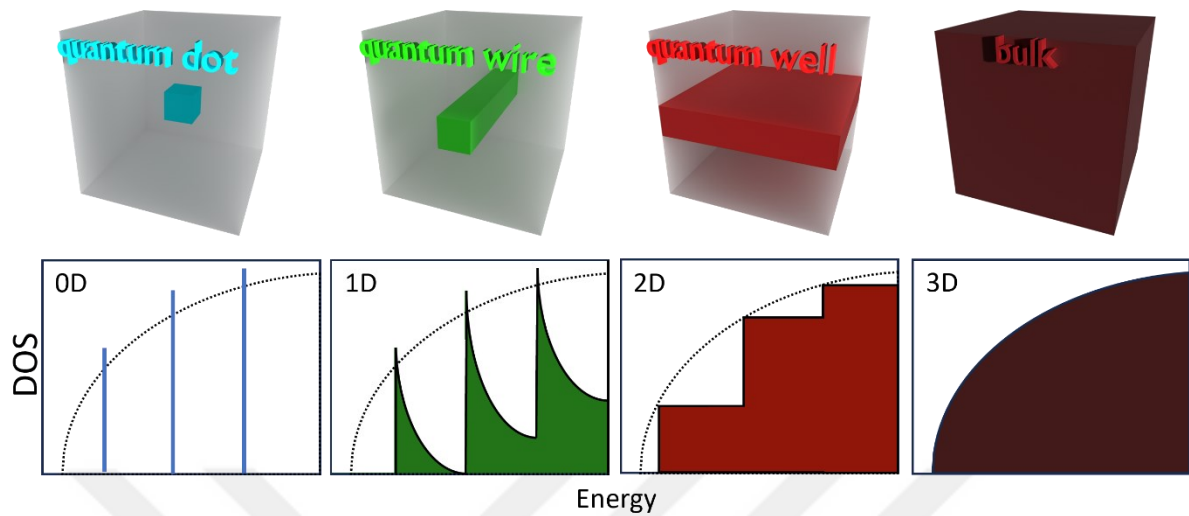


Figure 2.5. Density of states of confined semiconductors with 3D confinement (quantum dots), 2D confinement (quantum wire), 1D confinement (quantum well), and 0D confinement (bulk semiconductor).

The first achievement of 1D confinement in CSNCs (colloidal quantum wells or CQWs) was in 2006 when Taeghwan Hyeon developed wurtzite CdSe nanoribbons [36]. This was followed by Sandrine Ithurria's synthesis of zinc-blend CdSe nanoplatelets (NPLs) in 2008 [37], which is the material system of interest in the CQW literature and those will be the particle of interest in the rest of this thesis. Subsequently, other II-VI colloidal quantum wells with varying thicknesses were synthesized. These structures exhibit electronic properties similar to free-standing quantum wells, characterized by 1D confinement just in the direction of thickness and a step-function density of states (DOS) profile (Figure 2.5), which is also reflected in their absorption spectrum having distinct peaks for heavy and light hole transitions with the split-off feature, as presented in Figure 2.6. One fascinating feature of these colloidal quantum wells is the ability to control their thickness, which is the direction of confinement, with atomic precision. This precision results in very narrow emission spectra, with a full-width-at-half-maximum of less than 10 nm. In contrast, standard colloidal quantum dots typically have an FWHM of around 30 nm due to unavoidable size distribution. As a result, in a batch of synthesized CQDs, smaller dots emit at slightly lower wavelengths and larger dots at higher wavelengths, a phenomenon known as heterogeneous broadening. In the structure of a CQW, n number of chalcogenide layers are sandwiched between $n+1$ layers of group 12 transition metals so that each facet is terminated with metal atoms. Such structure is called “ $n.5$ ”

monolayer (ML) thick CQW. So far, CdSe CQWs with thicknesses ranging from 2.5 ML to 6.5 ML can be synthesized directly [13, 38-41]. Synthesis of 7.5 and 8.5 ML CdSe results in an inseparable mixture of 6.5, 7.5, and 8.5 ML thick CQWs [42].

As shown in Figure 2.6a, as the thickness of the CQWs increases absorption and the photoluminescence (PL) peaks shift towards higher wavelengths in a discrete manner. Their narrow photoluminescence bandwidths make CQWs a promising emitter for next-generation display applications with pure colors. In 1979, Keldysh proposed that the Coulomb interaction in 2D semimetals is enhanced due to the electric field's great extent of the leakage to the vacuum, where the interaction is unscreened [43], as illustrated in Figure 2.6b. This leads to an increase in the exciton binding energy in quantum wells. Additionally, the fraction of the electric field fringing out increases as the separation between the carriers is larger. The enhanced exciton binding energy and giant oscillator strength make the CQWs fast emitters and great absorbers. The absorbance of CQWs is further enhanced by their large lateral area per volume. The quasi-2D structure, where the carriers can move freely along the lateral area, helps suppress Auger recombination. Furthermore, the chemical strategies involving size control, surface chemistry modifications, heterostructure growth, and doping permit to tailor these properties required for a certain application and enhancing their optoelectronic performance.

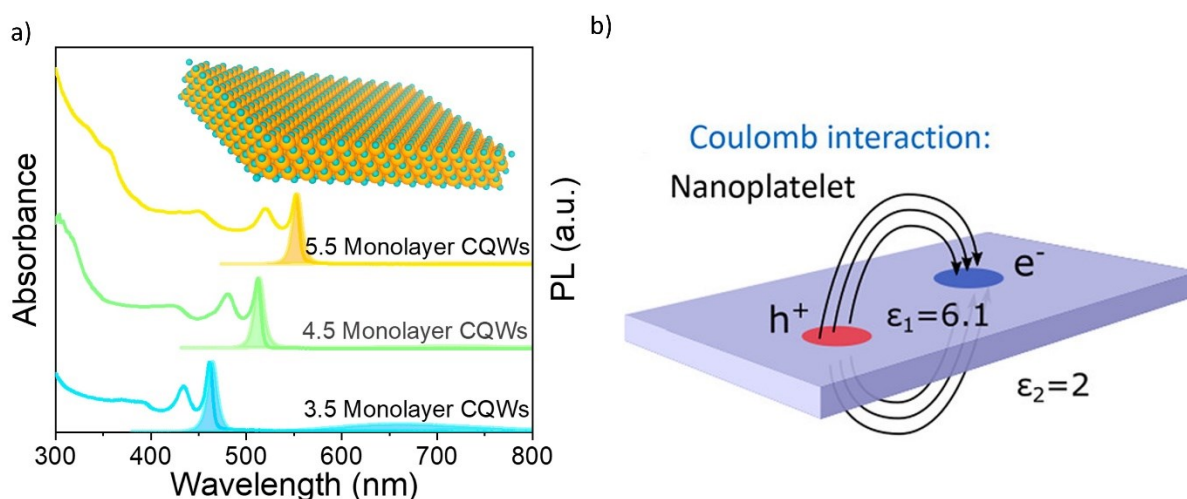


Figure 2.6. a) Absorbance and photoluminescence spectra of 3.5, 4.5, and 5.5 monolayer thick CQWs, b) an illustration depicting enhanced Coulomb interaction due to the excessive leakage of electric field to low dielectric medium, which screens the field less effectively. Adapted with permission from [8]. Copyright 2024 American Chemical Society.

The anisotropic shape with well-defined surface structure and precise thickness control makes CQWs a great subject for model studies of surface chemistry and optical phenomena. The anisotropic shape allows the generation of two types of heterostructures: (i) core/crown heterostructures which are obtained by the growth of secondary structure just on the periphery of core [44], and (ii) core@shell heterostructures [45], which involves encapsulation of the core with the secondary structure as in the case of core@shell CQDs. The greatest perk of the core/crown heterostructures is the ability to engineer wavefunctions without altering the confinement since there is no change in the thickness, which is the direction of the confinement. The crown structure provides additional absorption cross-section while passivating the surface dangling bonds on the periphery, which is the most defect-rich part of the CQWs [46-47]. The growth of the shell, on the other hand, passivates the trap sites all around the core, while being useful to tune the confinement and hence the emission wavelength. The intrinsic superiorities of CQWs, which allow further improvements via chemical approaches, make these CSNCs attractive materials for future light harvesting and light-generating applications.

2.1.3 Synthesis of CQWs

The modern synthesis of CSNCs involves the introduction of cation salts and anion precursors in the form of either elements or molecules to a high boiling point solvent along with ligands. The most general model explaining the formation mechanism of monodisperse CSNCs is named after Victor K. LaMer, who originally developed the model to describe the formation principles of monodispersed hydrosols [48]. As illustrated in Figure 2.7, according to the LaMer model, the formation of monodispersed nanoparticles should follow three phases with temporal separation, where each step is governed by the concentration of monomers constituting the particle and the existence of a seed in the reaction mixture. In the first phase, where there are no seeds, monomer concentration increases, either by swift presentation of monomers or decomposition of precursor molecules. As the monomer concentration reaches a certain level that surpasses the activation energy of nucleation, a burst of nucleation occurs in the second phase. Since this swift formation of seeds consumes monomers, the monomer concentration drops immediately so that no further nucleation can occur. In this third phase, the monomers with relatively low concentration attach to the surface of the seeds, which is called growth. The principles of the third phase are being implemented for shell growth, where the concentration of the precursors (monomers) is adjusted to avoid self-nucleation so that only

growth around the core is possible. Actually, this growth phase is an equilibrium state between the growth of nanoparticles and the dissolution of atoms from the nanocrystal.

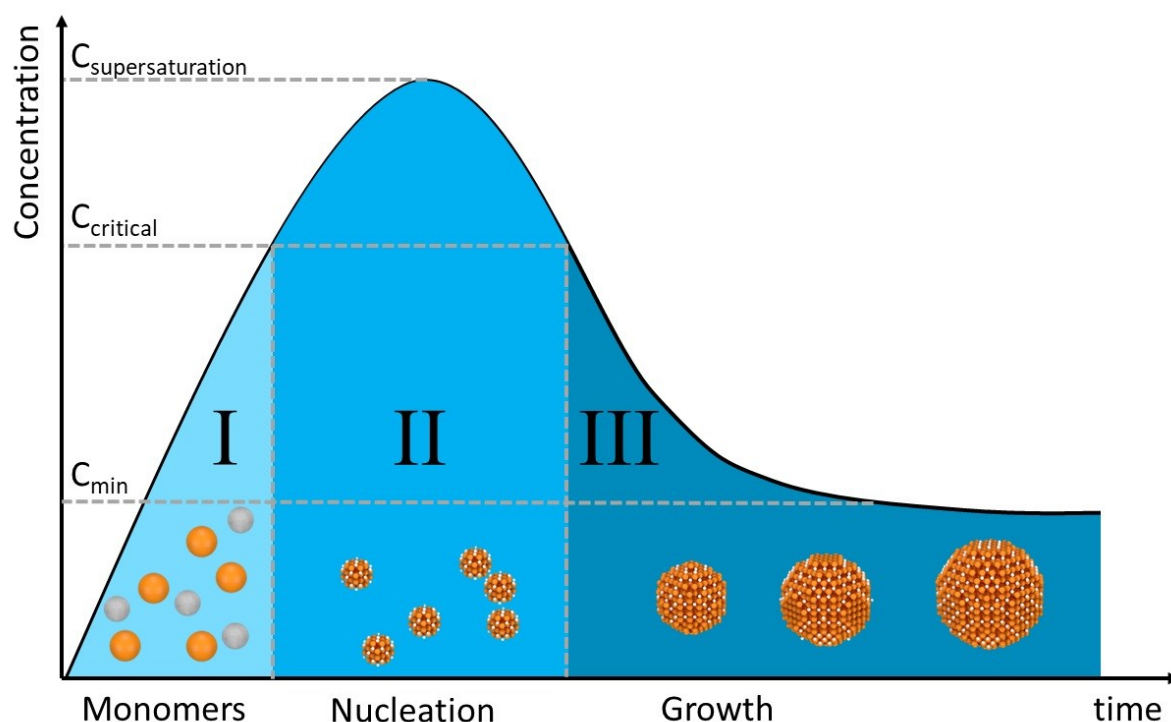


Figure 2.7. LaMer model, which suggests that temporal separation of nucleation and growth is mandatory to obtain monodisperse particles.

Shape control of the nanocrystals is a function of the surface energy, crystal structure, ligand, monomer concentration, and temperature. The first obtained shape diverged from spherical CSNCs (CQDs) was elongated ones, the nanorods [34]. The key parameters here were: (i) the crystal structure being wurtzite, where one facet ($00\bar{1}$) of the crystal is cadmium rich, (ii) the trioctylphosphine (TOP) solvent with hexadecylphosphonic acid ligands, and (iii) a relatively high concentration of monomers. Here, the solvent molecules and ligands are attached to the chalcogenide-rich facets of the crystal, decreasing their surface energy. Since the affinity of the solvent and ligands is low toward the cadmium atoms, the nanocrystal growth happens along this high-energy facet. Since growth and dissolution are an equilibrium reaction, a relatively high concentration of monomers should be present to favor the reaction towards growth. The syntheses of nanodisks [49], tetrapods [50] and octapods [51] follow similar principles. One alternative approach for shape control is the templated growth strategy, where the ligands form free-standing self-assembled-monolayers in reaction conditions, dictating an anisotropic growth [52].

However, the synthesis of zinc-blende CQWs with an anisotropic shape is a peculiar case since all of the facets are (001) planes with the same composition of atoms. The synthesis of 4.5 ML thick CQWs, which is the most established synthesis protocol, is as follows: cadmium myristate, elemental selenium powder, and octadecene as solvent are heated under an inert atmosphere (Figure 2.8). As the temperature increases, first cadmium myristate dissolves. Then, selenium dissolves and is activated. When the temperature approaches 200 °C, cadmium myristate decomposes to release cadmium atoms, which react with activated selenium species, and nucleation occurs. The nucleation phase can be observed by the color change of the mixture from transparent to deep orange. Then cadmium acetate salt, which has relatively low solubility, is swiftly introduced to the reaction mixture, and the temperature is increased to 240 °C. As the desired size, as a function of the growth time, is obtained, the reaction is quenched. The final reaction mixture includes 4.5 ML CQWs along with quantum dots, 3.5 and 5.5 ML CQWs, which can be separated by selective precipitation.

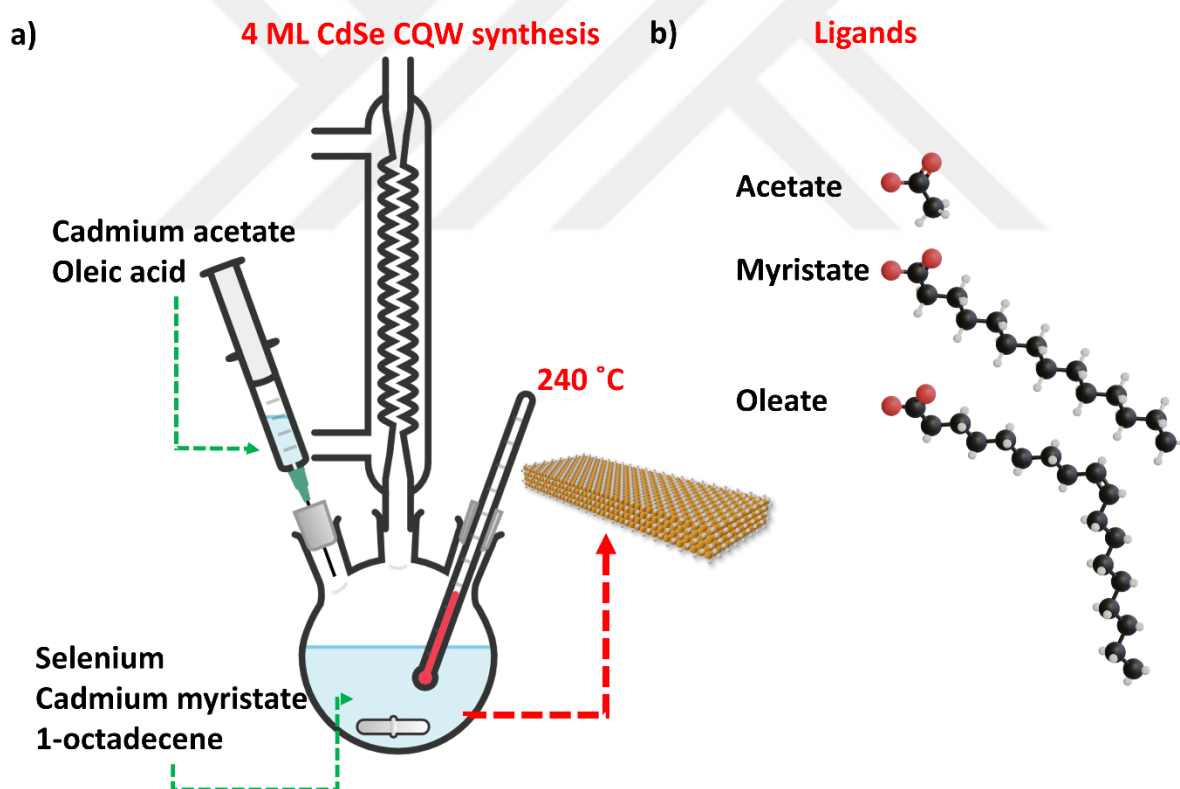


Figure 2.8. a) Synthesis protocol of 4.5 monolayer thick CdSe CQWs and b) the ligands present in the reaction medium during this synthesis.

First, it has been shown that there is no lamella to induce anisotropic growth at these reaction conditions. However, a fraction of the seeds during the nucleation phase exhibit slightly anisotropic shapes [53]. In line with this study, David Norris' group hypothesized that once

there is an anisotropy in the seed, the energy barrier of growth on the smaller facet is lower than the growth on the larger surface if the reaction is not limited by the concentration of monomers [54-55]. Once this growth barrier on a large surface is surpassed via reaction conditions such as the concentration of monomers and the temperature, CQWs can also be grown in thickness. For instance, the synthesis temperatures for 2.5, 3.5, 4.5, and 5.5 ML thick CQWs are 120, 170, 240 and 250 °C, respectively. However, after a certain thickness, the barrier for the thickness and lateral size growth becomes similar, and CQWs start to grow isotropically and become CQDs (Figure 2.9). More recently, the introduction of halides into the reaction mixture to modify the surface energy of CQWs has been shown to be a successful strategy for obtaining thicker CdSe CQWs (6.5, 7.5, and 8.5 ML) [40, 42].

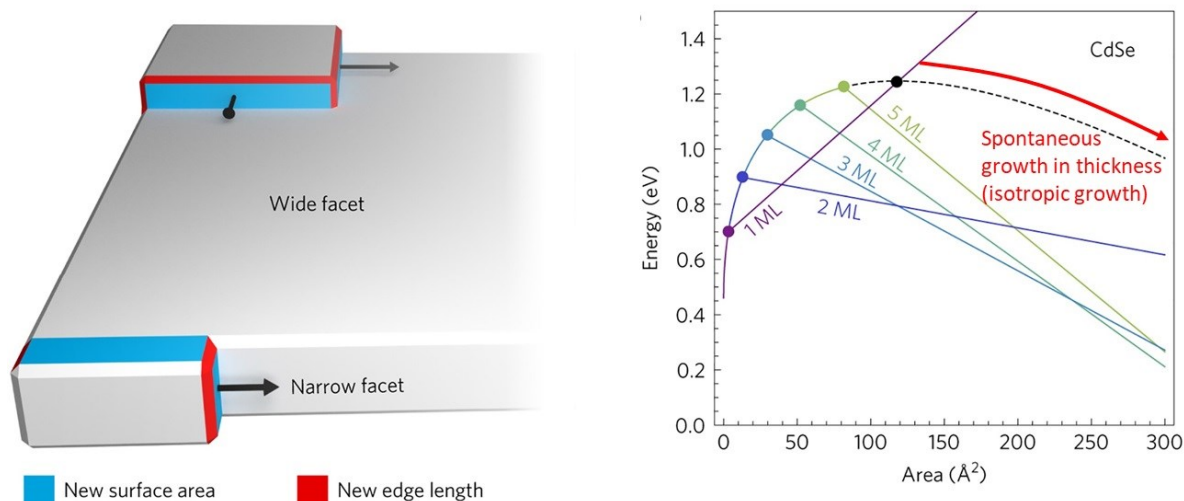


Figure 2.9. CQW growth modes on the wide and narrow facets of a nanocrystal with the corresponding energy profile. From [54]. Reproduced with permission from Springer Nature.

The synthesis of CQW heterostructures, as shown in Figure 2.10, may follow the mentioned principles of the growth phase of CQDs and CQWs. For instance, crown growth, namely a CdS crown, around the 4.5 ML CdSe core CQW, occurs under similar conditions of CdSe synthesis with a sulfur precursor instead of selenium. The size of the crown is mostly determined by growth time and the amount of monomer precursors. Multiple crowns with various elemental compositions around a single core can be easily synthesized [56]. This allows us to fine-tune carrier wavefunctions and electronic structures without altering the confinement.

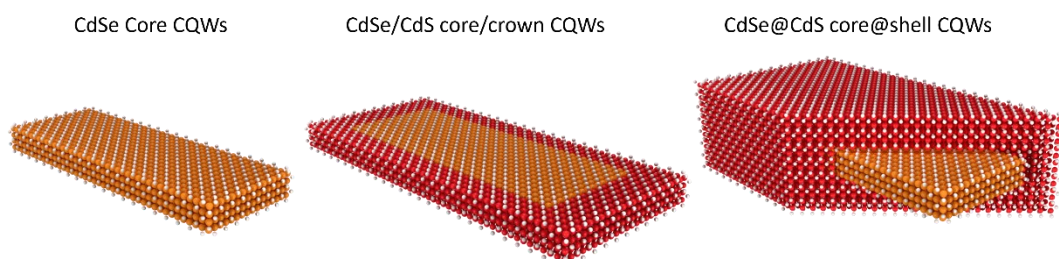


Figure 2.10. Illustrations for 4.5 monolayer thick CQWs and their core/crown and core@shell heterostructures.

In the case of shell growth, there are two main routes with their own perks: (i) hot-injection (HI) [57] and (ii) colloidal atomic layer deposition (c-ALD) [58] synthesis, the principles of which are illustrated in Figure 2.11.

Hot-injection shell growth, a seed-mediated growth technique, relies on the conformal coating of core CQWs with the shell material, achieved through surface reactions of monomers whose precursors decompose at relatively high reaction temperatures (approximately 300°C). Typically, cation salts are present at the beginning of the synthesis along with the ligands and solvent, while the anion precursor is slowly injected at high temperatures, giving the method its name. The high-temperature reaction conditions facilitate the atoms to settle their thermodynamically stable position in the structure, resulting in low defects and highly emissive and colloidally stable structures. The ratio, introduction order, and the amount of the precursors can be varied to adjust the elemental composition and the thickness of the shell to a great extent.

The colloidal atomic layer deposition method is a colloidal adaptation of the atomic layer deposition technique. It relies on self-limiting half-reactions, enabling material growth on another material with atomic precision. Since the outer surface of the CQWs is terminated with cadmium atoms, the introduction of a sulfur precursor with high affinity towards metals suffices for the conformal coating of sulfur atoms around the core. Since sulfur atoms cannot form multilayer structures, a single layer on the surface is guaranteed. Then, free sulfur ions from the reaction medium are removed with excessive washing procedures or phase transfer protocols to avoid multilayer formation by introducing cation salts. Then cation salts solution is introduced to the reaction mixture to complete the half-layer. These subsequent steps are repeated until the desired thickness of the shell is achieved. Apart from atomic precision over the thickness, the c-ALD method allows unprecedented control over the composition of each layer.

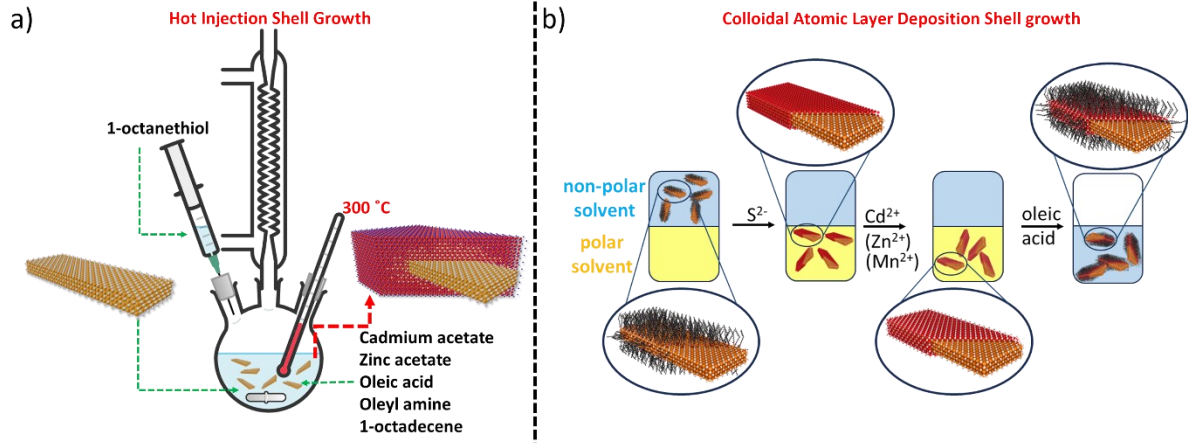


Figure 2.11. Synthesis protocols for the shell growth: a) Hot-injection and b) colloidal atomic layer deposition shell growth techniques.

The synthesis of zinc-blende CQWs showcases the complexity of achieving anisotropic growth in systems with uniform atomic compositions. Advances in the synthesis methods not only enhance the stability and emissive properties of nanocrystals but also allow for the creation of sophisticated heterostructures and for the implementation of multiple heterostructures in a single particle, such as core/crown@shell CQWs. This heterostructure enables fine-tuning of electronic and optical characteristics crucial for next-generation light-harvesting and light-emitting devices.

2.2 Optical Gain in CSNCs

The light amplification relies on optical gain, which is fundamental to lasing. As illustrated in Figure 2.12a, in a 2-level system consisting of a ground ($1S_h$) and an excited ($1S_e$) state, both with double degeneracy ($\omega_e = \omega_h = 2$), upon optical absorption of a photon with the bandgap energy, an electron is excited from the ground state to the excited state creating an exciton. A second incident photon with appropriate energy can interact with the material in that state in two ways: (i) either it will be absorbed and create a second exciton, a biexciton, or (ii) deplete the excited electron via stimulated emission, which is the process of generating a photon with identical characteristics to the incident one, a stimulated emission. When this 2-level system contains only one electron-hole pair, the absorption and stimulated emission probabilities are equal upon excitation. This state is known as optical transparency. Optical gain, or light amplification, happens when stimulated emission surpasses optical absorption. For a single particle, this requirement is met only when the CQD has a biexciton. Hence, the gain mechanism of the CQD is considered to be biexcitonic. In an assembly of CQDs, on the other hand, the gain occurs typically when the average per-particle excitonic occupancy, $\langle N \rangle$, is

slightly greater than 1. This state is known as population inversion. The gain threshold, $\langle N_{th,gain} \rangle$, for a two-level system with the ground state degeneracy ω_h and the excited state degeneracy ω_e , is met as $\langle n_{1S,e} \rangle + \langle n_{1S,h} \rangle = 1$, where $\langle n_{1S,e} \rangle = \langle N \rangle / \omega_e$ and $\langle n_{1S,h} \rangle = \langle N \rangle / \omega_h$ are average single-state occupation factors. These expressions result in $\langle N_{th,gain} \rangle = \omega_e \omega_h / (\omega_e + \omega_h)$. However, more realistic approach describing optical gain threshold is the three-state model, where a CQD can be unoccupied or occupied with one exciton or a biexciton, with probabilities of P_0 , P_X and P_{XX} , respectively, with $P_0 + P_X + P_{XX} = 1$ (Figure 2.12b). The condition for the gain threshold is $P_0 = P_{XX}$, which can be met as $P_X = 1$, if all the particles' occupancies are the same in the whole assembly. This is practically not possible, since the CQDs are excited with high-energy short optical pulses, where the distribution of excitons is predicted by Poisson statistics, $p_i = (\langle N \rangle^i / i!) e^{-\langle N \rangle}$. Here i ($0 < i < \infty$) is the number of excitons in a CQD, and p_i is the probability of this. To apply Poisson statistics to our three-state model, we assume that all multiexcitons contribute to optical gain as biexcitons, meaning $P_{XX} = 1 - P_0 - P_1$. If we rewrite the threshold condition of $P_0 = P_{XX}$, we obtain $1 - e^{-\langle N \rangle} (1 + \langle N \rangle) = e^{-\langle N \rangle}$, solution of which gives $\langle N_{th,gain} \rangle \cong 1.15$.

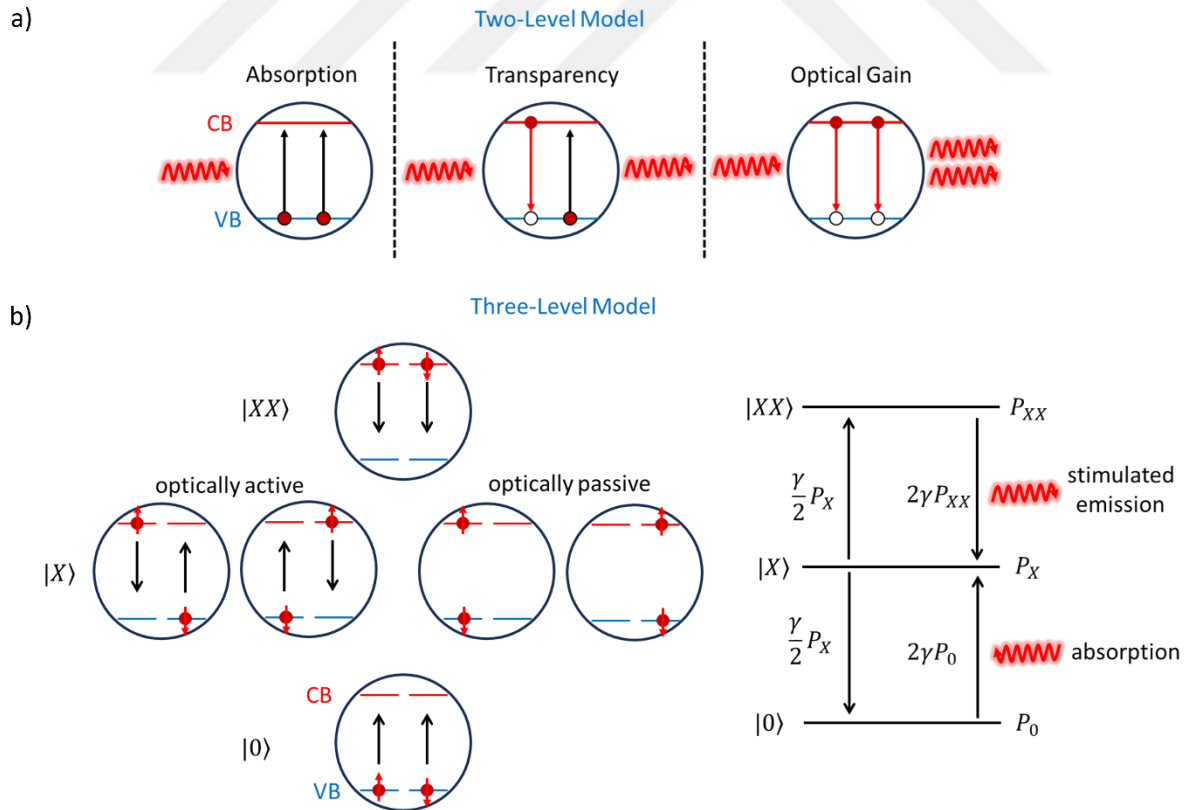


Figure 2.12. a) Two-level and b) three-level optical gain models for CQDs. The upward arrows indicate absorption while downward arrows indicate stimulated emission. γ is the rate of single

spin-allowed transition. Given the ground state, $|0\rangle$, and the biexcitonic state, $|XX\rangle$, two electrons (one spin-up and one spin-down) the rate of transitions from these states to single exciton state, $|X\rangle$, have rate coefficients of 2γ . However, the rate of transitions from single exciton states, $|1\rangle$, is $\gamma/2$, since only the half of the single exciton states are optically active. Figure adapted from: [19] DOI:10.1021/acs.chemrev.2c00865. Licensed under CC-BY-NC-ND 4.0.

However, the multiexciton requirement of optical gain and relaxed momentum conservation in CSNCs complicate the gain due to fast nonradiative Auger recombination. If we take our initial doubly degenerate model with two electron-hole pairs and excite with a photon, there are two possible pathways: (i) radiative electron-hole recombination resulting in a stimulated emission or (ii) an electron recombining nonradiatively with its hole by giving its energy to a third carrier, which would be either the electron or hole of the second exciton. The second case describes Auger recombination, which is a fast process depleting the excited electrons and suffering the population inversion, hence the optical gain (Figure 2.13). To sustain stimulated emission by compensating the Auger-related loss, a certain level of CSNC concentration is required. The required nanocrystal concentration (ρ) to meet this condition is determined by ensuring the rate of stimulated emission under gain saturation ($r_{SE,0}$) exceeds the rate of biexciton Auger decay ($r_{A,XX}$) = $1/\tau_{A,XX}$. The critical concentration ($\rho = \rho_{crit}$) is defined when these rates are equal, i.e., $r_{SE,0} = 1/\tau_{A,XX}$. The rate $r_{SE,0}$ can be expressed as $r_{SE,0} = \beta(c/n_r)G_0$, where G_0 is the saturated gain coefficient, c is the speed of light, n_r is the refractive index, and β is a dimensionless constant dependent on the QD-cavity coupling. If we define G_0 as $G_0 = \rho\sigma_{gain,XX}$ ($\sigma_{gain,XX}$: biexciton gain cross-section), we obtain $\rho_{crit} = n_r(\beta c\sigma_{gain,XX}\tau_{A,XX})^{-1}$. This can be simplified as

$$\xi_{crit} = n_r V_{NC} (\beta c \sigma_{gain,XX} \tau_{A,XX})^{-1} \quad (2.4)$$

where $\xi = \rho V_{NC}$ is the volume fraction of CQDs in the sample [59].

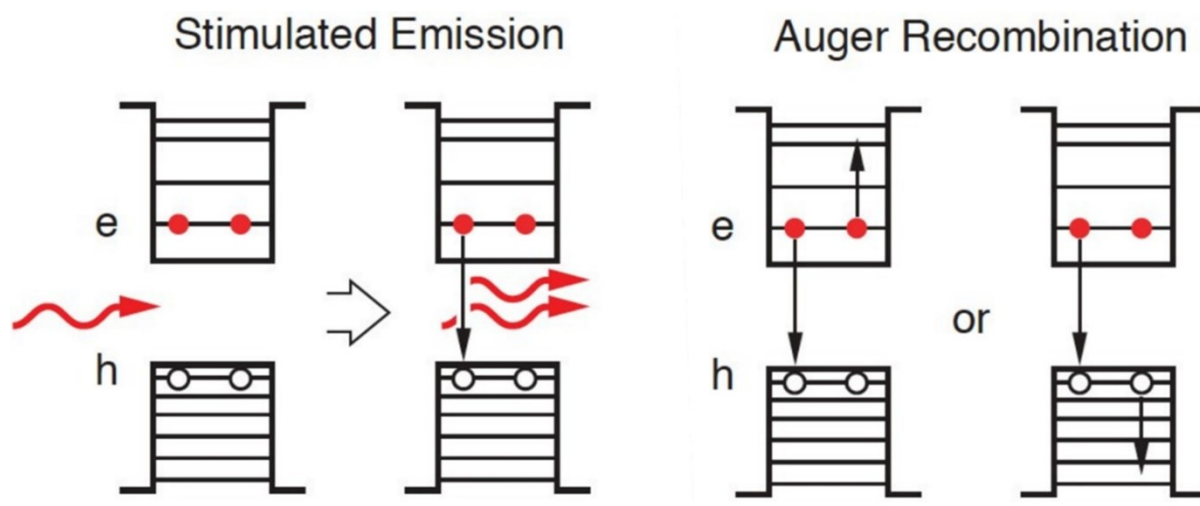


Figure 2.13. Stimulated emission (panel on the left) and nonradiative Auger recombination (panel on the right) pathways of an excited system. Figure reused from: [19] DOI:10.1021/acs.chemrev.2c00865. Licensed under CC-BY-NC-ND 4.0.

The optical gain studies of CSNCs rely on short-pulsed optical pump excitations. If the pulse duration, τ_p is significantly shorter than Auger lifetime, $\tau_{A,XX}$, Auger recombination does not affect the required pump fluence values. The per-pulse pump fluence, f_p , necessary for the optical gain is given by $f_{th,gain} = h\nu_p \langle N_{th,gain} \rangle / \sigma_{abs}$, where h is Planck's constant, ν_p is the pump laser's spectral frequency, and σ_{abs} is the absorption cross-section of the CQD. However, in the case of a continuous wave (cw) pump, Auger processes define the threshold pump fluence values. Before the system achieves optical amplification, depletion of the excited state is mostly governed by spontaneous radiative recombination and Auger, the time constant of which can be formulated as $\tau_{XX} = \tau_{A,XX} \tau_{r,XX} / (\tau_{A,XX} + \tau_{r,XX})$. On the other hand, the steady-state condition is formulated by the equation $P_{XX} / \tau_{XX} = \gamma_{exc} P_X$, where γ_{exc} is the excitation rate. This equation describes that the biexciton decay is compensated by the exciton-to-biexciton excitation. The same relationship is also valid between the 1st and 2nd levels of our 3-state model, $P_X / \tau_X = \gamma_{exc} P_0$. Combining these steady-state conditions yields $P_{XX} = \gamma_{exc}^2 \tau_{XX} \tau_X P_0$. Under threshold conditions, $P_0 = P_{XX}$, the threshold excitation rate is formulated as $\gamma_{exc,th,gain} = (\tau_{XX} \tau_X)^{-1/2}$. In terms of the intensity, $I = \gamma_{exc} h\nu_p / \sigma_{abs}$, the threshold intensity is expressed as $I_{th,gain} = (h\nu_p / \sigma_{abs}) ((\tau_{XX} \tau_X)^{-1/2})$ [19, 60].

2.2.1 Amplified Spontaneous Emission

Amplified Spontaneous Emission (ASE) is a process where spontaneous emission of light is amplified by stimulated emission within a medium that has a population inversion. The

efficient way of generating ASE is through exciting the gain medium with a high-energy short-pulsed pump with a stripe-shaped beam profile that acts as an optical waveguide facilitating the optical amplification along the long axis of the stripe. ASE can be regarded as cavity-less lasing and indicates that the material, if placed in an optical cavity, has the potential to lase.

The electromagnetic field should be effectively confined in the gain medium to sustain the ASE. To maximize this confinement, gain materials are generally deposited on a low refractive index substrate. The confinement factor, Γ , which is an important parameter on the ASE threshold, is the ratio of the mode power coupled to the total power [61]:

$$\Gamma = \frac{\iint_{al_{min}}^{al_{max}} \text{Re}\{\mathbf{E} \times \mathbf{H}\} dx dy}{\iint_{-\infty}^{\infty} \text{Re}\{\mathbf{E} \times \mathbf{H}\} dx dy} \quad (2.5)$$

having $al_{max/min}$ as the boundary of the gain medium, $\mathbf{E}$ as the electric field vector, and $\mathbf{H}$ as the magnetic field vector of the propagating wave. The modal gain coefficient of the material, $g_{mod}(\lambda)$, is directly proportional to the intrinsic material gain coefficient, $g_{i,material}(\lambda)$, by a factor of confinement factor, Γ : $g_{mod}(\lambda) = \Gamma g_{i,material}(\lambda)$ [62].

2.2.2 Lasing

If the gain material is implemented in a cavity, for instance, between two facing highly reflective mirrors with one having slightly lower reflectivity, a Fabry P rot cavity, the electromagnetic field distribution (pattern) at certain frequencies with very narrow linewidths, namely modes, resonates. As long as the population inversion is maintained and the gain beats the total loss per roundtrip, the stimulated emission is amplified with each reflection and ultimately exits the cavity as a very narrow, directional, and coherent beam, a process known as lasing. To sustain lasing the modal gain, g_{mod} , should compensate the losses occurring during reflection, $\alpha_{reflection}$ and propagation in the gain medium, α_{medium} . Figure 2.14 depicts the modes of the cavity, a broad spontaneous emission, and a narrower continuous stimulated emission (gain) profiles along with the level of loss. The lasing spectrum consists of discrete peaks at certain modes, where the gain overcomes the loss [63].

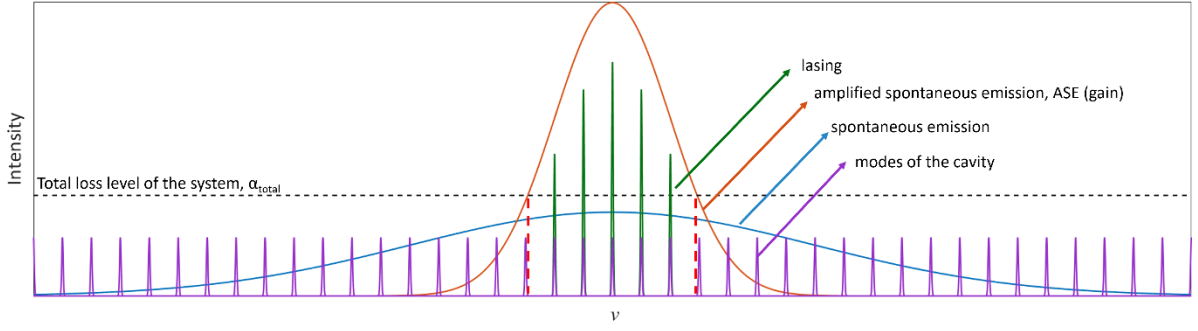


Figure 2.14. Modes of a cavity (magenta), spontaneous emission (blue), amplified spontaneous emission (orange), and lasing peaks (green) as a function of the spectral frequency. Lasing occurs only at the cavity modes where the gain exceeds the loss.

The efficiency of a cavity is characterized by the cavity photon lifetime, τ_c , and the quality factor, Q , where $\tau_c = [c_n(\alpha_{reflection} + \alpha_{medium})]^{-1}$ and $Q = 2\pi\tau_c\nu_0$. Here, c_n is the speed of light in the cavity and ν_0 is the resonant frequency [35]. An alternative approach to determine quality factor is to implement the equation $Q = \lambda/\Delta\lambda$, where λ is the lasing peak wavelength and $\Delta\lambda$ is the FWHM of that peak.

The lasing of CQDs requires a respective number of particles with biexcitons to compensate losses of the laser structure, and more importantly, fast Auger decay. It is assumed that the lasing occurs at half-saturated gain coefficient, $G_{1/2} = 0.5G_0$. Then, optical gain coefficient can be expressed as $G = G_0(P_{XX} - P_0)$ and $G = G_{1/2} = 0.5G_0$ is fulfilled as $2(P_{XX} - P_0) = 1$. Having these conditions and $P_0 + P_X + P_{XX} = 1$ along with aforementioned P_{XX} and P_X values which are γ_{exc} dependent, we obtain the threshold excitation rate as:

$$\gamma_{exc,1/2} = [1 + (1 + 12\tau_{XX}/\tau_X)^{1/2}] \quad (2.6)$$

If the biexciton lifetime is limited by the rate of Auger recombination, $\tau_{XX} = \tau_{A,XX}$, the Equation 2.6 becomes $\gamma_{exc,1/2} \approx 1/\tau_{A,XX}$, which corresponds to the excitation intensity $I_{1/2} = h\nu_p/(\sigma_{abs}\tau_{A,XX})$. Consequently, the ratio of the lasing threshold to the optical gain threshold can be estimated from $I_{1/2}/I_{th,gain} \approx \sqrt{\tau_X\tau_{A,XX}}$ [19].

Chapter 3

Optical Gain of Aqueous CQW Dispersions

This chapter of the thesis is based on the publication “Observation of optical gain from aqueous quantum well heterostructures in water,” S. Delikanli, F. Isik, E. G. Durmusoglu, O. Erdem, F. Shabani, B. Canimkurbey, S. Kumar, H. Dehghanpour Baruj and H. V. Demir, *Nanoscale* 14, 14895-14901 (2022). Reprinted with permission from [64]. Copyright 2022 Royal Society of Chemistry.

3.1 Motivation

In-solution optical gain can be highly advantageous owing to its potential practical applications, including sensing and detection [65-67]. Yet, there are only a few reports and demonstrations of in-solution optical gain and a limited number of in-solution lasing compared to optical gain and lasing studies using close-packed films of NCs [68-73]. This is primarily due to the low concentration of gain media possible in solution which is constraining the realization of ASE. The need for high concentration is principally a consequence of the difficulty of achieving ASE build-up time, which strongly depends both on the gain cross-section and the concentration of the gain material in-solution [74], faster than the Auger lifetime which is unfortunately very efficient in nanocrystals unlike bulk structures [74-75]. Nevertheless, solution-based gain using colloidal nanocrystals is very valuable because of its greater photostability thanks to the continuous renewal of the gain medium because of the constant movement of nanocrystals and ease of incorporation into various optical cavities. Such solution-based gain medium can be easily incorporated into optofluidic lasers for sensitive detection of chemicals and biological materials and on-chip imaging.

Recently, colloidal quantum wells have emerged as a favorable optical gain medium since they possess large absorption cross-sections [6, 38, 76], with continuously tunable emission [77-78], suppressed Auger recombination rates [6, 79], low optical gain thresholds [6, 80-81], long gain lifetimes [6], and large gain cross-sections [72-73]. Especially, their large gain cross-section makes them excellent candidates for in-solution lasing by supporting the gain condition and feasible levels of gain coefficients in solution [72]. Recently, ASE in solution and lasing in microfluidic channels have been demonstrated using CQWs dispersed in non-polar solvents with record low thresholds, almost one order of magnitude better than the previous lasing

demonstrations from colloidal nanocrystals [69, 72-73]. This low threshold optical gain from these CQWs is significantly important for realization of stable high-quality lasers in microfluidic devices for numerous applications, including biological and chemical sensors, flow cytometry and the development of advanced lab-on-chip (LOC) devices. In addition, recently introduced water-based semiconductor CQWs, which can be obtained by synthesizing them in organic solvents and then transferring them to water via ligand exchange, present an attractive platform for optical gain applications thanks to their photostability, highly efficient emission and soft confinement potential owing to their gradient alloyed shell [82]. Although these exciting aqueous CQWs present an extraordinary platform for in-solution optical gain, their optical gain properties have never been explored to date.

In this chapter, we demonstrate the achievement of optical gain in an aqueous medium using an advanced heterostructure of CdSe/CdS@Cd_xZn_{1-x}S core/crown@gradient-alloyed shell colloidal CQWs employing ultrafast transient absorption (TA) technique with a threshold of 3.4 $\mu\text{J}/\text{cm}^2$. These nanocrystals exhibit a long gain lifetime of 2.6 ns which makes them superior candidates for achieving optical gain under CW and quasi-CW pumping. This extremely long gain lifetime can be attributed to the smooth confinement potential suppressing the Auger recombination. We also demonstrated in-solution ASE from these carefully heterostructured aqueous colloidal nanocrystals using a capillary tube with a threshold of $\sim 120 \mu\text{J}/\text{cm}^2$. In addition, we show whispering gallery mode (WGM) laser with a threshold of $\sim 30 \mu\text{J}/\text{cm}^2$ obtained by incorporating films of our CQWs on a fiber using layer-by-layer approach by taking advantage of their 2D geometry, short mercaptopropionic acid (MPA) ligands allowing a higher packing density of CQWs and carboxylic end groups of their ligands causing hydrophilicity. The layer-by-layer approach leads to a uniform film on the lateral surface of the fiber and hence a much lower lasing threshold in this work compared to the previous report [83] in which films were obtained by assistance of capillary force. In this WGM laser, the lasing is strongly guided along the fiber and hence exhibits a spatially coherent emission. This solution-processed architecture of aqueous CQWs with their extraordinary properties makes excellent gain media for the design of CW-pumped lasers and the achievement of much needed optical gain in water is a major step forward for the development of advanced optofluidic lasers in bio-compatible environments.

3.2 Colloidal Synthesis and Experiments

Chemicals: Sodium myristate, cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), oleylamine (OLA), N-methylformamide (NMF), ammonium sulfide solution (40-48 wt. % in water), 1-octadecene (ODE), oleic acid (OA), selenium, hexane, acetonitrile, toluene, chloroform, ethylenediamine (EDA) and 3-mercaptopropionic acid (MPA) were purchased from Sigma-Aldrich.

Synthesis of cadmium myristate: Cadmium myristate was synthesized according to a previously published protocol with slight modifications [84]. In a typical synthesis, 6.26 g of sodium myristate and 2.46 g of cadmium nitrate tetrahydrate were separately dissolved in 500 and 80 mL of methanol, respectively. After complete dissolution, they were mixed and stirred vigorously for 3 h. Finally, the white cadmium myristate powder was precipitated by centrifugation. To remove any undesired impurities and/or side products, the precipitate was washed a couple of times with methanol. The final product was dried overnight under vacuum at room temperature and stored under ambient conditions.

Synthesis of CdSe core of CQWs: 4.5 monolayer CdSe CQWs (i.e. consisting of four Se atomic layers and five Cd atomic layers) were synthesized using a former procedure reported in the literature [84]. In this protocol, 68 mg of Se powder and 800 mg of cadmium myristate were added to 60 mL of ODE in a 100 mL three-neck flask and degassed at 95 °C for 1 h. Then, the temperature was set to 240 °C under the argon flow. At 195 °C, 200 mg of cadmium acetate dihydrate was added to the reaction. This solution was kept at 240 °C for 8 min. Finally, growth was terminated by adding 4 mL of oleic acid and quenched with a cold-water bath. Monodisperse 4.5 ML CdSe CQWs were obtained through size selective precipitation of the reaction mixture. The final product was stored in hexane.

Synthesis of crown growth precursor: A previously reported procedure was followed with slight modifications [84]. Typically, 480 mg of cadmium acetate dihydrate, 340 μL of OA, and 2 mL of ODE were loaded in a beaker. The solution was sonicated for 30 min at room temperature under ambient atmosphere. By continuous stirring at 160 °C and sonication at 100 °C alternately, a white homogeneous solution was obtained. After cooling the sample to the room temperature, 3 mL of 0.1 M sulfur in ODE was added to the mixture. The final solution was kept under constant stirring.

Synthesis of CdSe/CdS core/crown CQWs: A typical core-seeded synthesis method reported previously was used with slight modifications [84]. 4.5 mL CdSe core CQWs and 15 mL of ODE were introduced into a three-neck flask. The solution was degassed at 90 °C for 1h. Then, a certain amount of the growth solution was injected into the mixture at 90°C and degassed for 1h. After that, the solution was heated to 240 °C under argon flow and held at this temperature for 5 min to ensure the proper growth of crown. The reaction was quenched with a cold-water bath. The synthesized core/crown CQWs were precipitated by addition of 5 mL hexane and 3 mL ethanol and centrifugation. Finally, the precipitate was dispersed and stored in hexane.

Deposition of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ shell layers on CdSe/CdS core/crown CQW: $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ shell layers were grown on CdSe/CdS core/crown CQW to obtain CdSe/CdS@ $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ core/crown@Shell CQW by following a previously reported c-ALD recipe with some modifications [82]. 4 mL of NMF was added to the dispersion of CdSe/CdS core/crown CQWs in 1 mL hexane. Then, 40 μL of 40-48% aqueous solution of ammonium sulfide as sulfur shell growth precursor was added and stirred for 2 min. Growth of the sulfur layer was terminated by the addition of 1 mL acetonitrile and excess toluene (till the mixture became blurry) and the mixture was centrifuged. The precipitate was dispersed in NMF and the same cleaning procedure was repeated to remove unreacted precursor. Finally, the CQWs were dispersed in 4 mL of NMF. Cation precursor was prepared by mixing solutions of 0.4 M cadmium nitrate tetrahydrate and 0.4 M zinc nitrate hexahydrate in NMF by a desired volume fraction to obtain a gradient shell.

For the cation deposition, 1 mL of cation precursor mixture was added to CQW dispersion in NMF and the solution was stirred for 45 min. Growth of the cation shell layer was terminated by the addition of 1 mL acetonitrile and excess toluene (till the mixture became blurry) and the mixture was centrifuged. The precipitate was dispersed in NMF and the same cleaning procedure was repeated to remove unreacted precursor.

To increase number of shells, the aforementioned steps above were repeated. The fractions of the zinc to cadmium in cation precursors used in this work were 50:50, 95:5, 95:5 and 99:1 for the 1st, 2nd, 3rd and 4th shell layers, respectively. Lastly, CQWs were precipitated, and 5 mL of hexane and 100 mL of OLA were added and the mixture was stirred overnight. To remove excess ligands, the dispersion of CQWs was precipitated by addition of a minimum amount of ethanol and stored in hexane.

Ligand exchange: We followed a previously reported method to obtain CQWs that are dispersible in water [82]. Core/crown@shell CQWs in hexane were precipitated with addition of ethanol and centrifugation. The precipitate was redispersed in 3 mL chloroform. 1 mL of EDA was added to this mixture and stirred for 1 h under ambient conditions. Then, 3 mL of 0.15 M MPA in DI water was added. As the CQWs were transferred from chloroform to water phase, chloroform was removed with the help of a pipette and adding 10 mg of zinc nitrate hexahydrate to the CQWs in water.

3.3 Results and Discussion

In this work, we synthesized CdSe/CdS@Cd_{1-x}Zn_xS core/crown@gradient-alloyed shell (C/C@GS) CQWs by growing 4 monolayers of Cd_{1-x}Zn_xS shells on 4.5 monolayer thick CdSe/CdS core/crown CQWs using colloidal atomic layer deposition (c-ALD) technique [58, 82]. Then, we made them water dispersible by passivating their surface with MPA via ligand exchange as described in our previous work [82]. The quantum yield of these aqueous C/C@GS CQWs is approximately 90%. In this architecture, Cd_{1-x}Zn_xS gradient-alloyed shells grown on the seed CdSe/CdS core/crown CQWs provide a soft confinement potential and hole wavefunction is largely localized in the core region due to the large band-offset while electron is largely relaxed into the Cd_{1-x}Zn_xS shells layers as a result of small conduction band-offset and smaller effective mass [6, 82]. This spatial difference between the electron and hole wavefunctions generates a quasi-type-II band alignment. The schematic of C/C@GS CQWs together with the band-offsets of the heterostructure is depicted in Figure 3.1a. A representative transmission electron microscopy image of C/C@GS CQWs is provided in Figure 3.1b and energy dispersive spectroscopy (EDS) maps of cadmium, selenium, sulfur, and zinc from a single CQW (shown in the inset) are presented in Figure 3.1c. As can be seen in here, selenium is located only at the core but sulfur, zinc and cadmium are present all over the CQW as expected from alloyed shell of CdZnS in these CQWs [82]. The absorption and photoluminescence spectra of aqueous CQWs are shown in Figure 3.1d. The peaks appearing at 625 and 575 nm in the absorption spectrum are associated with the heavy-hole and light-hole excitonic transitions, respectively. The PL emission peak of these aqueous CQWs is located at 630 nm and the full-width-half-maximum (FWHM) of the PL is 20 nm.

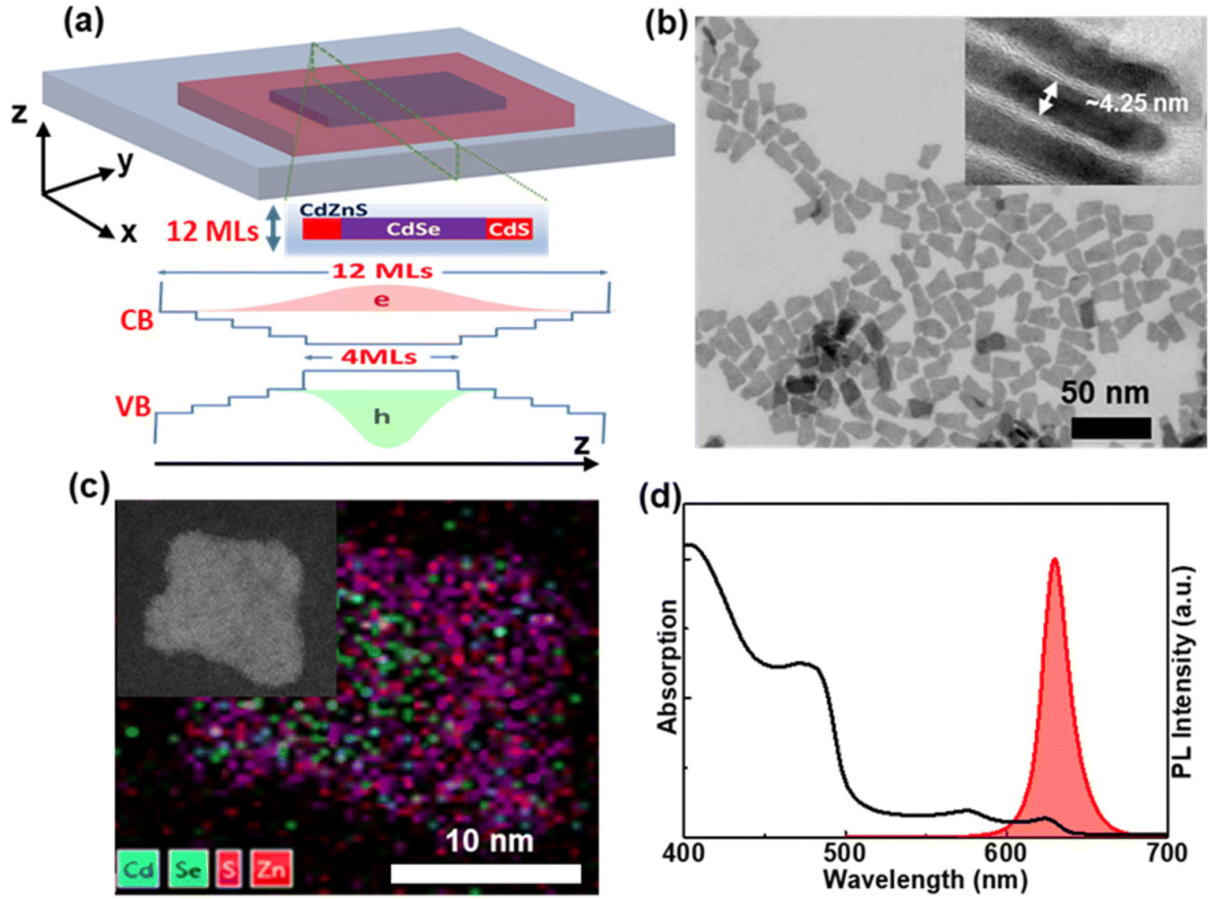


Figure 3.1. a) A schematic of CdSe/CdS@Cd_xZn_{1-x}S core/crown@gradient-alloyed shell colloidal quantum wells (CQWs) together with the band-offsets. b) A representative transmission electron microscopy (TEM) image of C/C@GS CQWs. c) EDS maps of cadmium, selenium, sulfur, and zinc from a single CQW (shown in the inset). d) Absorption and photoluminescence spectra of the CQWs. Used with permission of Royal Society of Chemistry (2024 Copyright), from [64]; permission conveyed through Copyright Clearance Center, Inc.

Figure 3.2a presents nonlinear absorption spectra $\alpha = \Delta\alpha + \alpha_0$, where $\Delta\alpha$ is the absorption bleach and α_0 is the absorption of the unexcited sample, parametrized with respect to the average number of generated excitons per CQW (given in the legend). In here, we used the absorption bleach spectra at ~ 15 ps. The average number of photogenerated excitons per CQW $\langle N_0 \rangle$ is calculated by using $N_0 = f \times \sigma$, where f is the pump fluence and σ is the absorption cross-section. Absorption cross-section of our sample is $2.0 \times 10^{-13} \text{ cm}^2$ and was calculated by following a method explained in our previous work [76]. The nonlinear absorption spectra gradually decrease as we increase the pump fluence as can be seen in Figure 3.2a and α becomes negative at the wavelengths within the proximity of the stimulated emission. This negative net absorption, $\alpha < 0$, signifies the occurrence of optical gain [74]. The optical gain occurs initially at 640 nm and then as the pump fluence is further increased, the peak of the net negative absorption slowly blue-shifts to 630 nm. This blue shift is a signature of stimulated emission

from higher order excitons [85-86]. In Figure 3.2b, the absorption α of our aqueous CQWs at the ASE peak as a function of the average number of photogenerated excitons per CQW $\langle N_0 \rangle$ is provided. The change in the sign of α indicates the threshold for achieving stimulated emission and thus our threshold for stimulated emission is $\langle N_0 \rangle \approx 1.4$ excitons which corresponds to pump fluence of $3.4 \mu\text{J}/\text{cm}^2$.

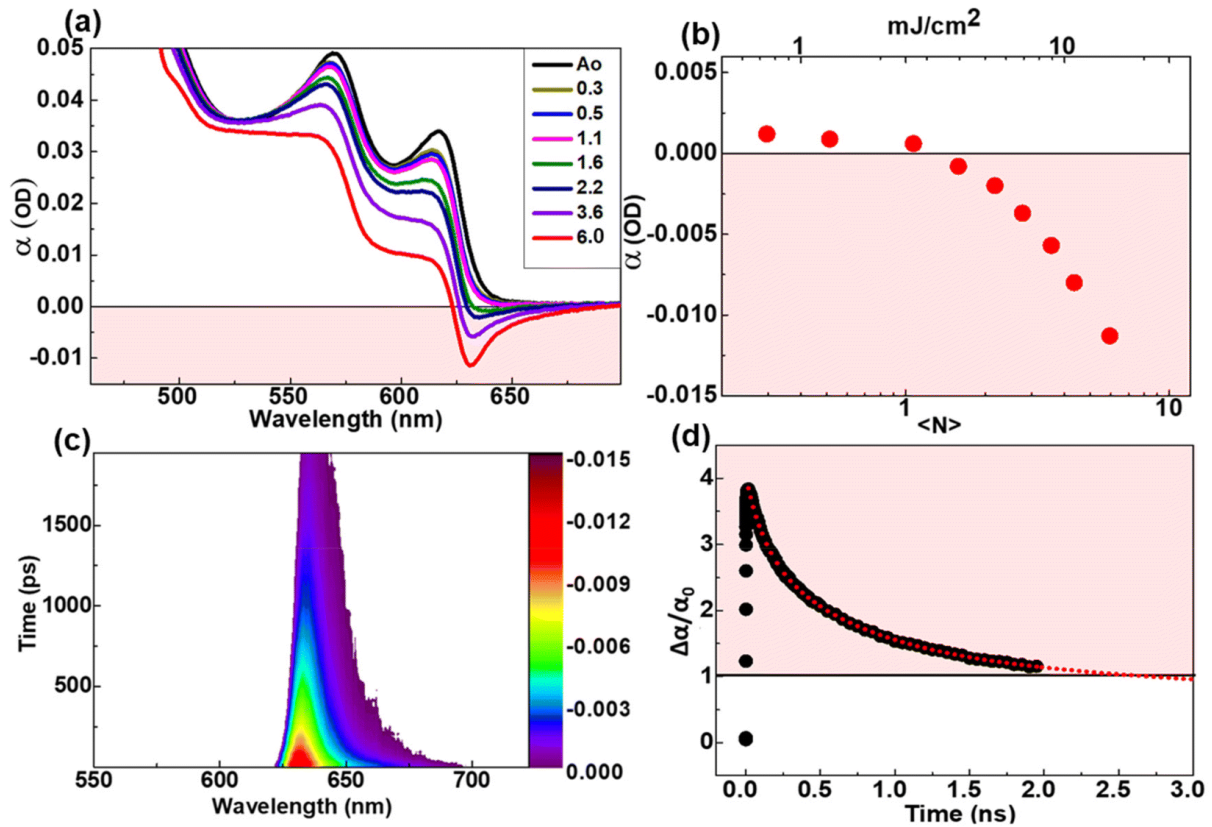


Figure 3.2. a) Nonlinear absorption spectra $\alpha = \Delta\alpha + \alpha_0$, where $\Delta\alpha$ is the absorption bleach and α_0 is the absorption of the unexcited sample, as a function of the average number of generated excitons per CQW. Red-shaded region shows where optical gain occurs ($\alpha < 0$) in this figure. b) Nonlinear absorption α taken at $t = 15$ ps as a function of the fluence and average number of generated excitons per CQW. c) 2D time-wavelength colored map of nonlinear absorption spectrum of our CQWs at the pump fluence of $15 \mu\text{J}/\text{cm}^2$, corresponding to $\langle N_0 \rangle \approx 6$ for the regions only under the optical gain. In c only the region exhibiting optical gain is shown and colored, the coordinates which are not under optical gain are colored as white. d) $-\Delta\alpha(\text{at } 640 \text{ nm})/\alpha_0$ as a function of the time at the pump fluence of $15 \mu\text{J}/\text{cm}^2$. In d we extrapolate the experimental data after 1.95 ns, which is our experimental temporal window, by fitting with three-exponential decay function, shown in dotted red curve. Used with permission of Royal Society of Chemistry (2024 Copyright), from [64]; permission conveyed through Copyright Clearance Center, Inc.

We also investigated the material gain and gain cross-section of these gradient alloyed CQWs. Material gain $g(pf, \lambda, t)$ at a specific pump fluence is given by

$$g(pf, \lambda, t) = \alpha(pf, \lambda, t) \times \mu(\text{at } 400 \text{ nm}) / \alpha_0(\text{at } 400 \text{ nm}) \quad (3.1)$$

where pf is the pump fluence, λ is the wavelength, t is the time, and μ (at 400 nm) is the intrinsic absorption coefficient at 400 nm [87]. Intrinsic absorption coefficient was calculated by dividing the absorption cross-section of our CQWs by its volume and the resulting μ (at 400 nm) is $1.35 \times 10^5 \text{ cm}^{-1}$ for our CQWs. The material gain $g(\text{pf}, \lambda, t)$ reaches 6000 cm^{-1} at the pump fluence of $15 \text{ } \mu\text{J}/\text{cm}^2$, which corresponds to $\langle N_0 \rangle = 6$. In addition, we obtained the gain cross-section of these aqueous CQWs. The gain cross-section per CQW (γ_g) can be calculated by

$$g_{\text{net}} = \gamma_g \times C - \alpha \quad (3.2)$$

where C is the concentration of CQWs and α is the optical loss coefficient [72]. For the case that we obtained $g_{\text{net}}(\text{pf}=15 \text{ } \mu\text{J}/\text{cm}^2) = 6000 \text{ cm}^{-1}$, C is $\sim 5 \times 10^{17} \text{ cm}^{-3}$. Here, we can easily assume that the net modal gain is close to the modal gain (g) since loss coefficient from the films of CQWs is very small (in the order of 10 cm^{-1}) [88] compared to the net modal gain. Then, γ_g ($\text{pf}=15 \text{ } \mu\text{J}/\text{cm}^2$) was calculated to be $1.2 \times 10^{-14} \text{ cm}^2$. This is smaller than the reported value from CdSe/CdS core/shell CQWs, which is likely obtained at higher fluences [72], but 1 to 2 orders of magnitude larger than those of QDs and nanorods [68, 74].

In Figure 3.2c, the 2D time–wavelength colored map of nonlinear absorption spectrum of our CQWs is provided at pump fluence of $15 \text{ } \mu\text{J}/\text{cm}^2$, corresponding to $\langle N_0 \rangle \approx 6$ for only the region under the optical gain. In this figure, while the coordinates that exhibit optical gain are colored and shown, the coordinates which are not under optical gain are kept white. The spectral position where the maximum gain occurs red-shifts as the time passes as can be seen from Figure 3.2c. Initially α is minimum (maximum in magnitude) at 630 nm, slowly shifting towards $\sim 640 \text{ nm}$ (at $\sim 2 \text{ ns}$). This spectral red shift of α over time is due to the reduction in the number of excitons with time in the CQWs after their initial generation with the femtosecond pulse. Likely, this is because of the Coulombic repulsive forces due to presence of multiexcitons. Then, as the number of excitons decreases with time, α eventually red-shifts spectrally. As can be seen in Figure 3.2c, α still stays negative during our measurement window of 1.95 ns which means our gain lifetime is longer than 1.95 ns. In Figure 3.2d, we present $-\Delta\alpha(\text{at } 640 \text{ nm})/\alpha_0$ as a function of the time at the pump fluence of $15 \text{ } \mu\text{J}/\text{cm}^2$. Since our sample was still under the gain within our window of measurement, we extrapolated the experimental data after 1.95 ns by fitting three-exponential decay function. The fit is also included in Figure 3.2d. Using our fit, we obtained a gain lifetime of 2.6 ns from our aqueous CQWs. This optical

gain lifetime is longer than the previously reported gain lifetimes of colloidal quantum wells [6, 89-90] and comparable to the best reported gain lifetimes of charged quantum dots [91] and quantum shells [92]. Such elongated gain lifetime in this system can be attributed to the longer Auger lifetimes as a result of the smooth potential confinement provided by the gradient alloyed shell [75, 93]. The Auger lifetimes are strongly suppressed in finely graded confinement potentials owing to the significant reduction in the strength of the intraband transition [75, 93].

To explore the in-solution ASE performance of our CQWs, CQWs dispersed in water were placed into a capillary tube having a core size of 300 μm by the assistance of capillary force and then optically pumped with a femtosecond mode-locked laser (pulse width ≈ 120 fs) at 400 nm and 1 kHz repetition rate using a stripe geometry with the help of a cylindrical lens. Emitted photons were collected by using an optical fiber connected to a spectrometer. Pump-fluence dependent ASE spectra from our aqueous CQWs are presented in Figure 3.3a. As presented in Figure 3.3a, at low pump fluences only the spontaneous emission with a FWHM of ~ 25 nm appears in the PL spectrum. However, as the pump fluence further is increased, a sharp ASE peak emerges at ~ 641 nm with a FWHM of ~ 10 nm for the pump fluences above the threshold and it becomes dominant as the fluence is further increased as can be seen in Figure 3.3a. The blue shift of the ASE can be attributed to the quasi-type-II nature of these CdSe/CdS@Cd_xZn_{1-x}S core/crown@gradient-alloyed CQWs, which leads to repulsive interactions in the biexcitonic regime. It is worth mentioning that the degree of such quasi-type-II behavior can be well controlled and fine-tuned by the use of alloying and geometrical parameters, as previously demonstrated in CdSe/Cd_{1-x}Zn_xS core/shell QDs, nanorods and CQWs [6, 94-95]. The emission intensity at the peak as a function of the pump fluence for the CQWs is presented in Figure 3.3b. The ASE threshold obtained in Figure 3.3b from the super-linear increase of the emission intensity and Figure 3.3a from the emergence of narrow ASE emission is ~ 120 $\mu\text{J}/\text{cm}^2$, which is slightly higher than the previously reported ASE threshold of CQWs dispersed in toluene [73]. This is likely due to the difference in the concentration of CQWs and possibly better optical confinement factor of the CQW solution in toluene which has a higher refractive index than water. This lower refractive index of water and low optical quality of the aqueous nanocrystals synthesized before are likely the reasons for the failure in achieving optical gain in water to date. Compared to the nanocrystals dispersed in non-polar solvents, such as hexane and toluene, the optical performance of the nanocrystals dispersed in water falls far behind [96-97].

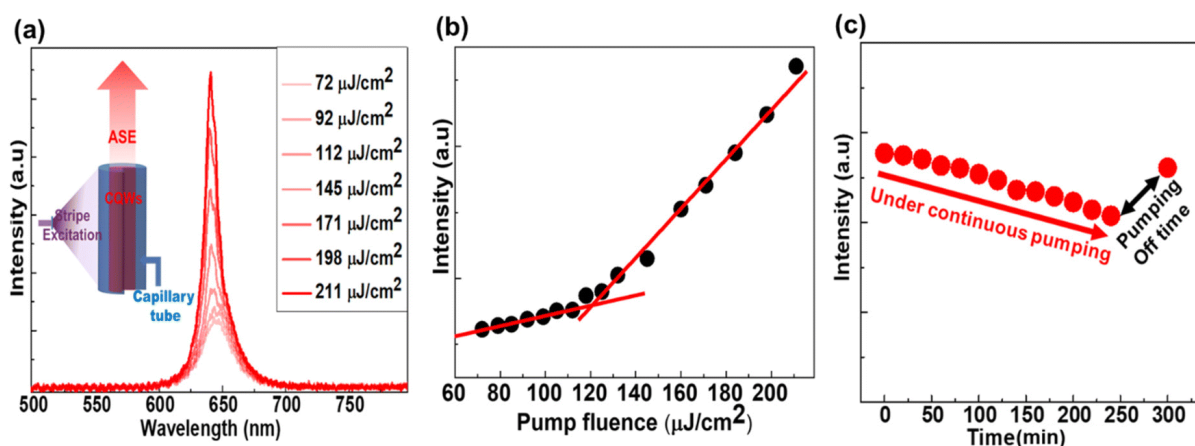


Figure 3.3. a) Pump-fluence dependent in-solution ASE spectra from aqueous CQWs in a capillary tube. The inset exhibit a schematic of CQW solution in the capillary tube optically excited using stripe geometry for ASE measurements. b) Emission intensity at the peak as a function of the pump fluence for aqueous CQWs. The crossing point of the fitted red lines in b indicates the ASE threshold. c) ASE intensity as a function of time. Used with permission of Royal Society of Chemistry (2024 Copyright), from [64]; permission conveyed through Copyright Clearance Center, Inc.

To study the stability of the light amplification in our aqueous CQWs, we pumped the sample above the ASE threshold for 4 h continuously. The stability test was performed under ambient conditions at a threshold of 190 $\mu\text{J}/\text{cm}^2$ using a femtosecond mode-locked laser having a pulse width of 150 fs and a 1 kHz repetition rate. We observed a decrease in the ASE intensity with time as presented in Figure 3.3c. However, this decrease in the ASE intensity was almost recovered after stopping the optical pumping of the sample for an hour. This phenomenon can be attributed to the dissipation of the heat which accumulated under continuous pumping. As a result, the decrease in the intensity of the ASE under continuous pumping is reversible and largely due to the change in the temperature of the surrounding environment unlike irreversible damage seen in QD microdrop lasers as a result of high fluences needed for obtaining ASE leading photo-oxidation [70]. Hence, our aqueous C/C@GS CQWs offer an effective architecture to considerably improve the optical gain stability problem of colloidal semiconductor nanocrystals thanks to their low in-solution ASE threshold and crown and shell layers for passivation and protection.

Owing to excellent optical gain performance of our engineered aqueous CQWs, we incorporated these CQWs as a gain medium into WGM laser. We obtained the WGM laser by depositing 6 monolayers of aqueous CQWs by layer-by-layer approach on a piece of coreless fiber having a diameter of approximately 125 μm by taking advantage of their 2D geometry and hydrophilicity owing to carboxylic end groups of their ligands. We achieved the deposition

of CQWs on fibers by using positively charged poly(diallyldimethylammoniumchloride) (PDDA) linker molecules between each CQW layer as presented in our previous work [82]. The layer-by-layer approach as shown in our previous work leads to uniform film deposition, which is important for lasing applications and other optoelectronic applications, such as light-emitting diodes. Briefly, the surface of the fiber was made hydrophilic by applying oxygen plasma and after that it was dipped into a PDDA linker solution for the attachment of linker molecules to the surface. Then, the fiber was dipped into aqueous CQW solution to attach the CQWs on top of the linker molecules. The process of attaching PDDA and CQWs was repeated 5 more times to reach the desired film thickness on the fiber. The scanning electron microscopy image of our WGM laser is displayed in the inset of Figure 3.4a, demonstrating that the CQW film obtained by layer-by-layer approach is smooth.

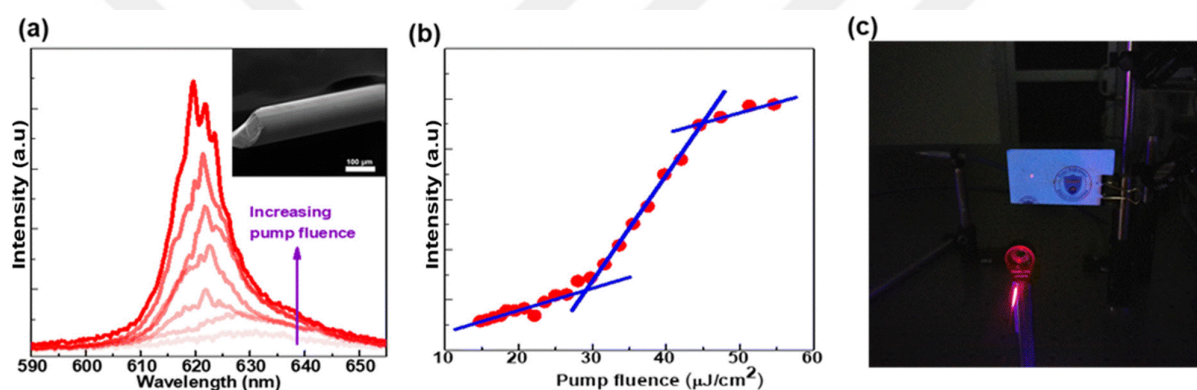


Figure 3.4. a) Luminescence spectra of the CQW integrated fiber. SEM image is given in the inset showing the smoothness of CQW film formation on the lateral sides of the fiber. b) Pump fluence dependent PL intensity of the CQW integrated fiber. c) Image of the resulting laser spot from the optically excited CQW integrated fiber. Used with permission of Royal Society of Chemistry (2024 Copyright), from [64]; permission conveyed through Copyright Clearance Center, Inc.

The emission spectra of the CQW-WGM laser at different pump fluences are given in Figure 3.4a. The WGM laser exhibits multimode laser output with each peak approximately having an FWHM of 1.5 nm corresponding to a Q-factor of ~ 413 . Emission intensity as a function of the pump fluence is presented in Figure 3.4b. The lasing threshold occurs at the pump fluence of $\sim 30 \mu\text{J}/\text{cm}^2$ as can be seen in Figure 3.4a and b with the emergence of a sharp peak and super-linear increase of the total intensity. This threshold is lower than the previous result on CQWs based WGM and can be attributed to the higher quality of aqueous CQWs, better film quality on the fiber used in this work obtained by layer-by-layer assembly unlike in the previous work in which the films were obtained by the help of capillary force [83] and short MPA ligands enabling higher packing density of CQWs. This lasing output saturates around $\sim 45 \mu\text{J}/\text{cm}^2$ as

can be seen in Figure 3.4b. The coherent laser emission of the WGM laser with a well-defined spatial profile is presented in Figure 3.4c. In this WGM laser, the lasing emission from WGM resonator is effectively guided along the fiber owing to strong waveguiding as also demonstrated in our previous work [83].

3.4 Summary

In conclusion, here we report in-water low-threshold optical gain from our carefully heterostructured aqueous CdSe/CdS@Cd_xZn_{1-x}S core/crown@gradient-alloyed shell CQWs with a threshold of $\sim 3.4 \mu\text{J}/\text{cm}^2$. These engineered hetero-CQWs exhibit extremely long gain lifetime of around 2.6 ns which makes them particularly advantageous as a gain medium for quasi-CW and CW lasing together with their low-threshold optical gain. This extremely long gain lifetime and ultralow optical gain threshold can be attributed to the smooth confinement potential as a result of their gradient alloyed shell. Using these aqueous CQWs, we also attained in-solution ASE with a threshold of $120.0 \mu\text{J}/\text{cm}^2$ using capillary tubes. In addition, we demonstrated a low-threshold WGM laser by depositing uniform film of CQWs on a fiber using layer-by-layer approach by exploiting their 2D geometry and hydrophilicity owing to carboxylic end groups of their ligands. In this WGM laser, the lasing is strongly guided along the fiber and hence exhibits a spatially coherent emission. This solution processed aqueous CQWs with their extraordinary electronic properties as a solution-based optical gain medium offers exceptional opportunities for the design of optofluidic lasers for sensitive detection of chemicals and biomedical applications. The achievement of in-water optical gain in this thesis work presents specifically a significant step for biological molecule analyses and detection in the living cells and tissues and other bio-compatible environment.

Chapter 4

Optical Gain of Giant CQWs

This chapter of the thesis is based on the publication ““Giant” Colloidal Quantum Well Heterostructures of CdSe@CdS Core@Shell Nanoplatelets from 9.5 to 17.5 Monolayers in Thickness Enabling Ultra-High Gain Lasing,” F. Isik, S. Delikanli, E. G. Durmusoglu, A. T. Isik, F. Shabani, H. Dehghanpour Baruj, and H. V. Demir, Small 2309494 (2024). Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.1 Motivation

CQWs exhibit very large absorption cross-sections that can easily surpass those of CQDs thanks to their large lateral dimensions and giant oscillator strength [13, 99]. Another important supremacy of CQWs over CQDs is their intrinsically suppressed Auger recombination processes due to their anisotropic shape and large volume [79]. Moreover, the advancements in the synthetic methods of CQWs allow us to engineer the depth and profile of the confinement barrier in core@shell heterostructures with precisely varied elemental composition. Exploiting the benefits from such custom-design heterostructures by the growth of a gradient-alloyed $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ shell on CdSe CQWs resulted in ultra-low amplified spontaneous emission threshold of $0.8 \mu\text{J}/\text{cm}^2$ [6]. On top of that, high density of states owing to quantum well like structure and slow multi excitonic Auger recombination processes at high pump fluences along with aforementioned intrinsic properties of CQWs have led to the achievement of giant modal gain coefficients as high as $6,300 \text{ cm}^{-1}$ with 4.5 monolayer thick CdSe CQWs [7]. Yet, the requirement of high gain coefficients to achieve gain in thin films of emitters has not been met, which would play a crucial role in realization of electrically-driven all-colloidal lasers since one of the main bottlenecks of such applications is the efficient charge injection to the emitter layer.

In this chapter, we show unprecedentedly high material gain coefficients of $g_i = 140,000 \text{ cm}^{-1}$ and gain cross-sections of $2.3 \times 10^{-13} \text{ cm}^2$ from our engineered “giant” CdSe@CdS core@shell hetero-CQWs of $\sim 600 \text{ nm}^2$ in lateral size possessing extended thickness up to 17.5 ML corresponding to $\sim 6 \text{ nm}$. Material gain coefficient is an intrinsic property of the gain materials, which is not affected by the external factors such as film thickness and/or film roughness unlike

modal gain coefficient, allowing us to make a fair comparison between different groups of gain materials [100]. We attribute this superior gain capability to the contribution of higher energy states to the gain along with an increased number of the states per energy owing to this giant size of CQWs, which also allows for more suppressed Auger recombination rates [75, 101]. We observe blue shift of the transient absorption spectra with the increasing pump fluence, which signifies the contribution of the higher energy states. Also studying the dependence of gain coefficients and optical gain thresholds on the thickness of the shell, we found that while the ASE threshold decreases with the deposition of consecutive layers of shell, the gain coefficient decreases with the further deposition of additional layers. The improvement in the ASE thresholds is due to the reduction of the nonradiative Auger recombination rates as a result of the volume scaling law, whereas decline in the density of emitters as a consequence of the excess volume increment causes the reduction of the gain coefficients [102-104].

These CQWs also present an exceptional platform for realization of in-solution lasing by supporting large feasible levels of gain owing to their large gain cross-section reaching to $2.3 \times 10^{-13} \text{ cm}^2$, which is 3 orders of magnitude larger than the ones of CQDs [74, 104-105]. Regarding that, we have also demonstrated low-threshold ASE from aqueous dispersion of these CQWs, which would be useful in optofluidic applications. Additionally, we have showed optically-pumped whispering gallery mode colloidal quantum well laser (WGM-CQW) with a lasing threshold of $8 \text{ } \mu\text{J}/\text{cm}^2$. Our WGM assisted-CQW laser exhibits highly polarized and stable emission which does not show any decline in the laser output during 4 hours of uninterrupted operation (12×10^6 laser shots).

As a follow-up study, we conducted TA and ASE measurements under high pump fluences on CQWs dispersed in hexane and water, respectively. This approach allowed us to investigate the effects of emitter packing density on the optical gain properties of CQWs. Our results revealed the presence of two distinct ASE peaks in the water dispersion, corresponding to the dual gain regions observed in TA measurements. This behavior was absent in the ASE measurements of CQW films, regardless of the pump fluence. These findings suggest that the packing density of CQWs plays a crucial role in the gain mechanism, with high packing density facilitating exciton cooling and hindering the observation of the second gain region.

4.2 Colloidal Synthesis and Experiments

Synthesis of cadmium myristate: Cadmium myristate was synthesized according to a previously reported recipe [106] 1.23 g cadmium nitrate tetrahydrate and 3.13 g sodium myristate were dissolved in 40 mL and 250 mL of methanol in separate bottles, respectively. Once they are completely dissolved, cadmium nitrate solution was added to sodium myristate solution and the mixture was stirred vigorously for 2 h with a magnetic stirrer. At the end of the synthesis, formed cadmium myristate, which is a white precipitate, was filtered and washed with methanol couple of times to remove unreacted species. Then the residue was dried under vacuum overnight.

Preparation of growth solution: The growth solution to obtain thicker CdSe NPLs were prepared by following a previously reported procedure [42]. 160 mg cadmium oxide, 40 mg cadmium chloride and 20 mL oleic acid were loaded into a 3-neck-flask and degassed at 95 °C under vacuum and constant stirring for half an hour. Then the temperature was raised to 200 °C under nitrogen atmosphere and let the reaction continue for 15 min. At the end of the 15 min, the reaction mixture becomes transparent or slightly yellow solution. At this point, the reaction was quenched with water bath and the product was stored in vials.

Synthesis of 4.5 ML CdSe CQWs with the lateral dimensions of 50×10 nm: The synthesis of these 4.5 ML CQWs was carried by following a previously reported method with slight modifications [37]. 150 mg cadmium myristate, 24 mg selenium powder and 15 mL ODE was loaded into a 3-neck flask and degassed at 100 °C for 10 min. Then, the temperature was raised to 240 °C under nitrogen atmosphere. As the temperature reached 198 °C, the mixture of 57 mg anhydrous cadmium acetate and 44 mg cadmium acetate dihydrate were added into the reaction mixture. After 10 min at 240 °C, the reaction was quenched with a water bath and 2 mL of oleic acid was injected. 4.5 ML thick CQWs were isolated from the other species by selective precipitation using ethanol as anti-solvent and hexane as the solvent. The TEM image and absorbance-PL spectra of these CQWs are provided in Figure 4.2a and c, respectively.

Synthesis of 7.5 ML thick CdSe CQWs: The synthesis of 7.5 ML thick CQWs was performed by following a previous report with slight modifications [42]. 170 mg cadmium myristate, 24 mg selenium powder and 15 mL of octadecene were loaded into a 3-neck-flask and degassed at 95 °C under vacuum for half an hour. Then the temperature was raised to 240 °C under inert atmosphere. When the color of the reaction mixture became deep orange (around 195 °C), 90

mg of anhydrous cadmium acetate was added to the reaction mixture and waited for the formation and lateral growth of 4.5 ML thick CdSe CQWs for 10 min at 240 °C. Then, the temperature was raised to 310 °C and preheated growth solution (at 150 °C) was injected into the flask as the temperature reached 280 °C. It took around 1 h to obtain the product containing mainly 7.5 ML thick CQWs which can be checked using absorbance spectra of the aliquots taken from the reaction mixture. At the end of the reaction, we removed the heating mantle and waited for the temperature to fall slowly. When the temperature dropped to 190 °C, we injected 2 mL of oleic acid and waited for the mixture cool down to room temperature. Finally, the product was collected and 20 mL of hexane was added and the mixture was centrifuged at 5,000 rpm for 6 min. The supernatant was discarded and the precipitate was dispersed in 20 mL of hexane. Then the dispersion was centrifuged with the same settings and the precipitate was discarded. 20 mL of ethanol was added to the supernatant and, after the centrifugation with the same settings, the supernatant was discarded and the precipitate was re-dispersed in hexane and stored.

Synthesis of CdSe@CdS core@shell CQWs by c-ALD method: To obtain core@shell heterostructures, we followed a previously reported colloidal atomic layer deposition method with slight modifications [58]. The 7.5 ML CdSe CQWs were washed several times with ethanol and methanol to remove any unreacted cadmium species. Then, they were re-dispersed in 1 mL hexane and 3 mL of N-methyl formamide (NMF) was added. After that, 40 μ L of ammonium sulfide (48-50% wt) solution was added and the mixture was shaken for 8 min. The product was precipitated by centrifugation after addition of 1 mL acetone and 30 mL toluene. Then, the precipitate was re-dispersed in 3 mL of NMF and the same washing procedure was repeated 3 times in total and dispersed in 3 mL of NMF at the end. After the sulfur layer coating, we added 2 mL of 0.4 M cadmium nitrate tetrahydrate solution in NMF and mix it for 45 min. Then the product was precipitated and washed with the same aforementioned cleaning procedure. The successive growth of sulfur and cadmium layers were repeated until desired thickness in terms of monolayers is achieved. At the end, the product was precipitated and after discarding the supernatant, 5 mL of hexane and 100 μ L of oleylamine was added to the precipitate. The mixture was sonicated and stirred overnight. To remove excess ligands the mixture was precipitated with ethanol with an amount of 25% of total volume and dispersed in hexane to be stored.

Ligand Exchange: To disperse the synthesized CQW heterostructures, we performed a ligand exchange protocol by following a previously reported recipe [82]. CQWs dispersed in hexane were first precipitated by the addition of ethanol and centrifugation; then, they were redispersed in 3 mL of chloroform. 1 mL of ethylene diamine was added to the dispersion and stirred for 1 h. Following, 3 mL of 0.15 M 3-mercaptopropionic acid in water was added to the mixture, and as the phase transfer occurred, the chloroform phase was removed. 10 mg of cadmium nitrate tetrahydrate was added to the CQW dispersion and stored.

Inductively coupled plasma mass spectroscopy (ICP-MS) measurement: To determine the concentration of the CQWs, first, we performed inductively coupled plasma mass spectroscopy (ICP-MS) on CQW with a known amount in terms of absorbance values. The CQWs were digested with nitric acid and diluted with deionized water so that the final solution had 2% nitric acid by volume. Concentration of cadmium atoms were obtained from Agilent 725 ICP-MS system.

Calculation of σ and μ_i : We calculated the absorption cross-section of CQWs using the relation:

$$\sigma(\lambda) = 2.303 \times A(\lambda) / (C_{\text{NPL}} \times N_A \times L) \quad (4.1)$$

where $A(\lambda)$ is the absorbance value at a specific wavelength, C is the concentration of absorbers in units of mol/cm^3 , N_A is the Avogadro's number, and L is the optical path length of the cuvette, which is 1 cm.

To calculate the concentration of CQWs by dividing the concentration of cadmium atoms obtained from ICP-MS measurement by the number of cadmium atoms per CQW. We estimated the volume of NPLs using TEM image and we calculated the number of cadmium atoms in a single NPL using the information that a unit-cell of CdSe which contains 4 cadmium atoms and have a volume of $0.216 \text{ \AA}^3$.

And finally, the intrinsic absorption coefficient was calculated using the expression of:

$$\mu_i(\lambda) = \sigma(\lambda) / V \quad (4.2)$$

where V is the volume of single CQW in units of cm^3 .

Determination of Γ : The refractive index data for CQWs was extracted from ellipsometry measurements similar to the methodology presented in a previously reported work [107]. CQW films were spin-coated from solution on quartz substrate. The ellipsometry data was collected for 400-1000 nm range with 3 nm steps for three different incidence angles (50-55-60). The thickness of the sample was found by selectively fitting 700-1000 nm range with a Cauchy model, where CQWs are non-absorbing. Keeping the thickness constant, 400-700 nm range was fitted with Kramers-Kronig-consistent dispersion curves. The complex dielectric function was decomposed into two Tauc-Lorentz oscillators and one Gaussian oscillator. The data analysis was performed using WVASE32 software package.

Guided modes for the spin-coated samples can be found by solving the wave equation for the asymmetric slab geometry of quartz-CQW-air. For these calculations, we used a waveguide calculation software (MODE Waveguide Simulator) for convenience. As CQW layer is the medium with the largest refractive index, the fundamental guided mode is guaranteed to exist as long as it is sufficiently thick. Propagation constants and mode profiles are found from the eigenvalue equations. The confinement factor of the fundamental mode, defined as the ratio of electromagnetic energy confined in CQW film to the total energy of the mode, was then calculated from the mode profiles.

Estimation of material gain, g_i , from variable stripe length (VSL) measurements: To obtain material gain coefficient values from the results of VSL measurements, we followed a previously reported equation: $g_i = g_{\text{mod}} / (\Gamma \times \%_{\text{volume}})$ where g_i is material gain coefficient, g_{mod} is modal gain coefficient (obtained with VSL measurements), Γ is the confinement factor (calculation of which is shown above) and $\%_{\text{volume}}$ is the percent volume occupation of the emitters in the film [87]. The value of the $\%_{\text{volume}}$ is given by the equation $\%_{\text{volume}} = A(\lambda) / (h_{\text{film}} \times \mu_i(\lambda))$, where $A(\lambda)$ is the absorption value at a specific wavelength, h_{film} is the thickness of the spin-coated CQW film and $\mu_i(\lambda)$ is the intrinsic absorption coefficient (the determination of which is explained above) of the CQW. In Figure 4.1, the absorption spectrum (a) and the cross-sectional scanning electron microscopy image of the spin-coated film (b) of 15.5 ML C@S CQWs as a representative sample are given. As depicted in Figure 4.1a, the absorption value of the CQW film at 400 nm is around 0.94 and the thickness of the film is 220 nm as shown in the Figure 4.1b. The intrinsic absorption coefficient of 15.5 ML C@S CQWs is determined to be $1.13 \times 10^5 \text{ cm}^{-1}$. Given the values, the percent volume occupation of CQWs

in this film is determined as 38%. By implementing this value in the former equation along with g_{mod} and Γ values, we obtained the material gain coefficient of the 15.5 ML C@S CQWs.

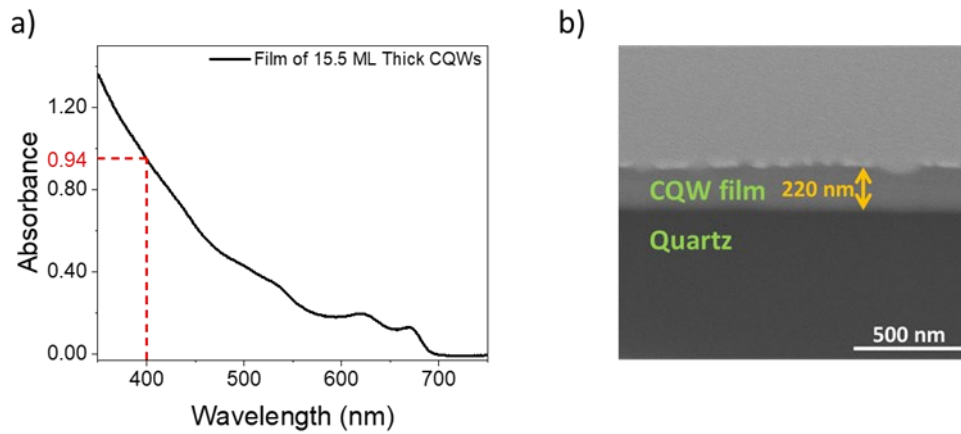


Figure 4.1. a) Absorption spectrum of the spin-coated film of 15.5 ML C@S CQWs with a thickness of 220 nm. b) Scanning electron microscopy (SEM) image of the film cross-section obtained with focused ion beam (FIB) etching. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

X-Ray diffraction spectrum of 13.5 ML C@S CQWs: The sample was prepared by drop-casting a concentrated CQW dispersion on the substrate and waited for the solvent to evaporate. The data was obtained using Panalytical Xpert Pro MPD.

4.3 Results and Discussion

We synthesized “giant” CQWs and analyzed their optical gain performances by the virtue of material gain coefficient, g_i , and number of excitons per CQW required to achieve gain, $\langle N \rangle_{\text{th}}$. Material gain coefficient is the gain coefficient of a fictional CQW matrix where the volume fraction of the CQWs is 1 and the threshold occupation [87], $\langle N \rangle_{\text{th}}$, is the average number of excitons per CQW that is required to reach optical transparency (here under the pump of a femtosecond pulsed laser), which is inherent to the gain material and thus recognized as a standard figure of merit to compare gain capability among different groups of such materials. To obtain giant CQW heterostructures we started with the synthesis of thickest reported CdSe CQWs following the recipe in the work of Christodoulou et al. with slight modifications [42]. We obtained a mixture of CQWs consisting of 6.5, 7.5 and 8.5 ML thick CQWs that cannot be separated with selective precipitation methods due to the fact that each species has a similar lateral size (and since the amount of the 7.5 ML CQWs is prominent, here we are going to call them as 7.5 ML CdSe CQWs). To investigate the role of the thickness of the core we also

synthesized 4.5 ML thick CQWs with a similar aspect ratio and a surface area so that the interplay of other parameters on optical gain can be isolated (Figure 4.2a and b).

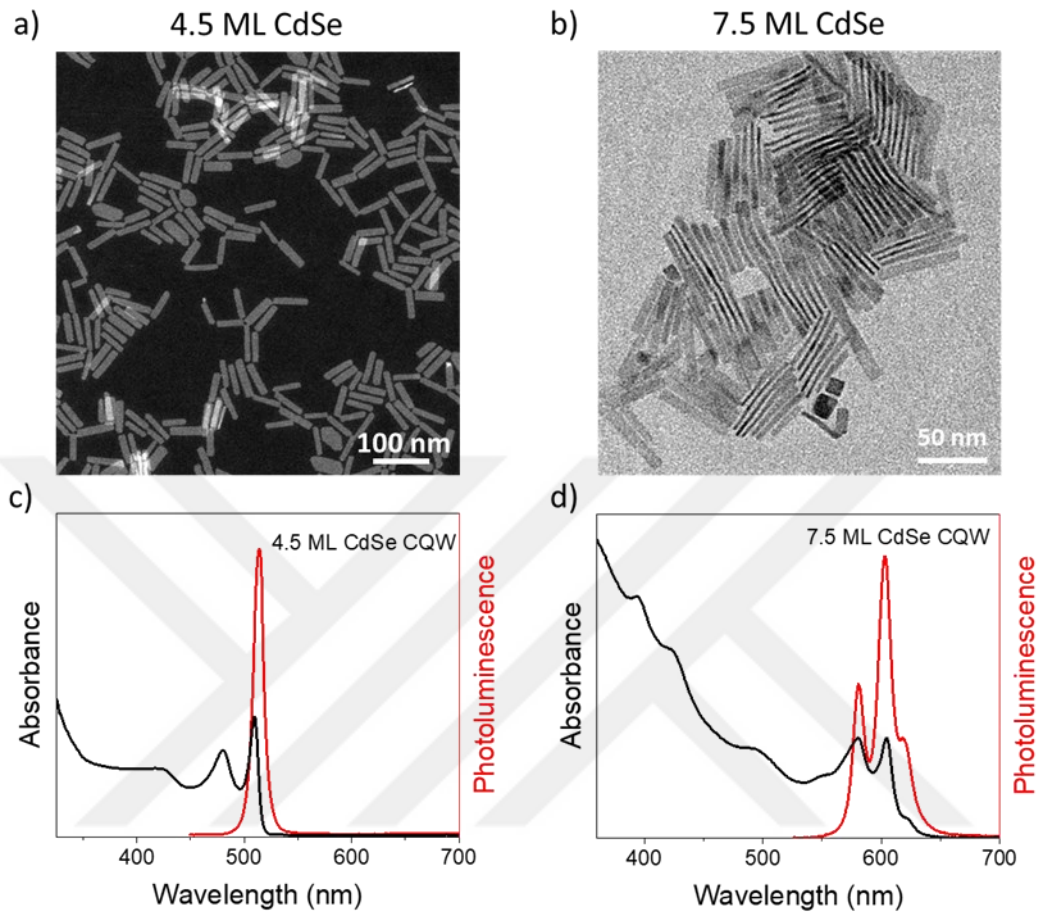


Figure 4.2. a) TEM image of 4.5 ML thick CdSe CQWs with similar lateral dimensions (50×10 nm) with 7.5 ML thick CdSe CQWs. b) TEM image of 7.5 ML thick CdSe CQW seeds. c) Absorption and PL spectra of the 4.5 ML CdSe CQWs d) Absorption and PL spectra of the 7.5 ML CdSe CQW seeds. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

The 7.5 ML thick CdSe CQWs we synthesized have average lateral dimensions of $10 \text{ nm} \times 50 \text{ nm}$ (Figure 4.2b). Then we coated these core CQWs with 1-5 MLs of CdS shell via colloidal atomic layer deposition (c-ALD) method [58] to systematically study the effect of the thickness of the shell on gain performances of the CQWs. In here, c-ALD method gives the opportunity to control the thickness of each additional layer with an atomic precision which is not possible by the hot-injection method [108]. A representative transmission electron microscopy image of 7.5 ML thick CdSe coated with 3 ML CdS shell (resulting total thickness of 13.5 ML) CQW heterostructure is shown in Figure 4.3a. As presented in the inset, the high-resolution close-up image indicates high crystallinity, even though the mentioned shell-growth technique relies on room- temperature reactions. X-ray diffraction spectrum of the core and core@shell CQWs

provided in Figure 4.4 depicts zinc-blende crystal structure with broad diffraction peaks due to the nano-size of the particles. With the growth of CdS shell the peaks are slightly shifted towards lower angles, which is attributed to the strain induced by the mismatch of the lattice constants between CdSe and CdS. The thickness of 13.5 ML CQWs that is presented in Figure 4.3b confirms successful shell growth with desired thickness where the lattice is expanded by a small margin so that the thickness has ended up to be 4.3 nm instead of 3.9 nm. This phenomenon of the lattice relaxation upon shell growth by c-ALD method was confirmed in the inset of Figure 4.3b with a larger lattice constant than the theoretical value, which was also observed in previous works [6, 82, 109].

The single photoluminescence peak of our thick-core@shell CQWs is a result of the reduction of quantum confinement energy with the deposition of shell layers and the relatively broad emission from the core@shell CQWs having a FWHM of >20 nm due to the strong electron-phonon coupling [82, 110] compared to the FWHM of ~ 10 nm from the core only NPLs. Also, one may consider the possible effect of electron shakeup processes [111], but in the case of these thick-core@shell CQWs, asymmetry -as a feature of electron shakeup- in the PL profile is not observed. The relaxation of the confinement can easily be followed by the red shift in the absorption and emission spectra with the increase in the number of the shells as can be seen in Figure 4.3c and d. In the inset of Figure 4.3c, the change of intrinsic absorption coefficients, μ_i , of the core@shell heterostructures with the variation of shell thickness is depicted. CQWs with shell thicknesses from 1 to 3 ML have similar μ_i values around $1.16 \times 10^5 \text{ cm}^{-1}$, but further addition of shell layers caused the intrinsic absorption coefficient values to decrease in a linear fashion. The narrowing of the full-width-at-half-maxima of the PL is pronounced within the CQWs with shell thicknesses increasing from 1 to 3 MLs but this effect diminishes for thicker shells as depicted in the inset of Figure 4.3d.

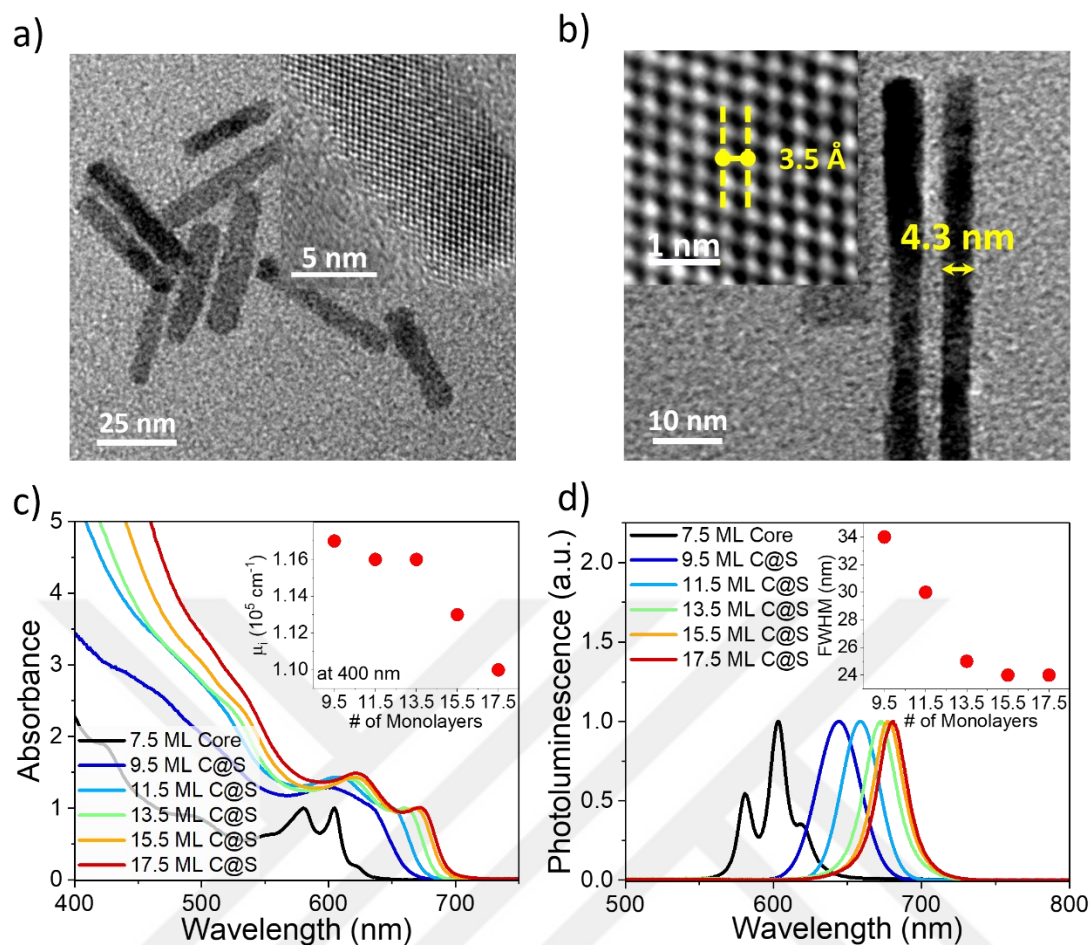


Figure 4.3. Structure and characterization of giant core@shell CQWs. a) 13.5 ML core@shell CQW: a TEM image where the inset shows a close-up shot with high crystallinity and b) TEM image depicting the thickness with an inset indicating a lattice fringe of 3.5 Å. c) Absorption spectra of 7.5 ML CdSe CQW seeds and its core@shell heterostructures with increasing thickness. The inset shows the intrinsic absorption coefficients, μ_i , of the core@shell heterostructures. d) Photoluminescence spectra of 7.5 ML CdSe CQWs and its core@shell heterostructures with increasing thickness. The inset depicts the FWHM values of the emission of the core@shell heterostructures. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

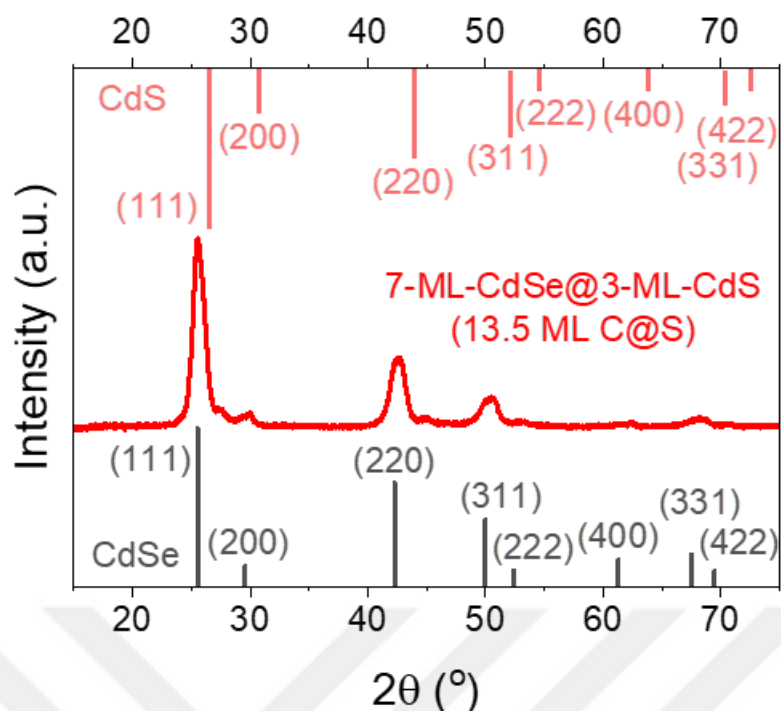


Figure 4.4. XRD spectrum of 13.5 ML C@S CQWs. The standard diffraction patterns of zinc-blende bulk CdSe (black) and CdS (red) are included as vertical lines at the bottom and the top (PDF2 of CdSe: 03-65-2891, CdS: 03-65-2887). Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

To analyze the optical gain performances of CdSe@CdS core@shell CQWs with increasing thicknesses, we performed amplified spontaneous emission measurements along with variable stripe length measurements on the spin-coated films of the CQWs and transient absorption measurements on CQWs in toluene under femtosecond pulsed laser excitation. Amplified spontaneous emission, variable stripe length (VSL) and transient absorption measurements were carried out using a femto-second mode-locked (pulse width ≈ 120 fs) pump laser at 400 nm wavelength with 1 kHz repetition rate. To obtain stripe-shaped beam profile for ASE and VSL measurements, a cylindrical lens was employed. The emission was collected by an optical fiber connected to the spectrometer.

The results of ASE measurements on 13.5 ML core@shell CQWs as a representative sample is shown in Figure 4.5a (while the results of the remaining samples are presented in Figure 4.6, Figure 4.7, Figure 4.8, Figure 4.9, and Figure 4.10). As the pump fluence increases, a narrow peak emerged around the wavelength of 691 nm, which is red-shifted away from the spontaneous emission (SE) peak at 679 nm. The FWHM value of SE is around 33 nm whereas the linewidth of the new emerging peak is just 7 nm, which is attributed to ASE. This is also endorsed by the super-linear increase in the integrated PL intensity with the further increase in

the pump fluence above the threshold pump fluence, I_{th} , of $9 \mu\text{J}/\text{cm}^2$ as shown in the inset of Figure 4.5a. In the inset, the exciton numbers, $\langle N_0 \rangle$, corresponding to the pump fluences are given where the threshold exciton occupancy, $\langle N \rangle_{th}$ is found as ~ 4 . $\langle N_0 \rangle$ is determined by the relation $\langle N_0 \rangle = \sigma \times f$ with σ being the absorption cross-section of the CQWs and f being the pump fluence in terms of the number of photons per area. Absorption cross-section is experimentally determined using the data from absorbance spectra, inductively coupled plasma mass-spectroscopy measurements and TEM imaging [76].

The threshold pump fluence, I_{th} , decreases as the thickness of the shell increases, as can be seen in Figure 4.5b. The fall in the threshold fluence within the first 3 MLs of shell is radical and this becomes insignificant afterwards. However, as depicted in the inset of Figure 4.5b, the threshold occupancy, $\langle N \rangle_{th}$, as a function of the shell thickness does not follow the same monotonous trend, rather it has a V-shaped profile where the lowest threshold is exhibited by the CQWs with 3 ML thick shell with the $\langle N \rangle_{th}$ value of 4. This behavior of the $\langle N \rangle_{th}$ indicates the increase of the absorption cross-section with the addition of layers, which is commonly observed in colloidal semiconductor nanocrystals (see the absorption cross-section of the CQWs increasing with the increasing shell thickness shown in Figure 4.11). Moreover, the V-shaped profile can be explained mainly as a result of two counteracting effects: (i) the suppression of Auger recombination which follows inverse proportionality to the thickness of the CQW and (ii) the introduction of additional defect sites, which induces non-radiative Auger processes, with the increasing number of shell layers [112-113]. There could also be possibly an additional adverse effect of strain build-up with increasing thickness of shell.

Next, we studied the behavior of ASE peak with the increasing pump intensity as shown in Figure 4.5c. The ASE peak becomes more asymmetric with the increasing pump fluence as can be seen in the figure. The asymmetric shape of the peak with a broader half on the blue side of the spectrum indicates the participation of higher energy states to the gain [85]. This hypothesis will be the backbone of the reasoning why these CQW heterostructures with thicker cores can reach unprecedentedly high gain coefficients. As depicted in the inset, half-width-at-half-maximum (HWHM) have similar values both for the red (red dots) and blue side (blue dots) of the peak at lower fluences. However, with the increasing pump fluence, the blue side expands to a greater extent.

The modal gain coefficients, g_{mod} , of the core@shell heterostructures with different shell thicknesses were determined via VSL measurements. VSL analysis stands on the exponential

increase of amplified spontaneous emission from the film of the material as the length of the stripe shaped pump beam increased, but VSL measurements should be properly executed to avoid probable pitfalls intrinsic to this method. In this regard, (i) we created a long beam stripe using optical components and used the center of the beam to minimize the effect of the intensity change depending on the Gaussian profile of the beam as we increase the slit width; (ii) we placed the slit close to the sample film to avoid intensity fluctuations caused by the interference of light passing through the slit; and (iii) we determined the modal gain coefficients, g_{mod} , by fitting the relation

$$I_{ASE,Integrated}(l) = A \times l + (\Omega/g_{mod})(e^{g_{mod} \times (l-l_{th})} - 1) \quad (4.3)$$

where $I_{ASE,integrated}(l)$ is the integrated intensity of the ASE emission, l is the stripe length of the pump beam, A is a constant proportional to the spontaneous emission power density for excitons, Ω is the fluorescence growing parameter, g_{mod} is the modal gain coefficient, and l_{th} is the threshold stripe length, which refers to the minimum stripe length required to achieve ASE [114-115]. We chose this expression instead of the gain saturation model [116] since we were working with relatively narrow slit widths and the small-signal gain model that we use only causes underestimation of the gain coefficient in the case of deviation [117].

Accordingly, the deduced modal gain coefficients, g_{mod} , of 13.5 ML core@shell CQWs -as a representative sample- at various pump fluence levels can be seen in Figure 4.5d where the dashed lines are the fits using the aforementioned expression. The VSL measurement results of the remaining samples are given fully in Figure 4.12. In Figure 4.5e, we present modal gain coefficients of the CdSe@CdS CQWs with increasing thickness of shell as a function of the pump fluence. Dashed lines are provided for eye guiding to depict the overall saturation behavior of modal gains with the increase of the pump fluence. The highest modal gain coefficient is observed from the CQWs with 3 ML shell, which is shown as green data points in the figure. The increase in the modal gain coefficient values as a function of the pump fluence gradually slows down. A similar trend was observed in CQWs previously [6-7]. One of the most remarkable results of these measurements is that the saturation pump fluences are at least 200 times higher than their gain threshold values, I_{th} . In QDs, the modal gain usually saturates at pump fluences twice the threshold value. The distinct behavior of the modal gain coefficients between the QDs and CQWs is attributed to the large density of states [118], slow Auger recombination rates [79, 102], and contribution of the excitonic molecules to the optical gain [87, 119].

The maximum achieved modal gain coefficients of each sample that are determined by the VSL measurements, are presented as black dots in Figure 4.5f. The films prepared for the measurement vary in thickness, and so does the confinement factor, Γ , of the films. Hence, we divided g_{mod} by the confinement factor to make a fair comparison of the gain coefficients between the core@shell particles for each sample with different film thicknesses. The results from the calculation of g_{mod}/Γ are shown in Figure 4.5f as blue dots. Since the confinement factor of the films of CQWs with 3 and 5 ML shells was close to the unity, they overlap with the measured data. The modal gain coefficients (black data points) and their confinement factor corrections (red data points) show a volcano shaped profile with 13.5 ML thick core@shell CQWs displaying the highest values. Finally, we determined the volume fraction of the CQWs in the film so that we can extrapolate their material gain coefficient, g_i [87]. The material gain coefficient of the CQWs, which are denoted as blue data points, remain constant within the first three samples with thinner shells and decrease with the addition of shell layers. A similar behavior was also observed from CdSe@CdS CQDs with the excessive increase in the thickness of the shell [104]. The drop in the g_i values is pronounced after the 3rd layer of the shell.

The maximum material gain coefficient of $140,000 \text{ cm}^{-1}$ is achieved with the CQWs, which is the highest material gain found among the colloidal emitters, to the best of our knowledge (see) [100]. This value corresponds to a gain cross-section per CQW, γ_g , of $2.3 \times 10^{-13} \text{ cm}^2$, which is 3 orders of magnitude larger than the best reported values of CQDs [74, 104-105]. It is calculated by the given equation $g_{\text{net}} = \gamma_g \times C - \alpha$ where g_{net} is the net material gain, C is concentration of CQWs in the medium, and α is the optical loss coefficient. Since the optical loss coefficient is very small in the films of CQWs, it can be neglected especially when a very high gain coefficient of theirs is considered [83]. The concentration of CQWs in the film is estimated to be $\sim 4.9 \times 10^{17} \text{ cm}^{-3}$.

Table 1. Material gains of different materials that are best in their classes under femtosecond optical excitation. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

Material	Material Gain (cm ⁻¹)
Organic dyes [120]	700
Perovskite CQDs [121]	2,000
II-VI CQDs [104]	2,800
Perovskite films [122]	3,200
Bulk AlGaIn [123]	6,000
II-VI nanowires [124]	10,000
Polymeric semiconductors [125]	12,000
Epitaxial InAs/GaAs QDs [126]	15,000
4.5 ML CdSe CQWs (band edge) [127]	15,000
4.5 ML CdSe CQWs [87]	76,000
Giant CQWs [98](This Study)	140,000

The reasonings we propose for the achievement of high gain coefficients are as follows: First, having thicker cores increases the number of states per energy, which follows a linear relation with the volume of quantum wells so that a larger number of states can contribute to the gain. In order to support this claim, we also determined the modal gain coefficients of 4.5 and 7.5 ML CdSe with similar lateral dimensions. The modal gain coefficient of 7.5 ML CdSe CWQs could reach 12,000 cm⁻¹, while it was only 3,500 cm⁻¹ in the case of 4.5 ML CdSe CQWs (Figure 4.1). This result was expected owing to the higher number of states per energy of thicker particles, which follows a linear relation with the volume of quantum wells so that a larger number of states can contribute to the gain. Then, growing an additional CdS shell monolayer around the CdSe core, which further adds energy states to our quantum object, helps

to suppress Auger recombination by pushing surface defect sites away, causing delocalization of electron wavefunction and increasing the volume. Slowing down the Auger recombination process permits the contribution of higher energy states to the gain, which in turn assists in obtaining large gain coefficients. However, the further increase in the thickness of shell results in the dilution of the packing of the emitters hence the drop of the material gain. Similar behavior was observed in CQDs, where the material gain is hampered by the increase in the shell thickness to a greater extent [104]. Moreover, additional shell layers are source of extra defect sites which again affects the population inversion in an adverse way. Hence, there is an optimum thickness of shell to achieve the best performing CQW as a gain system.

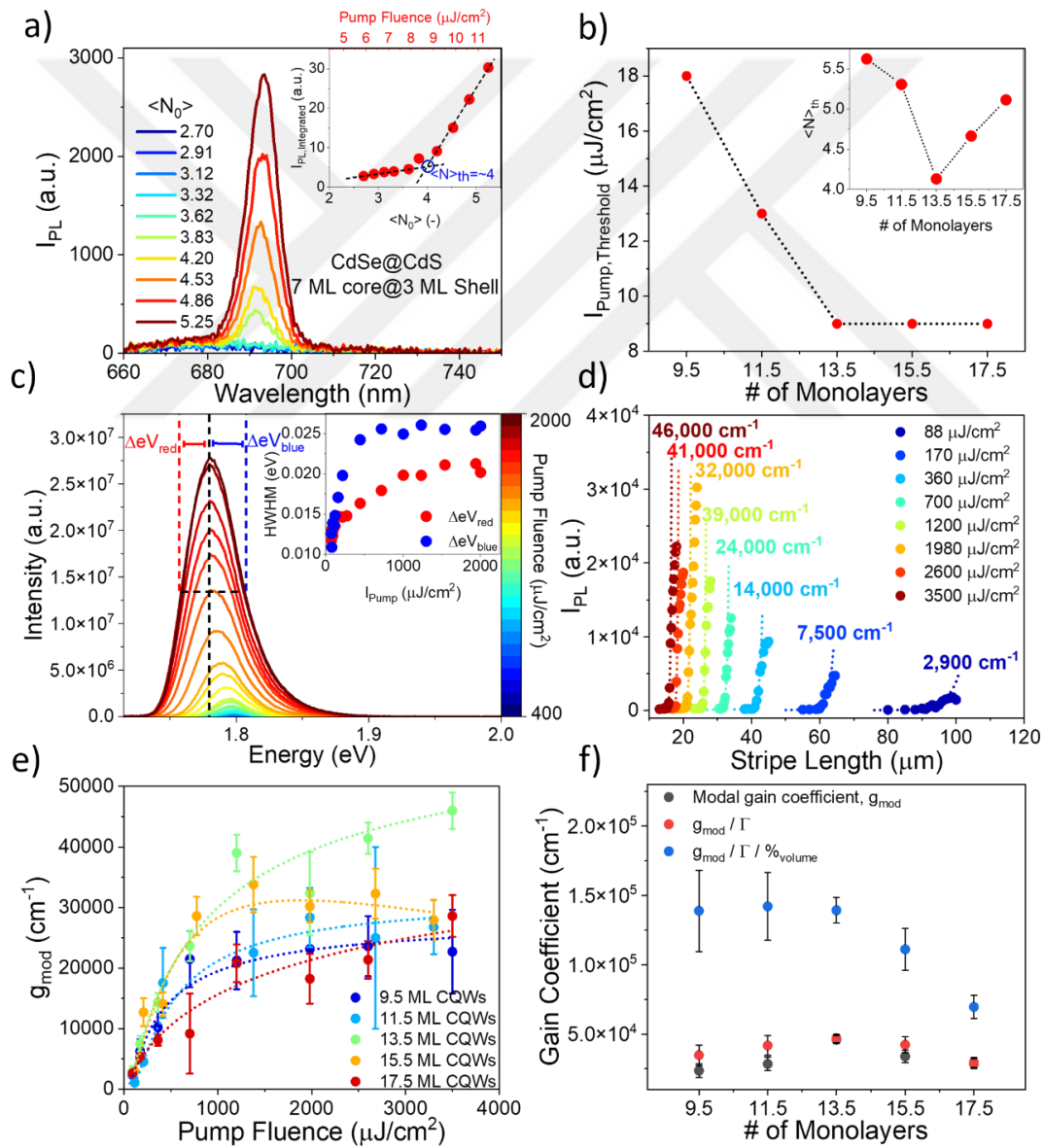


Figure 4.5. ASE and VSL results of core@shell CQW films. a) Pump-dependent ASE spectra of 13.5 ML core@shell CQW. The inset shows integrated PL intensity as a function of the

exciton occupancy per particle. b) ASE threshold values of the CdSe@CdS core@shell CWQs with the increasing number of shell layers in terms of the pump fluence. The inset depicts the same threshold values in terms of the threshold exciton occupancy per particle, $\langle N \rangle_{th}$. c) The evolution of ASE spectra of 13.5 ML core@shell CQW without spontaneous peak at the pump fluences reaching 2,000 $\mu\text{J}/\text{cm}^2$ where the blue side is broader. The inset shows the HWHM values of the ASE peak as a function of the pump fluence. d) VSL data of 13.5 ML core@shell CQWs at various pump fluences with the corresponding modal gain coefficients, g_{mod} . e) Modal gain coefficients of CdSe@CdS core@shell CQWS with increasing shell thickness as a function of the pump fluence. f) Maximum achieved modal gain coefficients, g_{mod} , of CdSe@CdS core@shell CQWS with increasing shell thickness (black dots), with their normalized values with respect to the optical confinement factors of the films (red dots) and to the volume fraction of CQWs on film (blue dots) which corresponds to the intrinsic material gain, g_i . Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

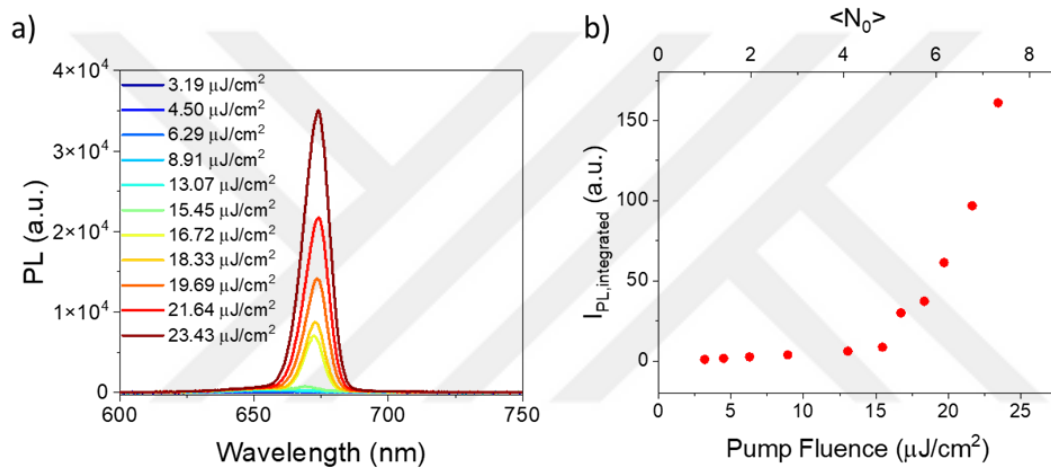


Figure 4.6. ASE measurement results of 9.5 ML C@S CQWs. a) Pump dependent ASE spectra. b) Integrated PL intensity as a function of the pump fluence (bottom axis) and exciton occupancy (top axis). Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

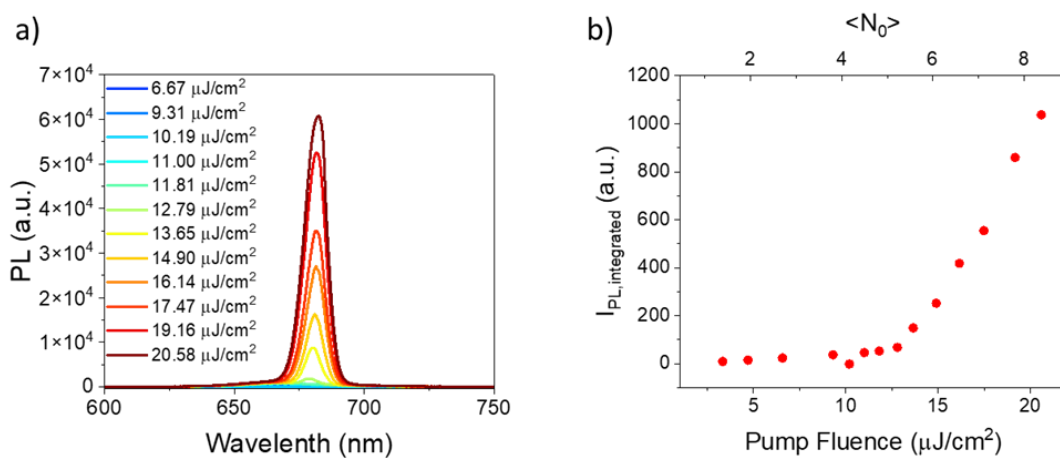


Figure 4.7. ASE measurement results of 11.5 ML C@S CQWs. a) Pump-dependent ASE spectra. b) Integrated PL intensity as a function of the pump fluence (bottom axis) and exciton

occupancy (top axis). Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

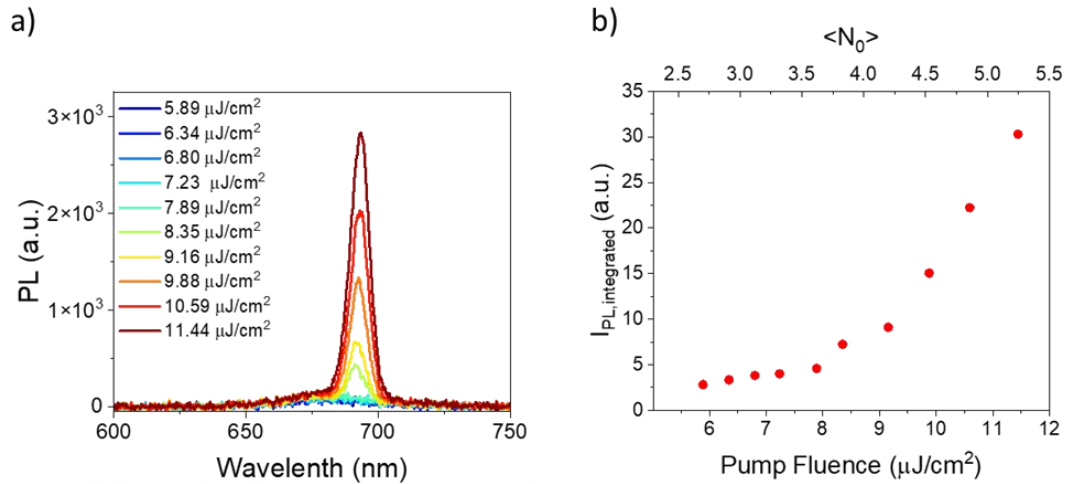


Figure 4.8. ASE measurement results of 13.5 ML C@S CQWs. a) Pump-dependent ASE spectra. b) Integrated PL intensity as a function of the pump fluence (bottom axis) and exciton occupancy (top axis). Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

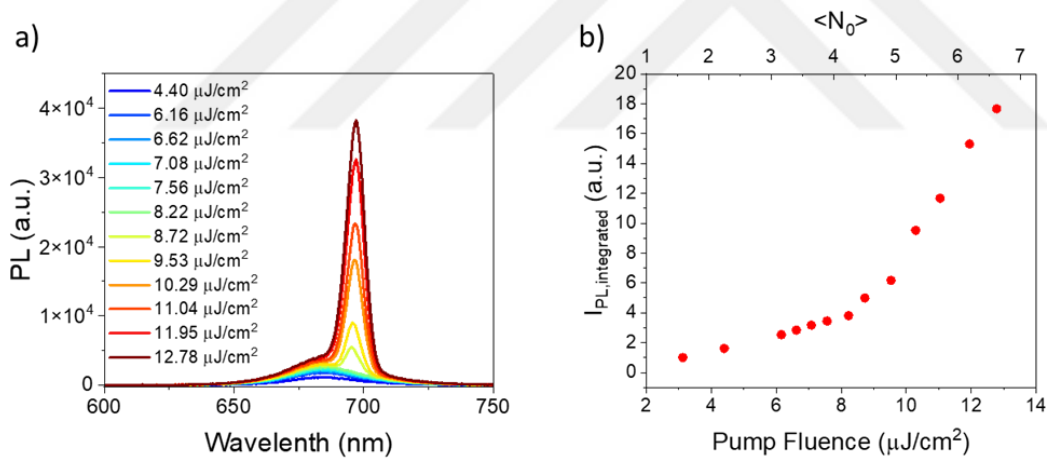


Figure 4.9. ASE measurement results of 15.5 ML C@S CQWs. a) Pump-dependent ASE spectra. b) Integrated PL intensity as a function of the pump fluence (bottom axis) and exciton occupancy (top axis). Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

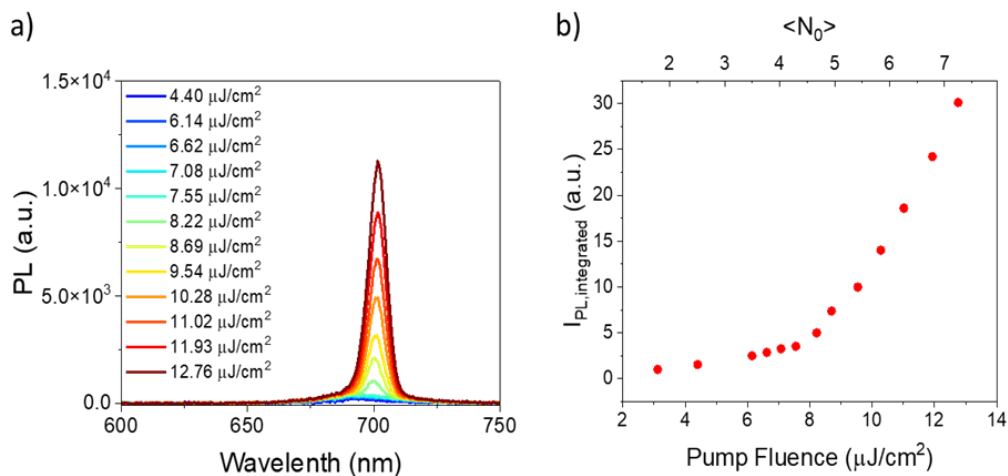


Figure 4.10. ASE measurement results of 17.5 ML C@S CQWs. a) Pump-dependent ASE spectra. b) Integrated PL intensity as a function of the pump fluence (bottom axis) and exciton occupancy (top axis). Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

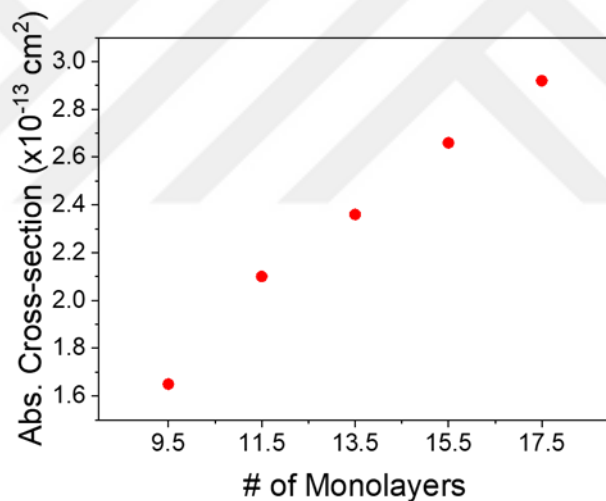


Figure 4.11. Intrinsic absorption coefficients, μ_i , of the core@shell heterostructures with increasing thickness. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

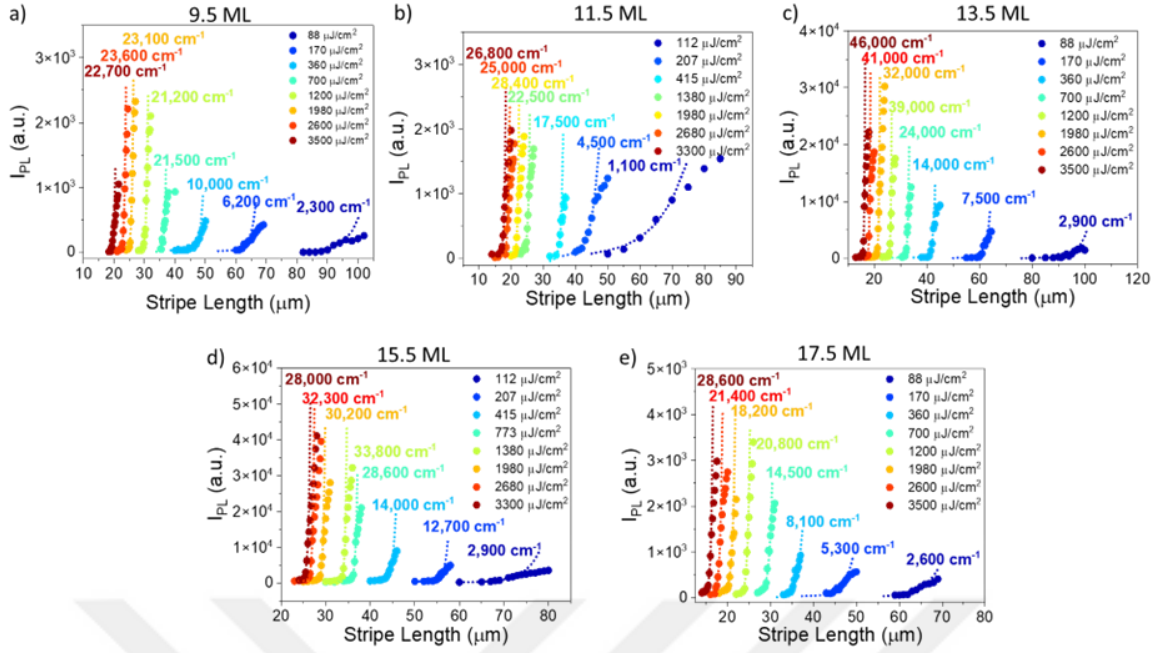


Figure 4.12. VSL measurement results of CdSe@CdS CQWs with increasing number of layers at various pump fluences. Exponential fits to determine modal gain coefficients, g_{mod} , are shown with dashed curves and the corresponding g_{mod} values are depicted with the same color of the curve. a) 9.5 ML C@S CQWs, b) 11.5 ML C@S CQWs, c) 13.5 ML C@S CQWs, d) 15.5 ML C@S CQWs, and e) 17.5 ML C@S CQWs. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

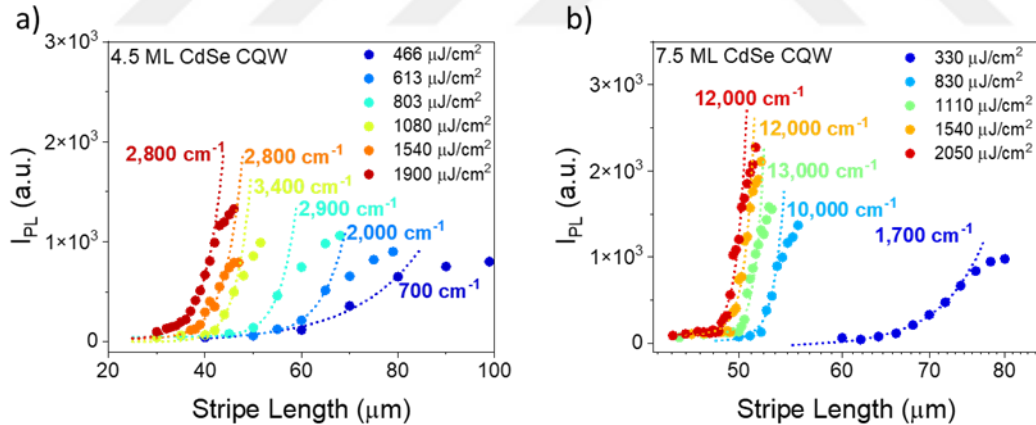


Figure 4.13. VSL measurement results of CdSe CQWs with 2 different thicknesses having similar lateral areas at various pump fluences. Exponential fits to determine modal gain coefficients, g_{mod} , are shown with dashed curves and the corresponding g_{mod} values are depicted with the same color of the curve. a) 4.5 ML CdSe and b) 7.5 ML CdSe. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

In consonance with the results obtained from ASE and VSL measurements, 13.5 ML core@shell CQWs attain the superior performance with the lowest ASE threshold in terms of the number of excitons required without suffering from a big drop in the gain coefficient. Hence, we have chosen them as the model CQW for the rest of this study. To acquire a deeper

understanding of the optical gain mechanism of our CQWs, we implemented femtosecond TA measurements through which temporal change in pump-induced absorption ($\Delta\alpha$) is deployed to calculate nonlinear absorption spectra ($\alpha=\Delta\alpha+\alpha_0$) at any given time, where α_0 is the absorption of the material without optical pump excitation. With increase in the number of generated excitons, the gradual bleaching in the absorbance outcompetes the value of α_0 which indicates the occurrence of gain [74].

Figure 4.14a shows the absorption bleaching of core@shell CQWs with 13.5 ML thickness at the delay time of 9 ps where the optical gain is achieved at around the threshold occupancy $\langle N_{th} \rangle = 3$ excitons per CQW. Any signal in the pale red area of Figure 4.14a indicates a net gain. As the intensity of the pump laser is increased, the negative peak of α grows and spectrally broadens. After a certain pump fluence additional peaks on the blue side of the main peak emerge following the initial peak at ~ 690 nm under the pump fluence slightly above the threshold. The peak at 660 nm prevails as the prominent one with further increase in the pump fluence.

In the TA measurements, the gain threshold pump fluences that are required to achieve gain in solution of CQWs are slightly lower than the value obtained from ASE on film measurements. This discrepancy is mainly due to the additional loss mechanisms from the film in which the CQWs reside. In Figure 4.14b, normalized absorption bleaching ($-\Delta\alpha/\alpha_0$) as a function of $\langle N_0 \rangle$ at the gain wavelength ($\lambda_{gain} \sim 690$ nm) is presented to depict the gain threshold. The value of $\langle N \rangle_{th} = 3$ is determined from the intersection of the measurement data with the horizontal dashed line at the level of $-\Delta\alpha/\alpha_0 = 1$, which indicates the optical transparency state.

In Figure 4.14c, we present 2D-time-wavelength map of the gain region of 13.5 ML core@shell CQWs for $\langle N_0 \rangle = 15.4$ in terms of the material gain coefficient, g_i , where the region is defined by the condition of $g_i > 0$. In this figure the area with the values $g_i < 0$ is displayed in white and the material gain at a specific wavelength for a particular pump fluence is given by:

$$g_i(f, \lambda, t) = \alpha(f, \lambda, t) \times \mu_i(400 \text{ nm}) / \alpha_0(400 \text{ nm}) \quad (4.4)$$

where f is the pump fluence, λ is the wavelength, t is the time, and $\mu_i(400\text{nm})$ is the intrinsic absorption coefficient at 400 nm provided in the inset of Figure 4.3c [87]. The gain lifetime of the CQW reaches the time interval of 600 ps, as can be seen in Figure 4.14c while that of QDs is around 100 ps [101, 128]. The spectral domain of the gain encompasses a broad range of 125 nm. Additionally, newly emerging gain regions that are depicted as three red stripes are more

pronounced in this figure. The gradual evolution of new gain regions as a function of the pump fluence is given in Figure 4.15 where the broadening on the red side of the spectrum is just 10 nm meanwhile it is 45 nm on the blue side. The continuous blue-shifting gain profile as the pump fluence increased suggests contribution of higher order excitonic states and indicates that the gain is of multi excitonic nature [86]. Even though there exist different models to explain the optical gain mechanism of CQWs, there is no conclusive consensus on any of them. Among these models are the purely excitonic gain model [129-130], the biexcitonic gain model [90, 131], excimer formation models [132], another model based on equilibrium between the excitons and excitonic molecules [127], and another on carrier cooling bottlenecks [87]. The most recent two of these reports focus on the explanation of high gain coefficients obtained by the CQWs. In the work of Geiregat et al. [127], it is attributed to the equilibrium of excitons and excitonic molecules owing to the large binding energies, which was studied by the means of TA measurements. As also discussed in this previous report, the exciton binding energy should decrease with the increasing thickness of CQWs, where the subject of this previous study, 4.5 ML CdSe CQW, is around 4-times thinner than our giant CQWs. In our study, we do not observe any TA peak maxima with positive OD values on the 45 meV range from the heavy hole peak, which is the exciton binding energy in 4.5 ML CdSe CQWs as seen in the previous work. Second, in the work of Tomar et al. [87], a nonexcitonic blue-shifted gain band leads to material gain up to $76,000 \text{ cm}^{-1}$ after the multiexcitonic band saturates around a material gain level of $18,000 \text{ cm}^{-1}$. In the current study, we do not observe full saturation of the multiexcitonic gain or a distinctively separated gain away from the band edge, which would otherwise indicate contribution from unbound charge carriers [87]. Our observations (from ASE and TA measurements) strongly suggest that the observed gain has a multiexcitonic nature, unlike a separate nonexcitonic blue-shifted gain band as previously reported in Ref 46. The highest gain region resides closely around the wavelength of 660 nm where the material gain coefficient, g_i , reaches $5,400 \text{ cm}^{-1}$ at the pump fluence of $33.5 \text{ } \mu\text{J}/\text{cm}^2$ ($\langle N_0 \rangle = 14$). As a result, in the current work, our findings indicate the contribution of higher energy states to the optical gain, which is facilitated by the suppression of Auger recombination, owing to the large size of our giant CQWs where the long gain lifetime is a clear indicator of slower Auger processes.

In Figure 4.14d, we plotted material gain coefficients, g_i , obtained from both TA and VSL measurements. The one extracted from TA measurements are shown as blue data points and red data points are extrapolated from VSL measurement results with the help of Γ and the

volume fraction of CQWs in the film. While in VSL, we were able to measure material gain coefficients with pump fluences up to $3,500 \mu\text{J}/\text{cm}^2$, in TA measurements we were only able to measure up to $35 \mu\text{J}/\text{cm}^2$. The internal reflection occurring at higher fluences prevented us from performing at high fluence in our TA system. However, when put together, one can easily follow the complementary results from both TA and VSL measurements and the continuing trend in g_i reaching record high levels of $140,000 \text{ cm}^{-1}$ with increasing pump fluence with the provided eye guiding curve.

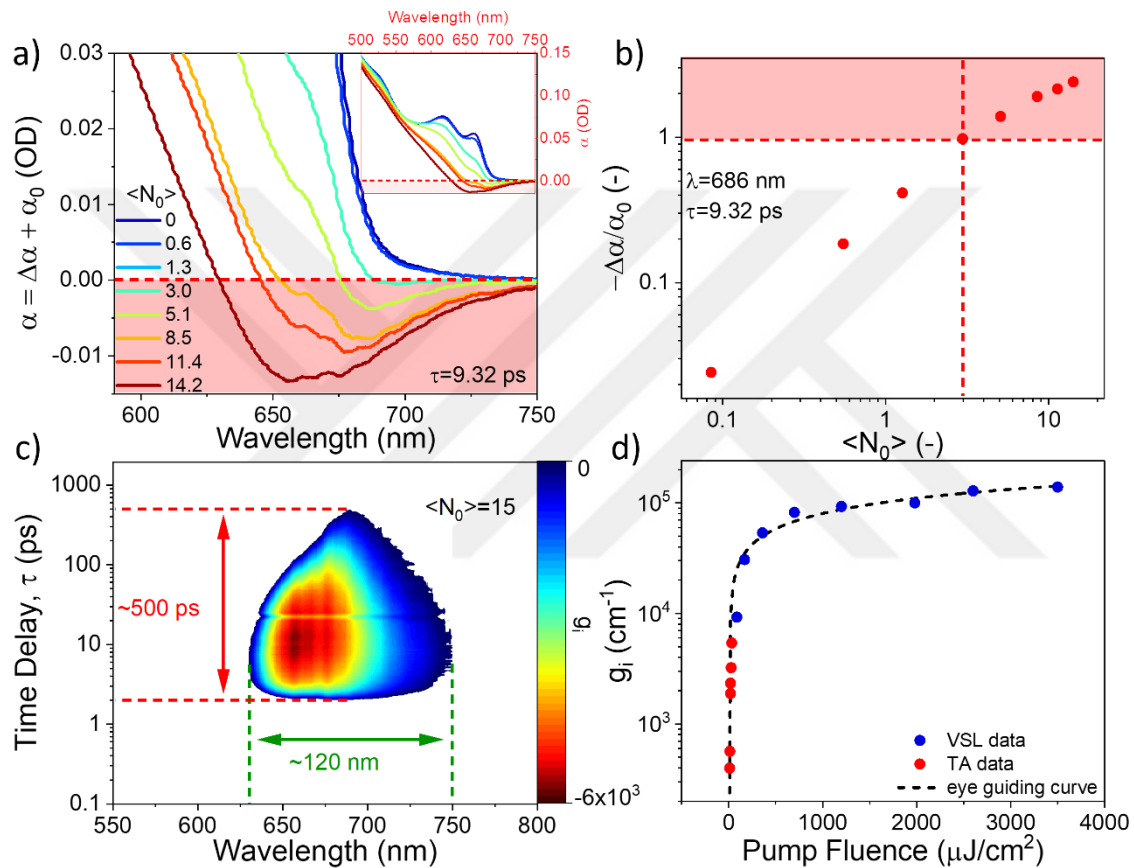


Figure 4.14. TA results of 13.5 ML core@shell CQWs as dispersion in toluene. a) Absorption bleaching of the CQW with the increasing pump fluence at the delay time, τ , of 9.3 ps. Dashed lines trace the blue-shift of the gain features. The inset depicts the same result in a broader range of the spectrum. b) $-\Delta\alpha/\alpha_0$ values at the wavelength, λ , of 686 nm and delay time, τ , 9.32 ps as a function of the exciton occupancy, $\langle N_0 \rangle$, where the $-\Delta\alpha/\alpha_0$ value of 1 corresponds to the gain threshold occupancy. c) 2D-time-wavelength map of material gain g_i of 13.5 ML core@shell CQWs for $\langle N_0 \rangle = 3$ where only $g_i > 0$ is shown indicating gain region. d) Material gain coefficients of 7.5-ML-CdSe@3-ML-CdS CQWs determined by TA measurements (red dots) and VSL measurements (blue dots) as a function of the pump fluence. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

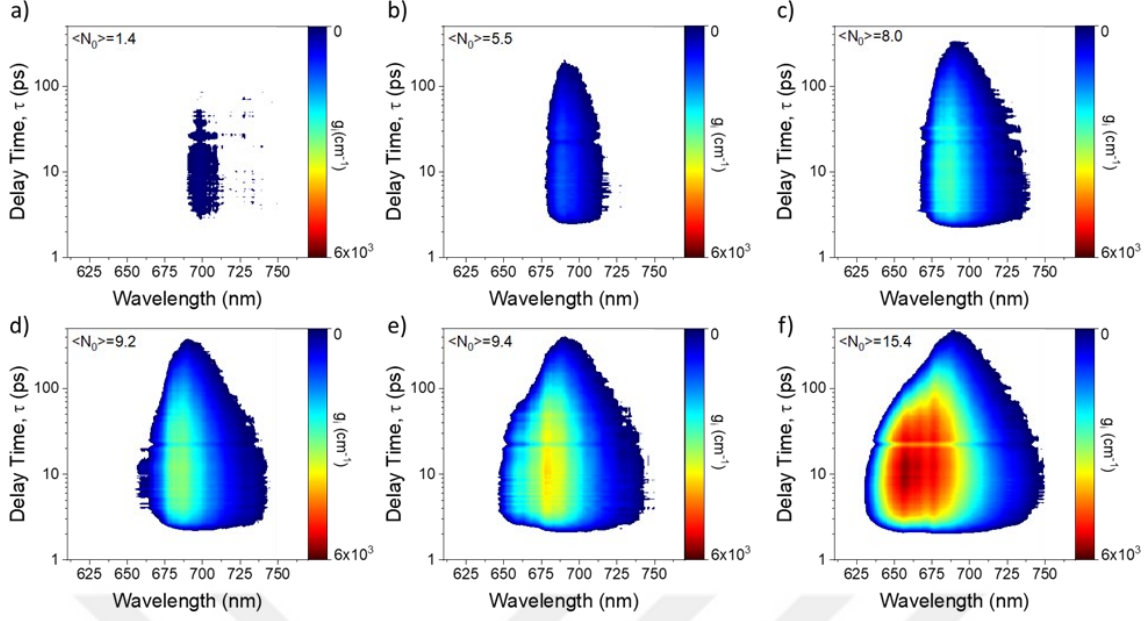


Figure 4.15. 2D-time-wavelength map of material gain g_i of 13.5 ML C@S CQWs for increasing $\langle N_0 \rangle$ values where only $g_i > 0$ is shown indicating gain region. a) $\langle N_0 \rangle = 1.4$, b) $\langle N_0 \rangle = 5.5$, c) $\langle N_0 \rangle = 8.0$, d) $\langle N_0 \rangle = 9.2$, e) $\langle N_0 \rangle = 9.4$, and f) $\langle N_0 \rangle = 15.4$. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

As a proof-of-concept demonstration, we incorporated 13.5 ML core@shell CQWs as the gain medium on the walls of a fiber having diameter of 125 μm to obtain a whispering gallery mode (WGM) assisted laser. This laser was produced simply by dipping the bare fiber, without any surface modification, to a highly concentrated solution of the CQWs in hexane. This resulted in the deposition of CQW film around the fiber thanks to the adhesion of CQWs on the fiber surface. The emission spectrum at various pump fluences shown in Figure 4.16a displays a multimode-lasing. However, close to the threshold, we observe a single-mode lasing with a FWHM of 0.9 nm at the wavelength of 676 nm as shown in the inset. This indicates that our WGM cavity has a Q-factor of ~ 750 . In Figure 4.16b, the output emission as a function of the pump fluence showcases a threshold pump fluence of 8 $\mu\text{J}/\text{cm}^2$. This is 4 times lower than the value obtained in a previous study of our group in which CQW heterostructure with 4.5 ML CdSe core having a laterally grown CdS crown and gradually alloyed 4 ML thick CdZnS shell were employed as gain medium [64], and the same level with the best performing WGM-CQW laser with having cavities with high Q-factor [133]. In Figure 4.16c, a multimode lasing emission from the WGM-assisted laser with a fine resolution of modes having a mode separation, $\Delta\lambda$, of ~ 1.1 nm is depicted (The mode numbers of the lasing peaks are given in Figure 4.17). Implementing the relation of $\Delta\lambda = \lambda^2/n_{\text{eff}}\pi D$, we have estimated the effective refractive index, n_{eff} , as 1.13 where the diameter of the fiber, D , is 120 μm and λ is the emission wavelength. The inconsistency of n_{eff} in this study with the reported refractive index of similar

CQW structures with $n \approx 1.80$ is due to the poor, patchy film formed on the fiber so that the electric field easily leaks to CQW-air and CQW-silica interphase [83]. The SEM image of the CQW-WGM laser depicting its diameter and the film quality is presented in Figure 4.18.

Next, we have studied the polarization of our laser emission by placing a linear polarizer with adjustable angle between the CQW-WGM laser and the spectrometer so that we can obtain the laser emission intensity as a function of the polarizer angle. As seen in Figure 4.16d we have well matched polarization data with the fitting of $\cos^2$ with a factor of the polarization [134], R , near unity indicating highly linearly polarized emission. In addition, we performed the stability test on our WGM assisted laser, the results of which are shown in Figure 4.16e. The intensity of emission was measured under pump (9×10^6 laser shots under 1 kHz repetition rate) fluence of several times higher than the threshold with time intervals of 15 min. Our CQW-WGM laser shows no trace of depletion in intensity even after 4 h of excitation, which makes our device one of the most stable colloidal lasers [6, 135]. The rise of intensity within the first 2 h can be attributed to annealing effect reported in previous studies [83, 136]. With a well-defined laser spot, the coherent laser emission of this WGM resonator with 13.5 ML core@shell CQWs is pictured in Figure 4.16f.

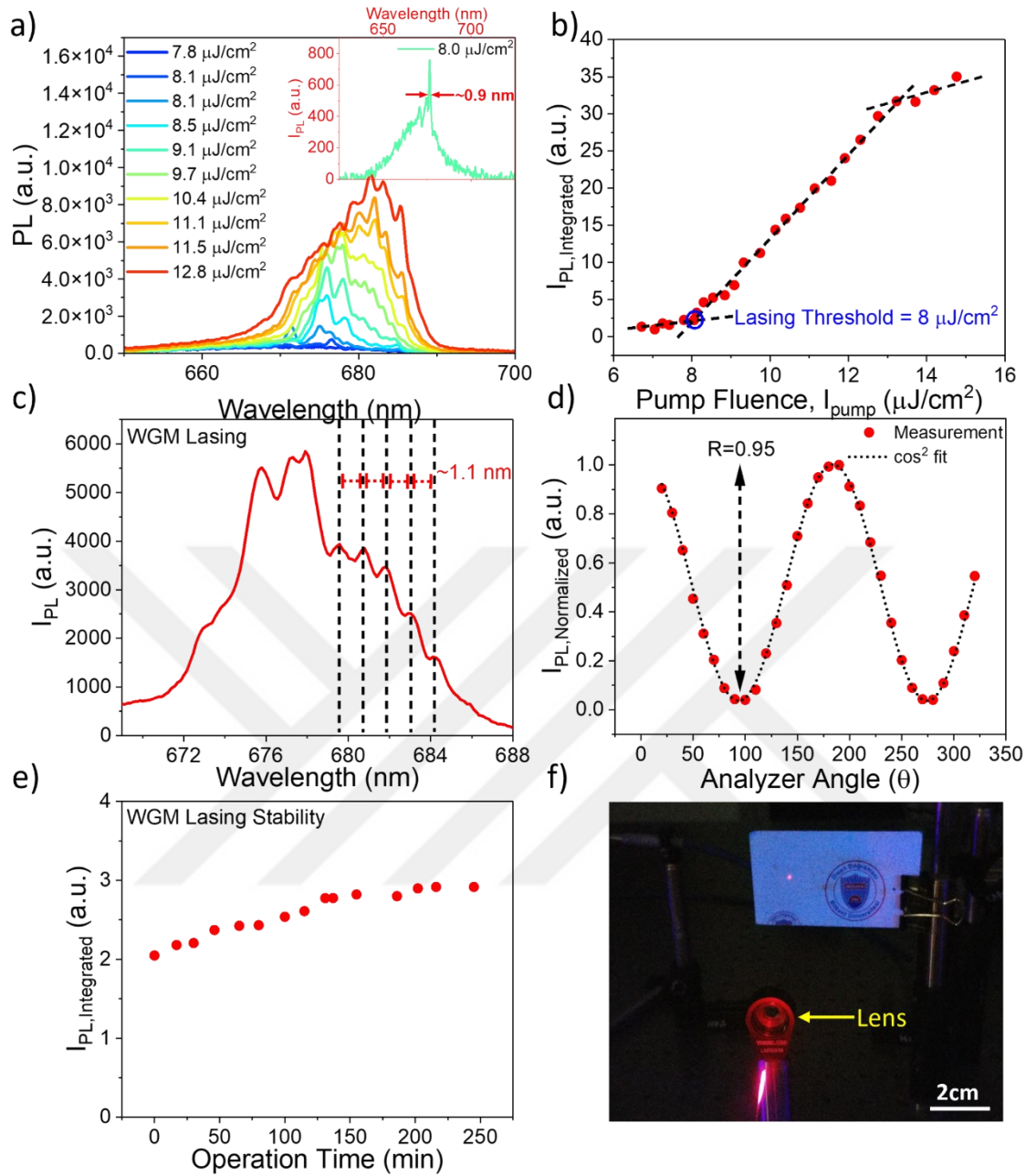


Figure 4.16. WGM assisted-CQW lasing performance of 13.5 ML core@shell CQWs. a) Pump-dependent WGM assisted lasing spectra of CQWs as a function of the pump fluence. The inset shows the lasing spectra at the threshold pump fluence with a FWHM of 0.9 nm. b) Integrated PL intensity of the lasing spectra with a S-shape behavior with increasing pump fluence. c) Lasing spectra with a mode separation of 1.1 nm. d) The normalized integrated lasing intensity of WGM assisted-CQW laser as a function of the polarizer angle, (θ), where the dashed curve is the $\cos^2(\theta)$ fit. e) Pump-dependent integrated lasing intensity under continuous excitation multiple times above the threshold value which shows no decrease even after 4 h operation duration. f) Image of WGM assisted-CQW laser emission depicting a well-defined lasing spot on the screen. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

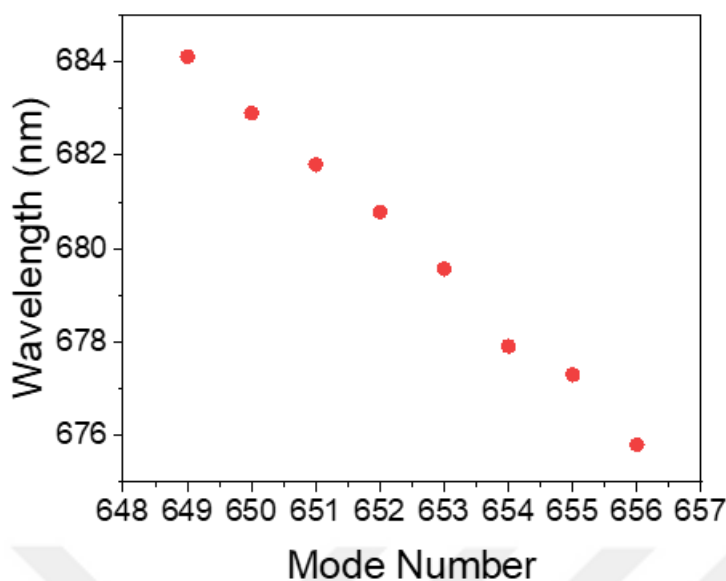


Figure 4.17. Mode numbers of WGM assisted lasing from 13.5 ML CdSe@CdS CQWs. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

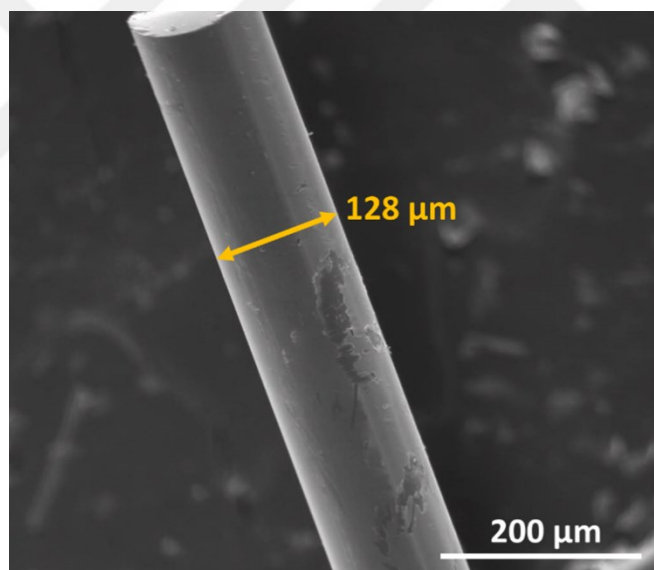


Figure 4.18. SEM image of CQW-WGM laser depicting irregularities and patchy film formation in the CQW film around the coreless fiber. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

Finally, we utilized these CQWs as a gain material dispersed in water to observe ASE in solution. In such applications the large gain coefficient is essential to achieve gain since the concentration of the emitters is lower than that in film by all accounts [74]. To achieve that, we first performed a ligand exchange protocol following a previous report so that we can disperse them in water [82]. Then we filled a capillary glass tube having an inner diameter of 250 μm with a concentrated CQW dispersion exploiting the cohesive forces. The ASE measurement of

the CQWs in water was performed with the same aforementioned femtosecond laser setup and pump-dependent ASE spectra of our CQW dispersion are shown in Figure 4.19a. An emerging narrow peak around the wavelength of 675 nm with a FWHM of 7 nm was observed as the pump fluence increases which is attributed to the ASE. The blue shift in the ASE of the dispersion compared to the ASE peak from the film is due to the possible surface etching of CQWs during the ligand exchange process [82]. In Figure 4.19b, integrated emission intensity as a function of the pump fluence is presented. The super-linear increase in the emission intensity after the threshold pump fluence of $480 \mu\text{J}/\text{cm}^2$ is another sign of the ASE. This is significantly lower than previously reported in-solution ASE thresholds from CQDs but higher than the ones of CQWs as dispersions in toluene. This higher threshold in water dispersion can be attributed to the lower refractive index of water than that of toluene so that the confinement of optical field is weaker. This demonstration of optical gain from the water dispersion colloidal emitters is a significant step towards the development of optofluidic lasers as sensing and imaging tools to detect chemical or biological agents.

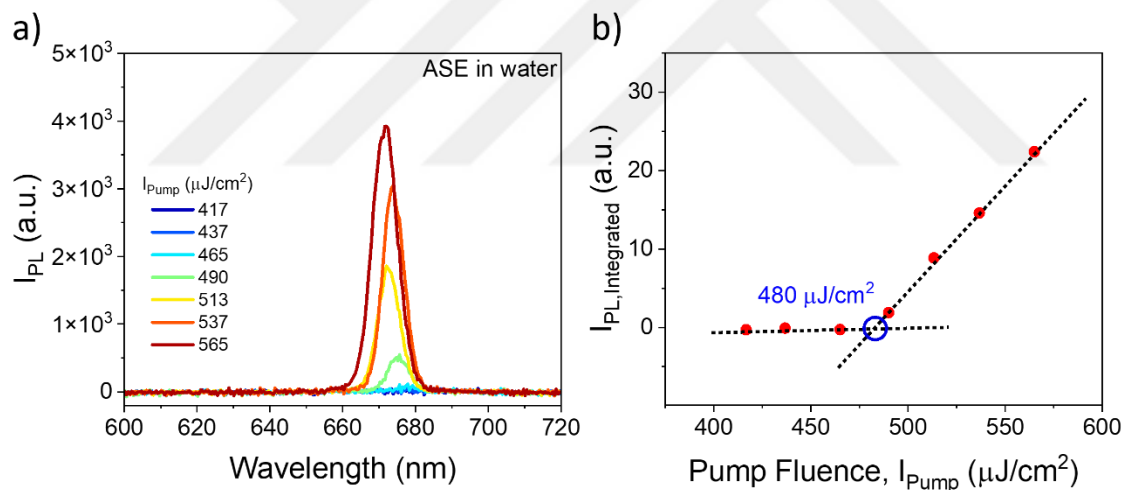


Figure 4.19. ASE of 13.5 ML core@shell CQWs as a water dispersion. a) Pump-dependent ASE spectra 13.5 ML core@shell CQW in water. b) Integrated PL intensity as a function of the pump fluence in water. Reprinted with permission from [98]. Copyright 2024 WILEY-VCH Verlag GmbH & Co.

As a follow-up study, we investigated the gain performance of the 13.5 ML CdSe@CdS in the solution phase under hard pump conditions. Here we probe the gain behavior with TA spectroscopy of these CQW heterostructures in hexane and ASE measurements in water. In Figure 4.20a, we present a 2D-time-wavelength map of the gain region of these 13.5 ML core@shell CQWs for $\langle N_0 \rangle = 110$ in terms of the material gain coefficient, g_i , where the condition of $g_i > 0$ defines the region. At such high exciton generation under hard pump

conditions, we observed two separate gain regions with their maxima at the wavelength of 686 and 645 nm, respectively. The gain region on the red side of the spectrum reaches a maximum gain level of $5,400 \text{ cm}^{-1}$ at the wavelength of 686 nm. The second gain region at higher energy shows a higher material gain coefficient of $9,000 \text{ cm}^{-1}$. The gain lifetime of the first gain region reaches the time interval of 100 ps, while the second one has a shorter gain life of 30 ps, as seen in Figure 4.20a. The first gain's spectral domain encompasses a broader range of 70 nm with respect to the second gain spanning 45 nm.

Figure 4.20b shows the absorption bleaching of core@shell CQWs with 13.5 ML thickness at the delay time of 9 ps. Any signal in the pale red area of Figure 4.20b indicates a net gain. Black dashed lines with these labels of HH and LH represent the heavy-hole and light-hole peak positions in the linear absorption spectrum, respectively. The separation between the HH and LH peaks is the same as the spectral distance between two gain regions, which indicates the contribution of the heavy hole and light hole energy levels to the optical gain.

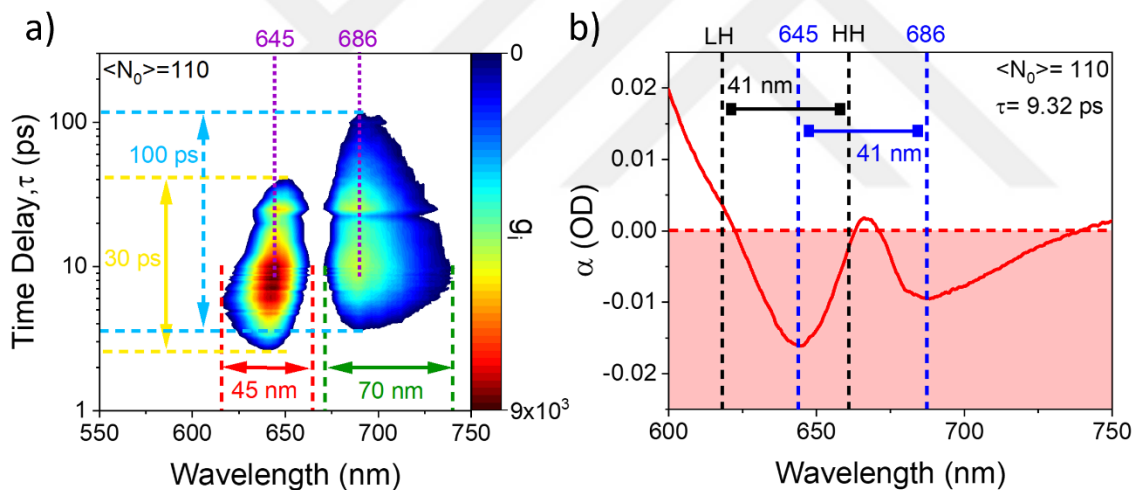


Figure 4.20. Transient absorption measurement results of 13.5 ML CQW heterostructures. a) 2D time-wavelength TA map depicting gain regions. b) Optical density (OD) values at a delay time of 9 ps. Black dashed lines labeled HH and LH are the heavy hole and light hole positions in the absorption spectrum, respectively.

When we performed ASE measurements on the films of the same sample, we observed ASE, which is indicated by the evolution of a narrow peak and superlinear increase in the integrated PL intensity with increasing pump fluence, as depicted in Figure 4.5a and its inset. As shown in Figure 4.5c, when we increased the pump fluence up until $2000 \mu\text{J}/\text{cm}^2$, we did not observe any significant change. As the pump fluence increases, ASE peak red-shifts primarily due to heating under pump conditions, and it broadens more towards the high energy side due to the contribution of higher energy states to the gain. Such behavior of observing two separate gain

regions in TA spectroscopy was previously reported on 4.5 ML thick CdSe CQWs [87]. However, in that report, the ASE spectra lacked a secondary gain peak.

Having two gain regions in the TA spectrum motivated us to mimic similar conditions for ASE measurements to observe two spectrally separate light amplifications. Since the high optical gain capability of the “giant” CQWs in this study enables strong gain in an aqueous environment with great stability, we studied the ASE behavior of aqueous CQW dispersions under high pump fluences.

As shown in Figure 4.21a and b, after a certain threshold pump fluence of $490 \mu\text{J}/\text{cm}^2$, a narrow peak occurs around 675 nm, which follows a super-linear increase in integrated PL intensity, indicating ASE. When we further increased the pump fluence and reached $630 \mu\text{J}/\text{cm}^2$, we observed an evolution of the second ASE peak at 645 nm. Observation of the second gain both in TA and ASE measurements performed on the dispersion samples and not in the films indicates the existence of a depletion mechanism for the carriers, which depends on the packing density of the emitters. When the CQWs have a relatively larger distance between them, the large number of hot carriers under high pump intensities cannot cool down to the band edge since these states are already occupied; hence, they show gain from higher energy states. However, there seems to exist a channel to deplete the excitons faster when the CQWs are in a densely packed film form so that we can only observe gain in one region.

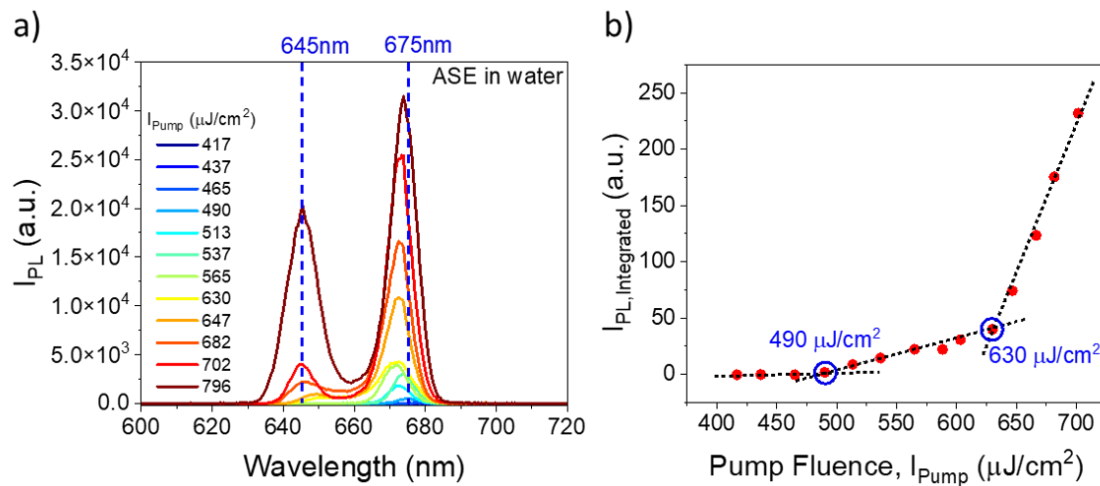


Figure 4.21. ASE measurements on CQWs in water dispersion under hard optical pumping. a) Pump-dependent ASE spectra of 13.5 ML CQW heterostructures in water. b) Integrated PL intensity as a function of the pump fluence.

4.4 Summary

This thesis work presents a systematical optical gain study of “giant” CQW heterostructures with tuned shell thickness exhibiting record high material gain coefficients reaching $140,000\text{ cm}^{-1}$ with large gain cross-sections. The high gain performance of these materials was mainly attributed to the suppressed Auger recombination processes and the high number of states per energy in this system owing to the large volume of the CQWs so that higher energy states could contribute to the optical gain. The role of higher states on the optical gain was deduced from the ASE and TA measurements. Exploiting the high gain coefficient of these materials, their use in a simple WGM-based laser resulted in a lasing threshold of $8\text{ }\mu\text{J}/\text{cm}^2$. Additionally, no sign of depletion observed in the laser emission indicates that the stability issues of colloidal laser devices are well addressed to the observed point of operation. Finally, we demonstrated ASE from these colloidal emitters in water as a proof-of-concept application utilizing their high gain coefficients. Moreover, we showed that the packing density of CQWs in the gain matrix affects the optical gain pathways. Observation of two gain regions in TA measurements and ASE measurements on CQW dispersions and not on the films indicates that the excitons recombine and deplete slower so that a higher energy state can contribute to the gain. Heat dissipation might also be another critical aspect affecting the carrier dynamics, where one would expect better cooling in dispersion. Surely, there is still room for improvement of these heterostructures by employing a soft potential barrier by growing gradient alloyed shells which would further suppress Auger recombination to obtain further lower thresholds and higher gain levels. These materials with extremely large modal gain coefficients may facilitate gain under continuous-wave excitation or even they can be possibly implemented in electrically-driven colloidal lasers.

Chapter 5

Engineering of Shell Composition for Optical Gain of Giant CQWs

5.1 Motivation

Implementation of CQW heterostructures in optical gain and lasing applications is an exciting avenue for the development of next-generation photonic devices. Optical gain is typically characterized by material parameters including gain threshold, gain coefficient and gain lifetime. Achieving low-threshold optical gain and high modal gain coefficients in CQWs is essential for the development of efficient and practical lasers. This has led to extensive research on the design and synthesis of CQWs with engineered structures and compositions with promising results in terms of gain threshold [6], coefficient [98] and lifetime values [64]. The synthesis of core@shell heterostructures of CQWs with carefully engineered architecture and composition is an effective approach to improve the optical gain performance of CQWs. The shell material and thickness play critical roles in determining the confinement of charge carriers, passivation of defect sites, suppression of nonradiative Auger recombination and other loss channels, and overall stability of the CQWs.

In this thesis, we systematically investigated the optical gain performances of core@shell CQW heterostructures with different shell compositions and thicknesses. Specifically, we focused on 7.5 ML thick CdSe CQWs coated with CdS, ZnS, and CdZnS gradient alloyed shells of varying thicknesses. By employing colloidal atomic layer deposition (c-ALD) [58], we achieve precise control over the shell thickness and composition, allowing us to systematically study their effects on the optical gain properties.

Our results demonstrate that the shell composition and thickness have profound impacts on the optical gain performance of CQWs. For instance, the introduction of a CdZnS gradient alloyed shell with a gradual increase in Zn content effectively reduces nonradiative Auger recombination rates and improves optical gain. This study also highlights the optimization in the shell thickness, where thinner shells suffer in suppressing Auger recombination, while too thick shells introduce additional defect sites and strain, which can adversely affect the gain threshold. By systematically varying the shell thickness, we aim to identify the optimal shell dimensions that maximize optical gain while maintaining the structural integrity of the CQWs.

The findings presented in this thesis provide valuable insights into the design principles for optimizing the optical gain properties of CQWs. The ability to achieve low-threshold optical gain and high modal gain coefficients in CQW heterostructures paves the way for their potential use in next-generation lasing applications. Furthermore, these results contribute to the broader understanding of the relationship between the structural parameters of CQWs and their optical performance, offering guidance for the development of colloidal photonic devices.

In conclusion, this study advances the field of CQW research by systematically elucidating the role of shell composition and thickness in enhancing the optical gain properties of core@shell CQWs. The insights gained from this work not only contribute to the fundamental understanding of CQW behavior but also open up new possibilities for their application in high-performance optoelectronic devices.

5.2 Colloidal Synthesis and Experiments

Synthesis of cadmium myristate: Cadmium myristate was synthesized following a previously reported method [106]. In separate bottles, 1.23 g of cadmium nitrate tetrahydrate and 3.13 g of sodium myristate were dissolved in 40 mL and 250 mL of methanol, respectively. After they were completely dissolved, the cadmium nitrate solution was added to the sodium myristate solution, and the mixture was stirred vigorously for 2 h using a magnetic stirrer. The resulting cadmium myristate, a white precipitate, was then filtered and washed several times with methanol to remove any unreacted species. Finally, the product was dried under vacuum overnight.

Preparation of growth solution: The growth solution for the synthesis of thicker CdSe nanoplatelets (NPLs) was prepared according to a previously reported method [42]. In a three-neck flask, 160 mg of cadmium oxide, 40 mg of cadmium chloride, and 20 mL of oleic acid were loaded and then degassed at 95 °C under vacuum with constant stirring for 30 min. The temperature was subsequently increased to 200 °C under nitrogen atmosphere, and the reaction continued for 15 min. The reaction mixture became a transparent or slightly yellow solution. The reaction was then quenched with a water bath, and the product was stored in vials.

Synthesis of 7.5 ML thick CdSe CQWs: The synthesis of 7.5 monolayer thick colloidal quantum wells was carried out according to a previously reported method with slight modifications [42]. In a three-neck flask, 170 mg of cadmium myristate, 25 mg of selenium

powder, 38 mg cadmium nitrate tetrahydrate, and 15 mL of octadecene were loaded and degassed at 95 °C under vacuum for 30 min. The temperature was then increased to 240 °C under nitrogen atmosphere. When the reaction mixture turned deep orange (around 195 °C), 100 mg of cadmium acetate dihydrate was added to the mixture. The formation and lateral growth of 4.5 ML thick CdSe CQWs were allowed to proceed for 25 min at 240 °C. The temperature was then raised to 310 °C, and 1 mL of the preheated growth solution (at 150 °C) was injected into the flask as the temperature reached 280 °C. The reaction proceeded for approximately 1 h to obtain primarily 7.5 ML thick CQWs, which was confirmed using absorbance spectra of aliquots taken from the mixture. At the end of the reaction, the heating mantle was removed, and the mixture was allowed to cool slowly. When the temperature dropped to 190 °C, 2 mL of oleic acid was injected, and the mixture was allowed to cool to room temperature. The product was collected, and 20 mL of hexane was added before centrifuging at 5,000 rpm for 6 min. The supernatant was discarded, and the precipitate was dispersed in 20 mL of hexane. The dispersion was centrifuged again under the same conditions, and the precipitate was discarded. Finally, 20 mL of ethanol was added to the supernatant and centrifuged again under the same conditions; the supernatant was discarded, and the precipitate was re-dispersed in hexane and stored.

Synthesis of CdSe@CdS core@shell CQWs by c-ALD method: To synthesize core@shell heterostructures, we modified a previously reported colloidal atomic layer deposition method [58]. The 7.5 ML CdSe CQWs were repeatedly washed with ethanol and methanol to eliminate any unreacted cadmium species. They were then re-dispersed in 1 mL of hexane and added to 3 mL of N-methyl formamide (NMF). Next, 40 μ L of ammonium sulfide (48-50% wt) solution was added, and the mixture was vigorously shaken for 8 min. Then, 1 mL of acetone and 30 mL of toluene were added to stop the reaction, and the product was precipitated by centrifugation at 6,000 rpm for 3 min. The precipitate was re-dispersed in 3 mL of NMF, and this washing process was repeated three times. The product is re-dispersed in 3 mL of NMF. Following the sulfur layer coating, we added 2 mL of 0.4 M cation salt solution in NMF and mixed it for 45 min. In the case of CdS and ZnS shell synthesis, the cation salts were cadmium nitrate hexahydrate and zinc nitrate tetrahydrate, respectively. For the gradient alloyed shell synthesis molar ratio of cadmium nitrate hexahydrate and zinc nitrate tetrahydrate were changed at each layer. The molar ratios of cadmium to zinc were as follows: 50:50 for the 1st layer, 10:90 for the 2nd layer, 5:95 for the 3rd layer, 1:99 for the 4th layer, and 0.1:99.9 for the 5th layer. The product was then precipitated and washed using the same cleaning procedure.

This cycle of adding sulfur and cadmium layers was repeated until the desired shell thickness in terms of the targeted number of monolayers was achieved. Finally, to cap the nanocrystals with long hydrocarbon chain ligands, the product was precipitated, the supernatant discarded, and 5 mL of hexane and 100 μ L of oleylamine were added to the precipitate. The mixture was sonicated and stirred overnight. To remove excess ligands, the mixture was precipitated with ethanol (25% of the total volume) and then dispersed in hexane.

Inductively coupled plasma mass spectroscopy (ICP-MS) measurement: We determined the concentration of CQWs using ICP-MS in addition to absorption spectroscopy and TEM imaging. First, we digested a known amount of CQWs, in terms of absorbance value, in nitric acid overnight at 80 °C. The solution was then diluted with deionized water to achieve a final acid concentration of 2% by volume. The ICP-MS measurement was carried out with Agilent 725 ICP-MS system.

Calculation of σ and μ_i : For the calculation of the absorption cross-section of CQWs, we implemented the following equation:

$$\sigma(\lambda) = 2.303 \times A(\lambda) / (C_{\text{CQW}} \times N_A \times L) \quad (5.1)$$

where $A(\lambda)$ is the absorbance value at a specific wavelength, C_{CQW} is the concentration [mol/cm³] of CQWs, N_A is the Avogadro's number [1/mol], and L is the optical path length [cm] of the cuvette, which is 1 cm.

We have calculated the concentration of CQWs following the previously reported procedure [98].

The intrinsic absorption coefficient is given by the equation:

$$\mu_i(\lambda) = \sigma(\lambda) / V \quad (5.2)$$

where V is the volume of single CQW in units of cm³.

5.3 Results and Discussion

We investigated the optical gain performance of our core@shell CQWs by systematically varying shell thicknesses and compositions. Our study focused on how these synthesis parameters influence the optical gain coefficient and threshold, two critical benchmarks that

determine the suitability of these materials for lasing applications. In our previous study [98], we have demonstrated that the thickness of the core in the CQW heterostructures plays a crucial role in achieving high optical gain coefficients owing to their high number of states contributing to the gain. Building on this finding, we first synthesized 7.5 ML thick CQWs as our core material, introducing nitrate, NO_3^- , ions using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ into the previously reported recipe [42]. This process yields a mixture of CQWs with the thicknesses of 6.5, 7.5, and 8.5 ML, which cannot be separated by selective precipitation due to their similar lateral sizes. Given the abundance in the amount of the 7.5 ML CQWs in the mixture, which is deduced from the relative intensities of the absorption peaks of each species as seen in Figure 5.1b, we refer to them as 7.5 ML CdSe CQWs. Scanning electron microscope (SEM) images of the synthesized 7.5 ML thick CdSe CQWs, which have average lateral dimensions of $13 \pm 2 \text{ nm} \times 24 \pm 6 \text{ nm}$, is presented in Figure 5.1a.

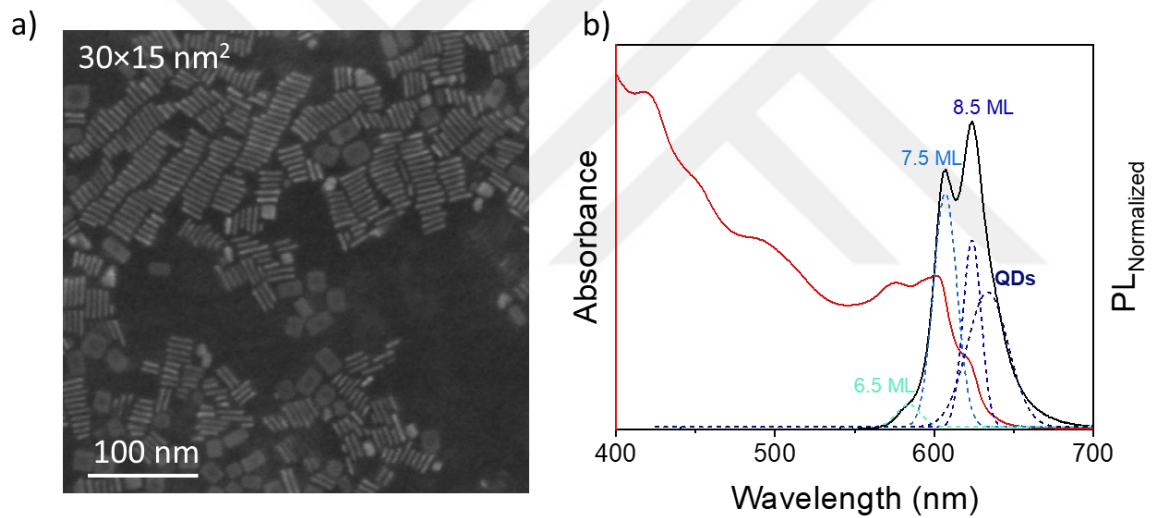


Figure 5.1. Structural and optical characterizations of 7.5-ML CdSe core CQWs: a) SEM image of 7.5-ML CdSe core CQW and b) absorption (red) and PL (black) spectra of 7.5 ML CdSe CQWs.

Then we coated core CQWs with CdS, ZnS, and CdZnS gradient alloyed shells with various thicknesses via colloidal atomic layer deposition to achieve precision in thickness and composition to systematically study the effect of both parameters on gain performances of the CQWs. Figure 5.2a shows the transmission electron microscopy (TEM) images of 7.5-ML-CdSe@3-ML-CdZnS as a representative sample having an average lateral area of $310 \pm 85 \text{ nm}^2$. Even though the PL of the core consists of multiple peaks belonging to 6.5, 7.5, and 8.5 ML thick CQWs (as seen in Figure 5.1b), the core@shell particles exhibit single photoluminescence (PL) peak with the growth of the shell layers, due to the reduction in

confinement energy [77]. Moreover, the broadening of the PL peaks with the growth of the shell contributes to the occurrence of the single peak PL. The growth of the shell inevitably causes the formation of defect sites, either due to lattice mismatch between the layers or disordered or missing atoms in the shell crystal. Especially core@shell heterostructures synthesized by the c-ALD method, which relies on room temperature reactions not allowing atoms to achieve thermodynamically stable positioning, are more prone to such defects. These defects enhance electron-phonon coupling, which results in the broadening of the PL peak [82, 110-111]. An additional cause of PL broadening in the core@shell heterostructured CQWs might be electron shakeup processes.

As depicted in Figure 5.2b, the red shift in the absorption and emission spectra with each additional shell layer is a clear indication of the relaxation in the confinement with the increase in the thickness of the shells. Additionally, the red shift of the spectra with each consecutive layer confirms successful shell growth. However, the amount of the shift among the samples with different shell compositions is not the same despite their same thickness. The shift in CQW heterostructures having shells richer in Zn content is slower due to the higher bandgap energy of ZnS. This induces a higher energy barrier in the shell, which confines the carrier wavefunctions more effectively. Figure 5.2c and d show the intrinsic absorption coefficients at 400 nm, $\mu_{i, 400 \text{ nm}}$, and the absorption cross-sections at the same wavelength, $\sigma_{400 \text{ nm}}$, of the CQW heterostructures having CdS, ZnS, and CdZnS gradient alloy shells with thicknesses ranging from 1 to 5 ML. The intrinsic absorption coefficient tends to decrease slightly with the increase in the shell thickness, mostly due to the decrease in oscillator strength. However, the introduction of Zn in the shell causes a relatively higher decrease. This might be caused by more separate energy levels of ZnS at high energy levels due to its large bandgap.

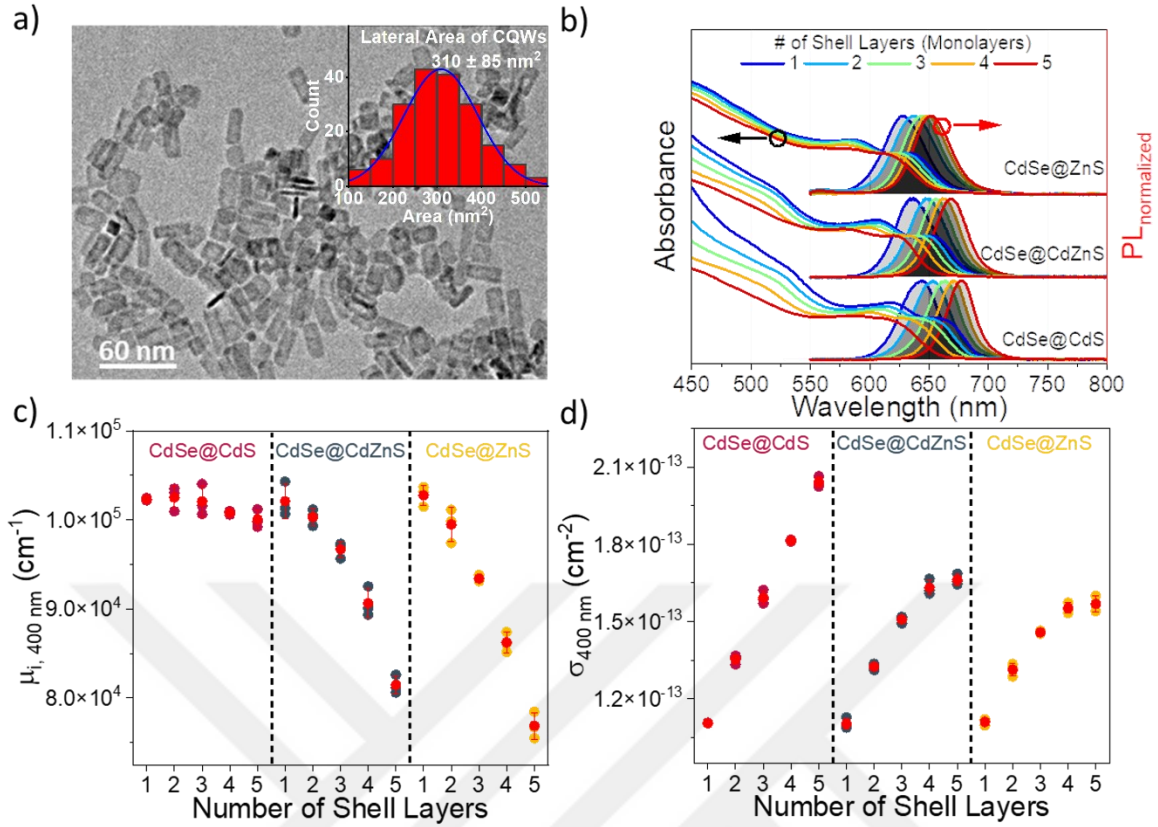


Figure 5.2. Optical characterizations of the core@shell CQW heterostructures. a) TEM images of 7.5-ML-CdSe@3-ML-CdZnS. The inset shows the histogram for the lateral area distribution of CQWs, b) Absorption and PL Spectra of the CQW heterostructures with 7.5 ML CdSe core and ZnS (top), CdZnS gradient alloyed (middle) and CdS (bottom) shell with thicknesses from 1 to 5 monolayers, c) intrinsic absorption coefficient values of the CQW heterostructures with 7.5 ML CdSe core and CdS (left), CdZnS gradient alloyed (middle) and CdS (right) shell with thicknesses from 1 to 5 monolayers, and d) absorption cross-section values of the CQW heterostructures with 7.5 ML CdSe core and CdS (left), CdZnS gradient alloyed (middle) and CdS (right) shell with thicknesses from 1 to 5 monolayers.

We performed amplified spontaneous emission measurements to study the optical gain threshold behavior of core@shell CQW heterostructure. The CQW films were prepared via spin coating technique to achieve uniform films with similar film thickness to bypass the effect of optical confinement factor, Γ , on the gain thresholds. We used absorbance spectra to adjust the thickness of the films, where the absorbance intensity is a function of the intrinsic absorption coefficient of the CQW, μ_i , packing density of the particles, and film thickness. Knowing the intrinsic absorption coefficients of the CQWs and assuming similar packing densities among the samples, we can estimate the relative intensity of the films to achieve similar film thicknesses. Figure 5.6a presents ASE measurement results of 7.5 ML CdSe@5 ML CdZnS heterostructured CQWs as a representative sample. The occurrence of the narrow peak at 710 nm after the pump fluence reaches $5.6 \mu\text{J}/\text{cm}^2$, which has a $\sim 17 \text{ nm}$ red-shift with

respect to the spontaneous emission peak at 693 nm. Additionally, at the same pump fluence level of $5.6 \mu\text{J}/\text{cm}^2$, which is the gain threshold pump fluence, I_{th} , the integrated PL intensity follows a super-linear increase (see inset of Figure 5.6a). Both of these indicators are clear signs for light amplification related to ASE.

The ASE measurement results of all the core@shell structures with the number of shell layers from 1 to 5 are presented in Figure 5.3, Figure 5.4 and Figure 5.5, which belong to CdSe@CdS, CdSe@CdZnS and CdSe@ZnS, respectively. The threshold pump fluence (I_{th}), regardless of the shell composition, decreases as the thickness of the shell increases as can be seen in Figure 5.6b. The fall in the threshold fluence follows a hyperbolic trend. This behavior of I_{th} is mainly the result of two counteracting effects: (i) the suppression of Auger recombination, which follows inverse proportionality to the thickness of the CQW of the particle to some degree [102, 137] and (ii) the introduction of additional defect sites with the increase of the numbers of shell layers. Regarding the role of the shell composition on the ASE threshold values, CQWs with ZnS shells have the highest threshold values. This is due to the larger lattice mismatch between CdSe and ZnS, which induces lattice strain at the interface. The strain-caused trap states result in higher Auger recombination rates and, hence, higher thresholds. The lattice strain between CdSe and CdS is lower but it does not show the lowest threshold among the samples. This is due to the relatively low energy barrier of CdS, which allows carrier wavefunctions, especially electron wavefunction, to leak to the surface trap sites to some extent. Having a CdZnS alloyed shell with gradually increasing Zn content with shell thickness reduces the lattice mismatch and confines the carrier wavefunction better with a smooth energy barrier, resulting in decreased Auger recombination and lower ASE thresholds.

Figure 5.6c shows VSL measurement resulting in the highest modal gain coefficients, g_{mod} , of each CQW heterostructure with 3 ML of a shell with different compositions. The obtained modal gain coefficients followed a similar trend of ASE thresholds as a function of the shell composition, having the highest level of $26,000 \text{ cm}^{-1}$ from CQWs with CdZnS gradient alloyed shell, which was followed by the ones having CdS shell ($26,000 \text{ cm}^{-1}$) and ZnS shell ($9,000 \text{ cm}^{-1}$). The similarity in the trend between ASE thresholds and g_{mod} as a function of the shell thickness signifies the role of nonradiative Auger processes in these values, where the smooth confinement barrier of CdZnS gradient alloyed shell suppresses Auger due to the reasons mentioned above.

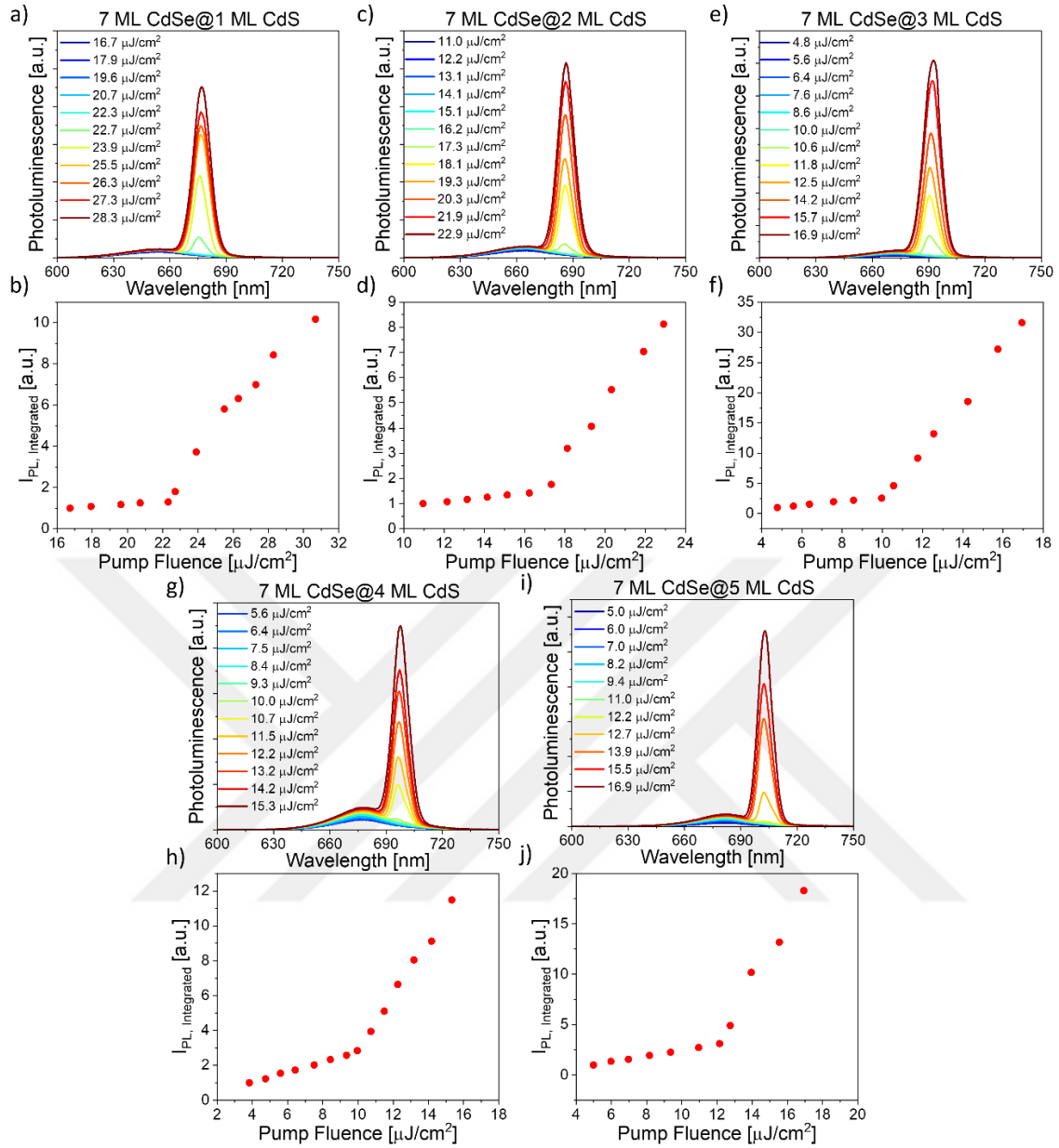


Figure 5.3. ASE measurement results of CdSe@CdS CQWs. PL spectra at increasing pump fluences and related integrated PL values as a function of the pump fluence of CdSe@CdS core@shell CQWs with a, b) 1 ML; c, d) 2 ML; e, f) 3 ML g; h) 4 ML; and i, j) 5 ML shell thicknesses, respectively.

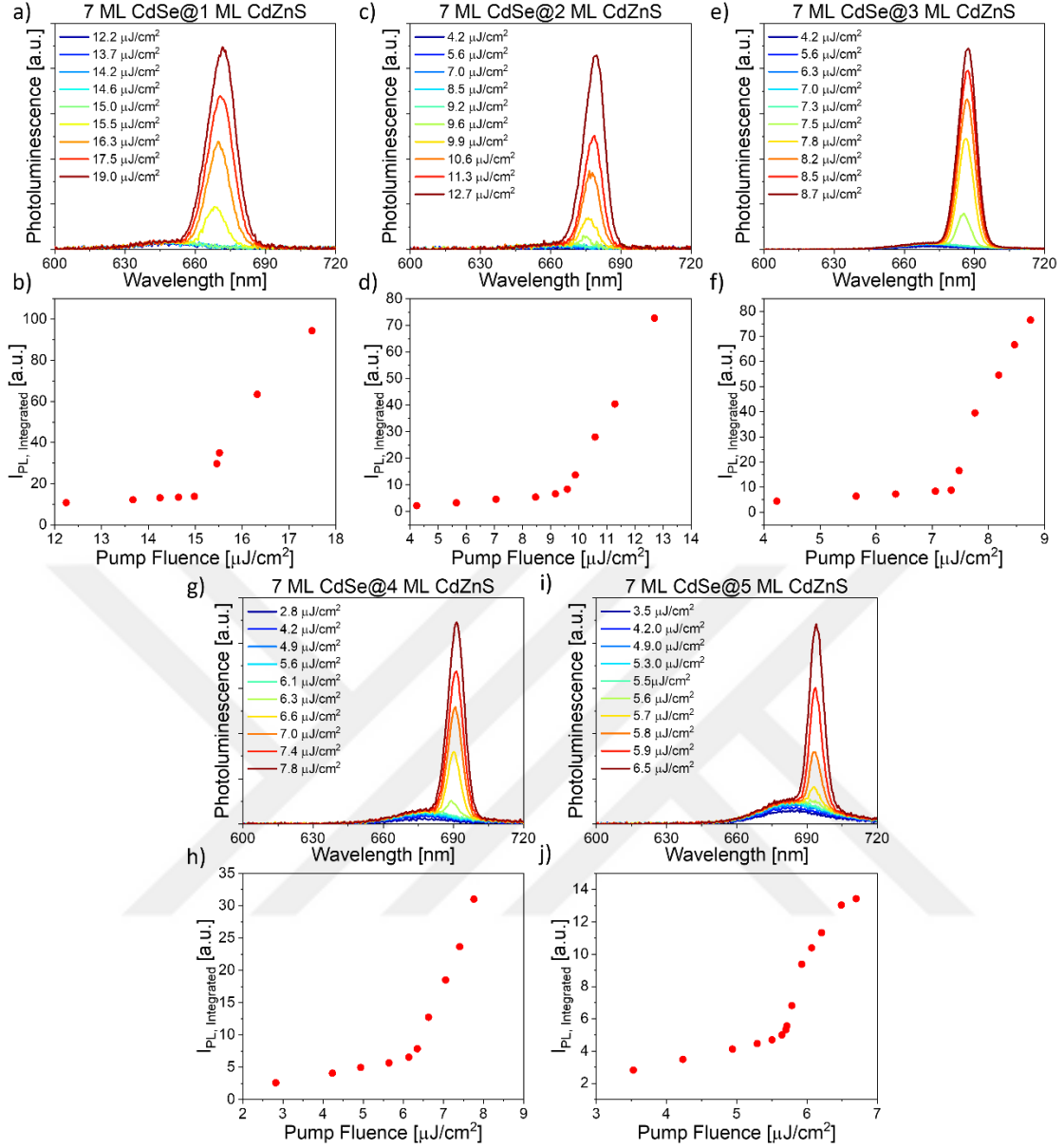


Figure 5.4. ASE measurement results of CdSe@CdZnS CQWs. PL spectra at increasing pump fluences and related integrated PL values as a function of the pump fluence of CdSe@CdS core@shell CQWs with a, b) 1 ML; c, d) 2 ML; e, f) 3 ML g; h) 4 ML; and i, j) 5 ML shell thicknesses, respectively.

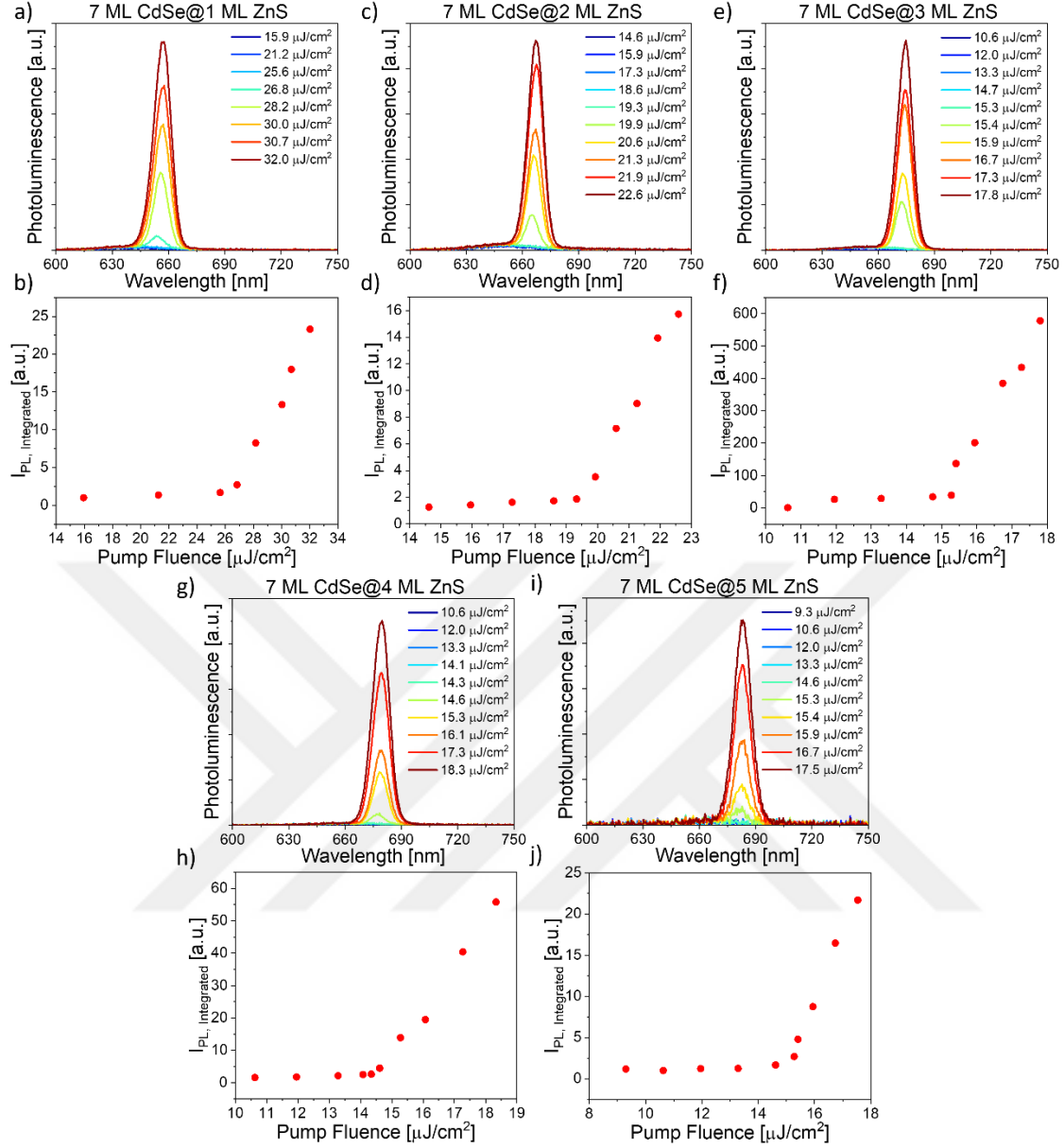


Figure 5.5. ASE measurement results of CdSe@ZnS CQWs. PL spectra at increasing pump fluences and related integrated PL values as a function of the pump fluence of CdSe@CdS core@shell CQWs with a, b) 1 ML; c, d) 2 ML; e, f) 3 ML g; h) 4 ML; and i, j) 5 ML shell thicknesses, respectively.

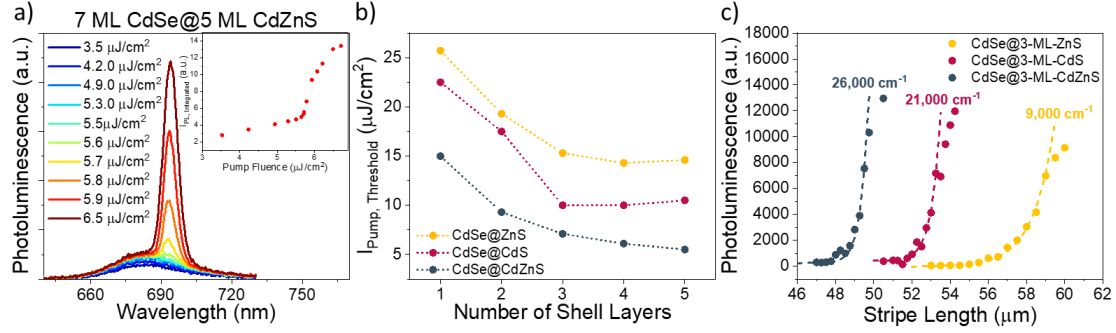


Figure 5.6. ASE results of core@shell CQW films. a) Pump-dependent ASE spectra of 7.5-ML-CdSe@5-ML-CdZnS core@shell CQWs along with the a) integrated PL intensity as a function of the pump fluence in the inset, b) ASE threshold values of CdSe@ZnS (light green), CdSe@CdS (green) and CdSe@CdZnS (blue) core@shell CWQs with increasing shell thickness, c) VSL measurement results of CQW heterostructures with 3 ML shell with a composition of CdZnS (most left curve), CdS (middle curve) and ZnS (most right curve).

5.4 Summary

In this thesis work, we synthesized II-VI heterostructured colloidal quantum well heterostructures with different shell composition and thickness via colloidal atomic layer deposition to achieve high material gain with low amplified spontaneous emission thresholds to obtain superior materials for lasing applications. To achieve such properties, we have first synthesized thicker CdSe cores with a low aspect ratio for the CQW heterostructure, which is the core material. Thick cores are a crucial design element for achieving high gain coefficients since the thickness of the CdSe increases the available energy states to excite increase, and hence, high material and modal gain coefficients are attained. Then, we coated core CQWs with CdS, ZnS, and CdZnS shells using the c-ALD method. We implemented the c-ALD method to grow the shell to accomplish excellent well control over the thickness and elemental composition at each layer independently.

The conducted work presents a systematical study of ASE and VSL performances of core@shell CQW heterostructures with various shell compositions and thicknesses where the lowest threshold is achieved with 7.5-ML-CdSe@5-ML-CdZnS core@gradient-alloyed-shell CQWs and the highest modal gain coefficient is achieved by the CQW heterostructures with CdZnS gradient alloyed shell. This result is attributed to the suppression of nonradiative Auger recombination owing to the volume scaling law and smooth energy barrier, which was obtained by the gradual increase of the Zn amount in the shell. Previously we have reported record high gain coefficients from CdSe@CdS core@shell CQW heterostructures using thick cores [98]. These CQWs with gradient alloyed shells, with their lower gain thresholds compared to the

values in the mentioned previous work and high gain coefficients, may enable gain under continuous-wave excitation and could potentially be used in electrically driven colloidal lasers.



Chapter 6

Cubic Quantum Shells

6.1 Motivation

Weakly confined colloidal semiconductor nanocrystals are a new class of materials that draw attention owing to their unique photophysical properties [138]. Relatively large-sized semiconductor nanocrystals, a.k.a. giant quantum dots, have been already studied in detail, especially for the prospect of their optical gain and lasing applications [139]. The nonradiative Auger recombination process, which is the bottleneck for optical gain in confined systems, follows an inverse relationship with the volume of the particle. This relationship is coined as the universal volume scaling law [140]. This was the motivation for studies on the giant QDs. However, the optical gain in these structures still mainly followed a similar biexcitonic gain mechanism as in confined systems, still suffering from the Auger recombination process being the fastest component of nonradiative loss [104].

Heterostructured colloidal quantum wells, so-called nanoplatelets, on the other hand, demonstrated superior optical gain performances in terms of optical gain thresholds [6], material gain coefficients [98], and gain lifetimes [64], which are three main parameters to quantify the optical gain performance of an active gain material. Still, the gain mechanism of these structures is under debate if it follows a similar biexcitonic gain mechanism [130] and/or excitonic molecules contribute [127] to the gain and/or it is non-excitonic [87]. Even it is unclear if the long gain lifetime is limited by the Auger recombination or by a radiative process [141].

Another class of colloidal semiconductors are quantum shells, which are quantum wells in terms of mode of quantum confinement [142]. The difference between these quantum shells and nanoplatelets is that quantum shells are close-looped and do not have edge sites, which are considered to be the most irregular sites hosting trap sites. It has been recently shown that slow recombination of multicarrier species in these structures is observed, and they were, hence, great candidates for scintillation and lasing applications. The gain lifetime of these materials is shown to be a record-high 6 ns, which is outpacing competing planar platelet-in-box systems [141].

One of the main motivations of this work is to synthesize cubic quantum shells which do not suffer from the variation of facets throughout the structure, which is unavoidable in spherical systems. The variation in facet geometry induces differences in the interface between the layers and this is generally a source of trap sites in colloidal semiconductor nanocrystal heterostructures. Additionally, the corners of these cubes might have unique energy states that can be utilized in optical gain. Their large size reaching a weakly confined regime will help to obtain bulk-like gain where the Auger recombination process is a bottleneck. Moreover, cubic structures are more prone to form superstructures, which can demonstrate collective optical phenomena, as shown in cubic perovskite QDs [143]. Here, we have synthesized weakly confined cubic quantum shells with various shell thicknesses to systematically study the role of each segment on the photophysical properties and find the optimum structure for desired applications.

6.2 Colloidal Synthesis and Experiments

Preparation of Se-ODE precursor: The Se-ODE precursor with a selenium concentration of 0.03 M was prepared using a previously reported method [138]. First, 25 mL of 1-octadecene (ODE) was loaded into a three-neck flask and degassed under vacuum at 95 °C for 30 min. The temperature was then increased to 250 °C under nitrogen atmosphere. Upon reaching 250 °C, a mixture of 236.88 mg (3 mmol) selenium powder and 5 mL ODE was injected dropwise. After the selenium completely dissolved, the temperature was lowered to 200 °C and maintained for 4 h. At the end of the 4 h, the reaction was quenched with a water bath, and the final solution was diluted three times with ODE.

Preparation of S-ODE precursor: S-ODE precursor with 0.1 M sulfur concentration was synthesized using a previously established method [138]. 48.105 mg (11.5 mmol) sulfur was mixed with 15 mL of ODE and sonicated for 20 min.

Preparation of S precursor for CdS cubic core synthesis: This precursor was prepared according to a method reported earlier [138]. 5 mL of S-ODE precursor, 3.3 mL oleic acid, and 1.5 mL ODE were mixed in a vial.

Preparation of S precursor for CdS cubic shell synthesis: The preparation of S precursor for CdS cubic shell synthesis was carried out according to a previous method [138]. 5 mL of S-ODE, 477.67 μ L of oleic acid and 4.5 mL ODE were mixed in a vial.

Preparation of stearyl chloride solution: The stearyl chloride solution was prepared by following the previously reported method with slight modifications [138]. 506.55 μL (454.38 mg, 1.5 mmol) stearyl chloride was mixed with 15 mL ODE by sonication. The mixture was then diluted further with ODE so that the optical density of the mixture at 400 nm becomes 0.2.

Synthesis of spherical CdS seeds: The synthesis of CdS seeds was performed by following a previously reported synthesis protocol with slight modifications [138]. 1.6 mmol (424 mg) of cadmium acetate dihydrate, 4 mL of oleic acid, and 24 mL of ODE were loaded into a 100 mL three-neck flask and degassed at 95 °C under vacuum for 1 h. The reaction temperature was then increased to 230 °C under nitrogen atmosphere. At 230 °C, 1 mL of S-ODE precursor was swiftly injected. When the first excitonic peak in the absorption spectrum of the aliquots reached 434 nm, the heating mantle was removed. Once the temperature dropped to room temperature, the reaction mixture was divided into two centrifuge tubes, and 17.5 mL of acetone was added to each before centrifuging at 8,300 rpm for 6 min. The supernatant was discarded, and the precipitates were redispersed in 3 mL of toluene. Then, 12 mL of methanol was added to the mixtures. After centrifugation at 8,300 rpm for 5 min, the supernatants were discarded, and this washing step was repeated two more times. The precipitates were then redispersed in 1 mL of toluene, and 4 mL of methanol was added. These mixtures were heated to 80 °C, centrifuged at 8,000 rpm for 5 min, and the supernatants discarded. This washing step was also repeated twice more before redispersing the precipitates in 3 mL of ODE.

Synthesis of cubic CdS cores: For the synthesis of cubic CdS cores, a previously reported method with some modifications was followed [138]. 0.2 mmol (90 mg) of cadmium acetate dihydrate, 1.2 mmol (386.5 μL) of oleic acid, and 9 mL of ODE were loaded into a 50 mL three-neck flask and degassed at 95 °C under vacuum for 1 h. The temperature was then increased to 270 °C under nitrogen atmosphere. At 270 °C, 0.4 mL of stearyl chloride solution and 1 mL of 20.4 OD (at the first excitonic peak) spherical CdS seeds in ODE were swiftly injected into the reaction mixture, and 4 mL of S precursor for CdS cubic core synthesis was injected with a rate of 0.6 mL/h. At the end of 4 h, the PL peak reached 507.6 nm, and the heating mantle was removed. When the temperature fell to 80 °C, the reaction mixture was centrifuged at 4,000 rpm for 1 min, and the supernatant was discarded. To remove spherical particles, the precipitate was redispersed in 6 mL of toluene, the mixture was centrifuged at 4,000 rpm for 1 min, and the supernatant was discarded. This washing step was repeated two more times. The final precipitate was redispersed in 6 mL of toluene, heated to 80 °C, and

centrifuged at 4,000 rpm for 1 min. The supernatant was discarded, and this washing protocol was repeated two more times. Finally, to remove excess ligands and unreacted species, the precipitate was redispersed in 3 mL of toluene, and this mixture was mixed with an equal volume of methanol before heating to 80 °C and centrifuging at 4,000 rpm for 5 min. This step was performed three times in total. The final product was redispersed in ODE to be used as core material in subsequent syntheses.

Synthesis of cubic CdS@CdSe Core@Shell quantum dots: 85 mg of cadmium acetate dihydrate, 0.7 mmol (236.999 mg) of erucic acid, 0.7 mmol (120.582 mg) of capric acid, and 9 mL of ODE were loaded into a 25 mL three-neck flask and degassed at 90 °C for 30 min under vacuum. The reaction temperature was then increased to 270 °C under nitrogen atmosphere. At 270 °C, 750 μ L of stearoyl chloride solution and 1 mL of 15 OD (at 400 nm) cubic CdS core in ODE were swiftly injected. Following these injections, 3.6 mL (for thin CdSe), 9.6 mL (for mid CdSe), or 15 mL (for thick CdSe) of Se-ODE precursor was injected at a rate of 1.8 mL/h. At the end of the injection, the heating mantle was removed, and as the temperature fell to 80 °C, an equal volume of isopropanol was added to the reaction mixture, which was then centrifuged at 6,000 rpm for 3 min. The supernatant was discarded, and the precipitate was redispersed in 3 mL of toluene. 3 mL of methanol was then added to this dispersion, and the mixture was heated to 80 °C and centrifuged. The supernatant was discarded, and the same washing step was repeated two more times. Finally, the precipitate was redispersed in 1 mL of ODE.

Synthesis of cubic CdS@CdSe@CdS Core@Shell@Shell quantum dots: 85 mg of cadmium acetate dihydrate, 0.7 mmol (236.999 mg) of erucic acid, 0.7 mmol (120.582 mg) of capric acid, and 9 mL ODE were loaded into a 25 mL three-neck flask and degassed at 95 °C for 30 min under vacuum. Then, the reaction was set to 270 °C under nitrogen atmosphere. Once the temperature reaches this level, 750 μ L of stearoyl chloride solution and 1 mL of cubic CdS@CdSe core@shell quantum dots, which were dispersed in ODE, were swiftly injected into the flask. This was followed by the dropwise addition of S precursor for CdS cubic shell synthesis with a rate of 0.6 mL/h. The amount sulfur precursor required for the thin, middle and thick CdS shell was 0.2, 0.4 and 1.2 mL, respectively. At the end of injection, the heating mantle was removed and as the temperature fell to 80 °C, an equal amount of isopropanol in volume was added to the reaction mixture, which was then centrifuged at 6,000 rpm for 3 min. The supernatant was discarded and the precipitate was redispersed in 3 mL of toluene. 3 mL of

methanol was then added to this dispersion and then, this mixture was heated to 80 °C and centrifuged. The supernatant was discarded and the same washing step was repeated two more times.

6.3 Results and Discussion

To obtain weakly confined quantum shell heterostructures, we first synthesized spherical 3 nm sized CdS semiconductor nanocrystals using the previously reported recipe with slight modifications [138], the transmission electron microscopy images, and absorption/photoluminescence spectra of which are presented in Figure 6.1a and b. These spherical CdS seeds with an average diameter of 3 nm show very narrow emission around 450 nm with a narrow full-width-at-half-maximum (FWHM) of 18 nm. Additionally, the absorption spectrum has well-defined, narrow, and separated excitonic peaks, which infers very narrow size distribution.

Following this step, we continued to grow CdS around these seeds via a high-temperature seed-mediated growth reaction, which involves cadmium acetate dihydrate salt as a cation precursor, oleic acid as ligands, sulfur-octadecene-oleic acid mixture as a sulfur source and stearyl chloride-octadecene mixture to achieve a cubic shape. Chloride ions are known to promote the nanoparticles with well-defined facets and cubical shapes by modifying the surface energy of the nanocrystals with certain crystal structures [144-145]. The transmission electron microscopy image and absorption/photoluminescence spectra of cubic CdS nanocrystals are depicted in Figure 6.1b and c. The average size of these particles is 8 nm. Even though the size distribution is narrow, which can be easily inferred from narrow emission at 505 nm with an FWHM of 16 nm, the absorption spectrum has no defined features but just some shoulders.

To grow a CdSe shell around presynthesized cubic CdS quantum dots, we followed a similar approach of abovementioned seed-mediated growth, where cadmium acetate dihydrate was our cadmium source, the selenium-octadecene mixture was our anion source, stearyl chloride was presented to keep the cubic shape during the synthesis. Here, we used a mixture of erucic acid and octanoic acid as stabilizing ligands instead of using just oleic acid to be able to further grow these particles. To achieve a homogeneous growth in colloidal synthesis, it is mandatory to sustain well-dispersed nanoparticles in reaction conditions, which is provided by the presentation of ligands such as oleic acid and oleylamine as typical molecules to the reaction mixture. However, as the size of particles increases, it becomes challenging to maintain

colloidal stability with mainstream ligand systems. Hence, we used a mixture of ligands with various hydrocarbon chain lengths, referred to as entropic ligand mixtures [146-147], which stabilize particles in solutions by maximizing the intramolecular entropic effects. These entropic ligand systems can improve the solubility of various nanocrystals by 10^2 – 10^6 [146]. The average particle size of cubic CdS@CdSe quantum dots, the TEM image of which is presented in Figure 6.1e, is around 12 nm. The drastic shift in the photoluminescence reaching 715 nm with an FWHM of 43 nm is another sign of successful shell growth. Since CdSe has a lower bandgap and it creates a quasi-type-II band structure with CdS, where electrons can be easily delocalized in the whole structure, and holes are mostly localized in CdSe, the recombination mainly occurs in CdSe. So, the emission wavelength is not limited by the bulk bandgap of the CdS core but by the CdSe shell. The sudden increase in the FWHM of emission does not follow the trend where the overall size distribution of particles is narrow. When the TEM images are closely inspected, the thickness of the CdSe shell on 6 facets of the cubes is not equal, and each facet can contribute to emission separately, which might cause a widening in emission. Another cause might be the different photophysical phenomena occurring at weakly confined regime. This aspect will be further studied by computational and spectroscopic methods in near future.

To complete the whole structure, we have grown a secondary CdS shell around cubic CdS@CdSe quantum dots following the similar approach above using the sulfur-oleic acid-octadecene mixture as an anion source instead of a selenium-octadecene mixture. The dimensions of the whole structure reach 20 nm. With the growth of the shell, PL does not shift but FWHM slightly decreases (Figure 6.1a and b), which might be due to the passivation of surface trap sites inducing electron-phonon coupling in addition to the emission from shallow trap sites.

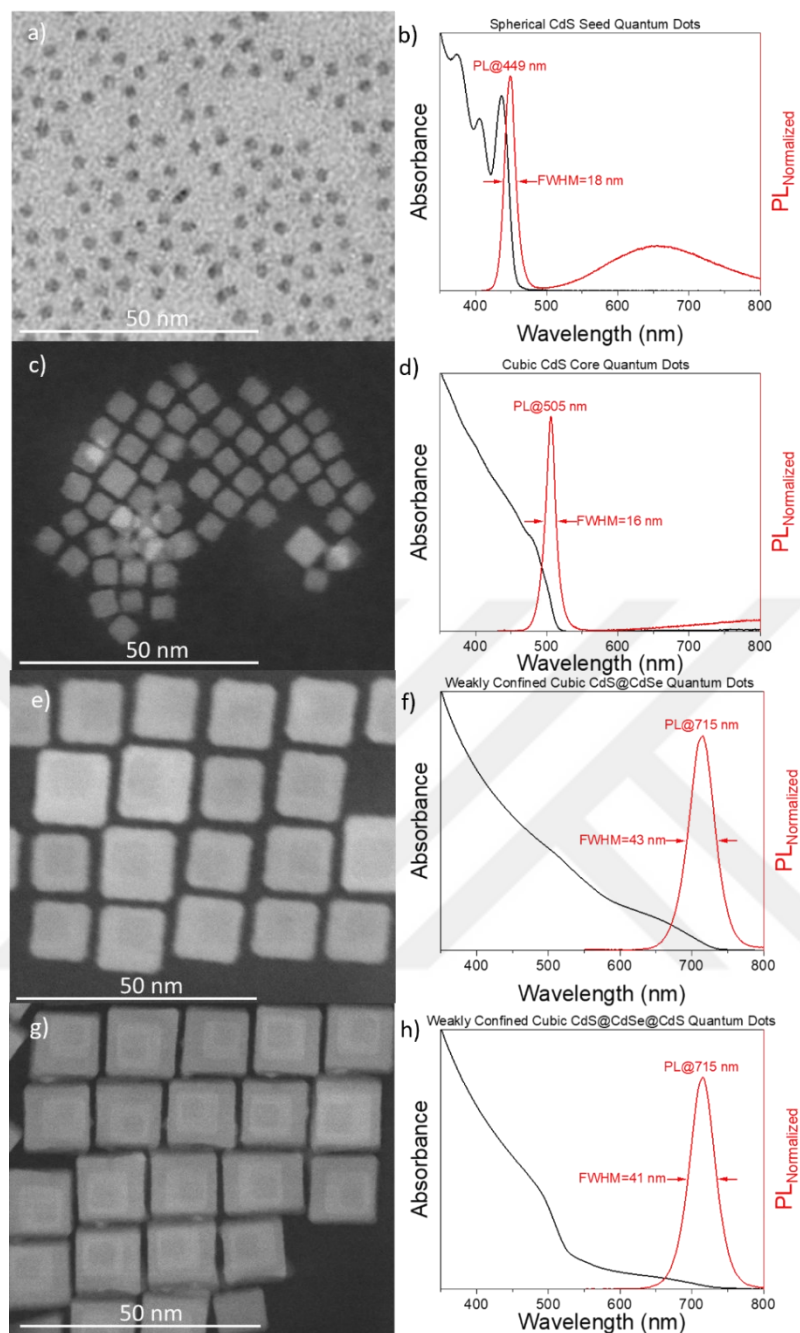


Figure 6.1. a) TEM image of spherical CdS seed QDs. Adapted with permission from [138]. Copyright 2024 American Chemical Society. b) Absorption (black) and PL (red) spectra of spherical CdS seed QDs. c) TEM image of cubic CdS core QDs. d) Absorption (black) and PL (red) spectra of cubic CdS core QDs. e) TEM image of cubic CdS@CdSe core@shell QDs. f) Absorption (black) and PL (red) spectra of cubic CdS@CdSe core@shell QDs. g) TEM image of cubic CdS@CdSe@CdS core@shell@shell QDs. h) Absorption (black) and PL (red) spectra of cubic CdS@CdSe@Shell core@shell@Shell QDs.

In Figure 6.2, a detailed structural analysis using high-resolution TEM images along with EDS mapping is presented. The layers of CdS and CdSe are clearly seen in the TEM images which is further confirmed from the elemental map obtained by the EDS measurement.

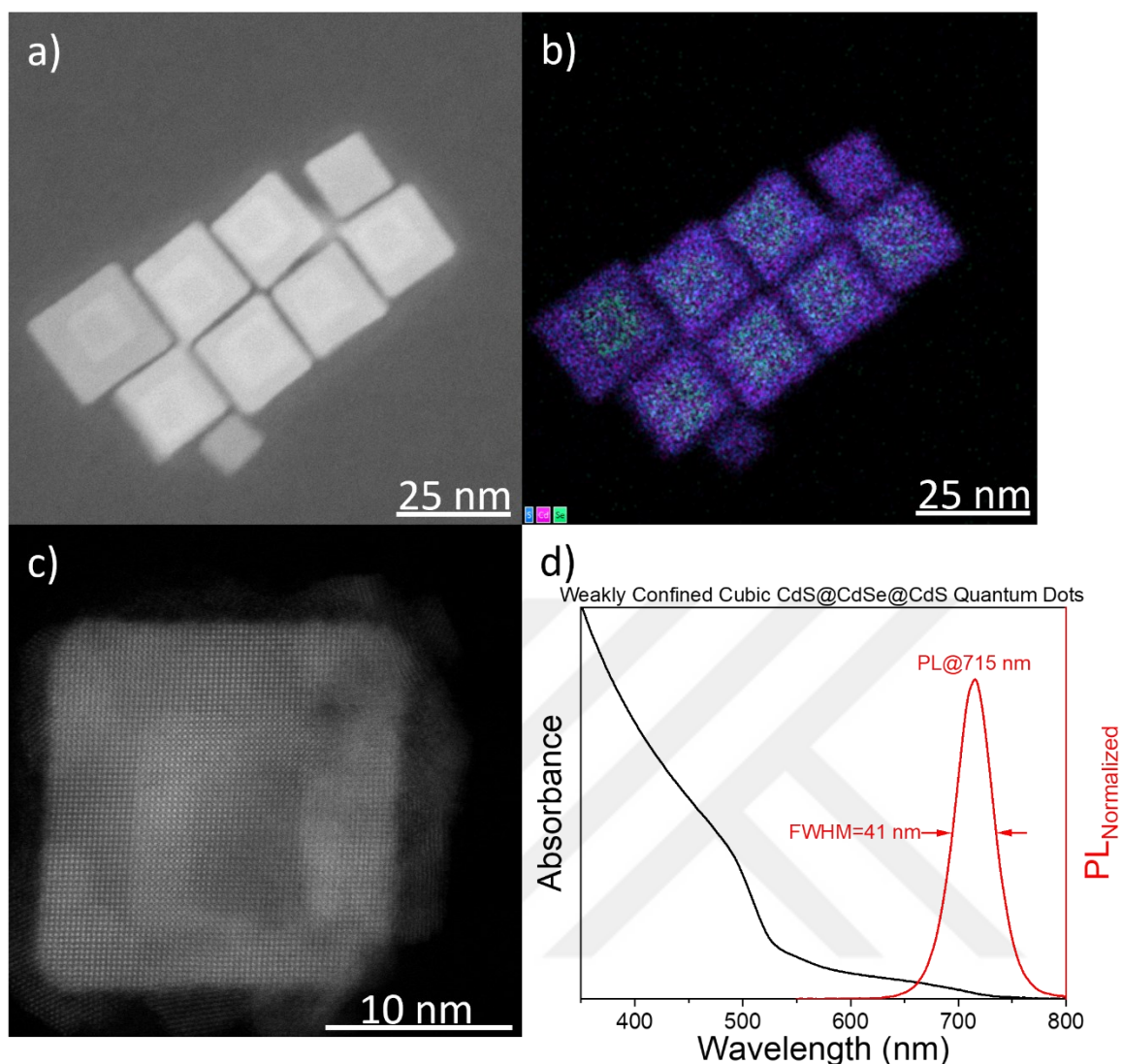


Figure 6.2 Structural characterization of cubic CdS@CdSe@CdS quantum dots. a) High-resolution scanning transmission electron microscopy image. b) EDS elemental map of weakly confined cubic CdS@CdSe@CdS quantum dots. c) High-resolution scanning transmission electron microscopy image of a single particle. d) Absorption and PL spectra.

Lastly, to study the effect of CdSe and CdS shell layer thicknesses on the photophysical properties of these structures, we synthesized structures with thin, medium, and thick CdSe and CdS layers by controlling the amount of anion precursor and growth time during the synthesis. The list of samples prepared is presented in Table 1. In the case of thin CdSe shell, the thickness of the secondary CdS shell causes a red shift in the absorption and PL spectra. However, the secondary shell growth on quantum dots with intermediately thick CdSe layer does not cause a shift in the spectra. This indicates that the large size of the quantum object is approaching the bulk limit. Only a thin CdS shell can be grown on the cubic QDs with thick CdSe layer since the size of CdS@CdSe is already near the limit to be able to be stabilized with the ligand system used here.

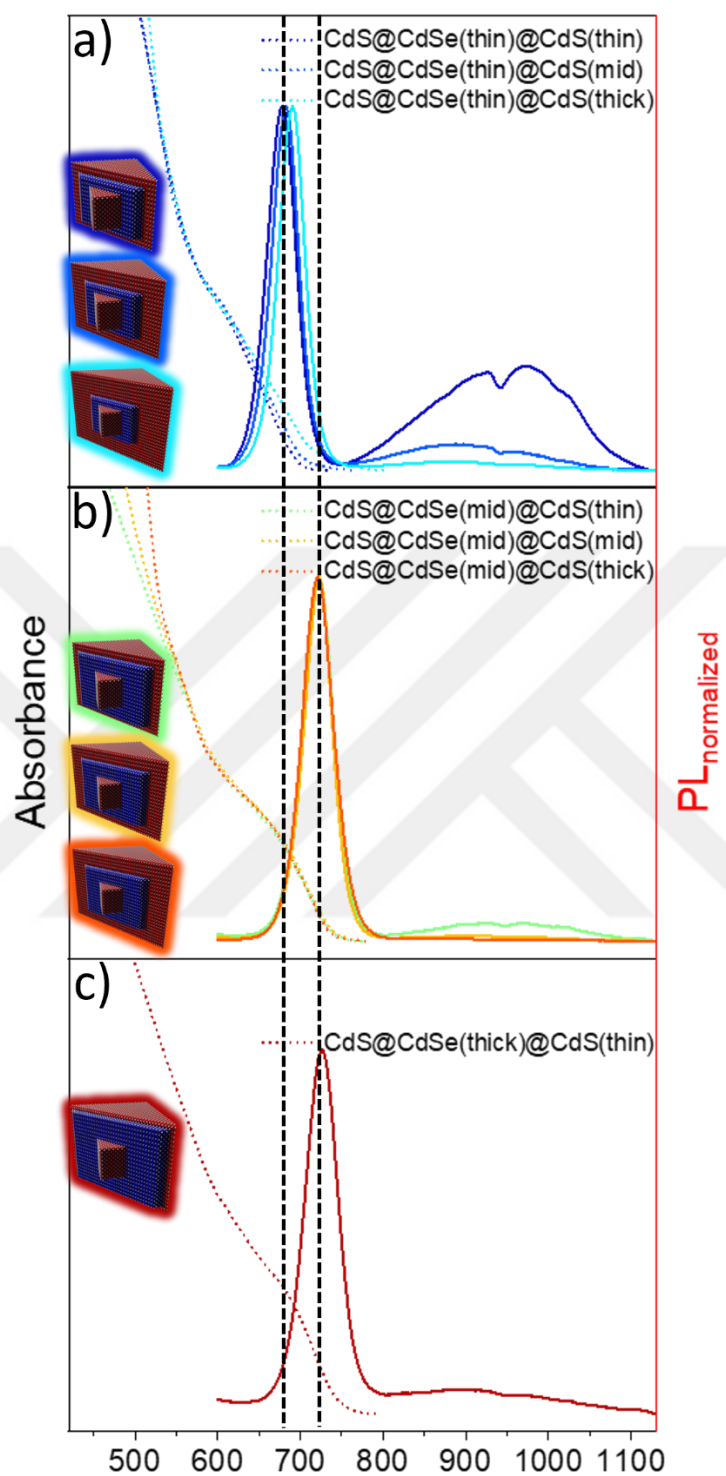


Figure 6.3. Absorbance and PL spectra of colloidal cubic quantum dot heterostructures having various thickness of CdS shells with a) thin, b) medium range and c) thick CdSe quantum shells.

6.4 Summary

In this research, we synthesized weakly confined cubic CdS@CdSe@CdS core@shell@shell structures with dimensions reaching 20 nm. The relatively low bandgap CdSe shell is sandwiched between wide bandgap CdS core and shell. Such structures are also referred to as quantum shells, which are quantum well-like structures owing to the mode of quantum confinement. We have implemented seed-mediated high-temperature growth reactions to obtain these weakly confined cubic quantum dot heterostructures. We have used stearyl chloride during these seed-mediated growth reactions to obtain a cubic shape. The biggest challenge in achieving large, uniform-sized particles during colloidal synthesis is to sustain the colloidal stability of the particles via ligands. The mainstream ligands for such reactions, such as oleic acid or oleylamine, are not enough to stabilize the particles during the synthesis. So, we have used a mixture of carboxylates with different hydrocarbon chain lengths, such as oleic acid, erucic acid, and decanoic acid. Such ligand systems are referred to as entropic ligand mixtures, which stabilize particles in solutions by maximizing the intramolecular entropic effects. These entropic ligand systems can improve the solubility of various nanocrystals by 10^2 – 10^6 . Additionally, we synthesized a set of core@shell@shell heterostructures with various combinations of primary and secondary shell thicknesses. The aim of this work is to study the photophysical properties of weakly combined cube-shaped quantum shells and the role of structural parameters in their performances.

Chapter 7

Conclusion

7.1 Concluding Remarks

In this thesis, we investigated the relationship between CQW structure and optical gain properties to understand the underlying mechanism governing light amplification. We have synthesized carefully engineered CQW heterostructures implementing synthesis protocols that allow precise control of the dimensions and composition at the atomic level. These synthesis protocols enabled us to generate a library of CQW heterostructures with systematically varied structural and elemental parameters. Probing their optical gain performance using advanced spectral and spectro-temporal methods, such as transient absorption spectroscopy, amplified spontaneous emission, and variable stripe length measurements, helped us to unveil the structure-property relationship. We benefitted from the obtained data to optimize CQW heterostructures for optical gain applications. Here, we reported CQW heterostructures with ultralow gain threshold and long gain lifetime, enabling the observation of light amplification in water dispersion, which is challenging due to the low concentration of emitters compared to their film counterparts and low refractive index of the medium suffering from the reduced optical confinement. Then we demonstrated an unprecedentedly high gain coefficient from “giant” CQW heterostructures owing to their thick core large lateral size, which results in an increased number of available states contributing to gain and suppressed Auger recombination. Following this, we fine-tuned the confinement barrier of these CQW heterostructures to further improve gain threshold values. Finally, we synthesized novel CQW heterostructures in the form of quantum shells, which entails a cubic shape having well-defined surface morphology with an overall size approaching the bulk limit.

In water, low-threshold gain was achieved from carefully engineered $\text{CdSe/CdS}@_{\text{Cd}_x\text{Zn}_{1-x}\text{S}}$ core/crown@gradient alloyed shell CQWs. A CdS crown laterally grown on the 4.5 ML thick CdSe core facilitated exciton funneling while passivating defect rich periphery of the starting core and increasing the absorption-cross section of the overall structure. Following, a gradient alloyed shell with increasing zinc concentration at each layer was grown on the core/crown heterostructure. While the shell is passivating surface trap sites and confining the wavefunction within the whole structure, the gradient results in a smooth confinement barrier, which is an effective strategy to successfully suppress Auger recombination. From this heterostructure, we

obtained an ultra-low ASE threshold of $\sim 3.4 \mu\text{J}/\text{cm}^2$ and an extremely long gain lifetime of around 2.6 ns. Inspired by these results, we transferred our CQW heterostructures to water via a ligand exchange protocol and achieved ASE from their dispersion. The achievement of in-water optical gain in this thesis work presents specifically a significant step for biological molecule analyses and detection in living cells and tissues and other bio-compatible environment.

In this thesis, we also unveiled that the thickness and lateral size of the core, along with shell thickness, play a crucial role in the material gain of CQW heterostructures. Here, we synthesized CdSe@CdS core@shell CQW heterostructures with 7.5 ML thick cores having lateral areas of 450 nm^2 and 1- to 5-ML thick CdS shells, which were grown via colloidal atomic layer deposition. The large size of CQWs results in an increased number of states whose contribution to the gain is facilitated by the suppressed Auger recombination following a volume scaling law. From these heterostructures, we achieved a record-high material gain coefficient of $\sim 140,000 \text{ cm}^{-1}$, which is unprecedented among all colloidal semiconductor nanocrystals. Exploiting their high gain coefficients, we obtained very stable ultra-low WGM-based lasing with a threshold of $8 \mu\text{J}/\text{cm}^2$, even with the low quality of our cavity. Encouraged by the stability of our materials under optical pump, we investigated the optical gain behavior of our materials under hard pump conditions, which resulted in spectrally separated two light amplifications at the same time. These materials with extremely large modal gain coefficients may facilitate gain under continuous-wave excitation or even they can be possibly implemented in electrically-driven colloidal lasers.

To lower the optical gain threshold values of CQW heterostructures with thick cores, we systematically studied the role of composition and thickness of the shell on optical gain. Implementing colloidal atomic layer deposition, we grew CdS, ZnS, and gradient alloyed CdZnS shells on 7.5 ML CQWs with various thicknesses. The lowest gain threshold was achieved with core@gradient-alloyed-shell CQWs, which also showed the highest modal gain coefficient among all. This result is attributed to the suppression of nonradiative Auger recombination owing to the volume scaling law and smooth energy barrier, which was obtained by the gradual increase of the Zn amount in the shell.

Last, we synthesized weakly confined cubic CdS@CdSe@CdS core@shell@shell quantum dot heterostructures with variable shell thicknesses. Since the low bandgap is sandwiched between large bandgap CdS, this structure is akin to quantum wells with 1D confinement. In

the weakly confined regime, achieved by the large dimensions reaching 20 nm, the momentum conservation is expected to be partially recovered, which is relaxed in confined systems. This recovery of momentum conservation is supposed to minimize Auger recombination. To synthesize such large particles, we implemented entropic ligand systems during the synthesis to achieve colloidal stability in reaction conditions, which is crucial to obtain uniform size distribution.

Overall, the outcome of this thesis advances the prevailing knowledge about the structure-property relationship of CQW heterostructures specifically for optical gain applications. We believe these findings will strongly help the realization of high-performance-colloidal nanolasers in the future, which will benefit numerous fields of applications such as on-chip communication and data processing, wearable sensors, 3D displays, advanced holography, and biosensing.

7.2 Contributions to the Literature

The first author/equal contribution journal publications during the thesis study include:

1. **F. Isik**, S. Delikanli, E. G. Durmusoglu, A. T. Isik, F. Shabani, H. Dehghanpour Baruj, H. V. Demir, ““Giant” Colloidal Quantum Well Heterostructures of CdSe@CdS Core@Shell Nanoplatelets from 9.5 to 17.5 Monolayers in Thickness Enabling Ultra-High Gain Lasing” **Small**, 2024, 2309494 [98]
2. S. Delikanli, **F. Isik**, E.G. Durmusoglu, O. Erdem, F. Shabani, B. Canimkurbey, S. Kumar, Dehghanpour Baruj, H. V. Demir, “Observation of Optical Gain from Aqueous Quantum Well Heterostructures in Water,” **Nanoscale**, 2022, 14, 14895-14901 [64]

In addition to the presented work in this thesis, there are other journal publications to which contributions were made:

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4. M. A. Masharin, T. Oskolkova, **F. Isik**, H. V. Demir, A. K. Samusev, S. V. Makarov, “Giant Ultrafast All-Optical Modulation Based on Exceptional Points in Exciton–Polariton Perovskite Metasurfaces” **ACS Nano**, 2024, 18, 3447-3455 [149]

5. T. Bozkaya, **F. Isik**, I. Bozkaya, S. Delikanli, E. Unal, H. V. Demir, "Light-sensitive monolayer-thick nanocrystal skins of face-down self-oriented colloidal quantum wells," **Nanoscale**, 2023, 15, 17583-17588 [150]
6. F. Shabani, M. Ahmad, S. Kumar, S. Delikanli, **F. Isik**, A. Bhattacharya, A. Petrou, H. V. Demir, "Thermodynamic Silver Doping of Core/Shell Colloidal Quantum Wells Imparted with Paramagnetic Properties Emitting at Near-Infrared" **Chemistry of Materials**, 2023, 35, 4159-4170 [151]
7. S. Delikanli, B. Canimkurbey, P. L. Hernández-Martínez, F. Shabani, A. T. Isik, I. Ozkan, I. Bozkaya, T. Bozkaya, **F. Isik**, E. G. Durmusoglu, M. Izmir, H. Akgun, H. V. Demir, "On the Rational Design of Core/(Multi)-Crown Type-II Heteronanoplatelets" **Journal of the American Chemical Society**, 2023, 145, 12033-12043 [56]
8. H. Dehghanpour Baruj, I. Bozkaya, B. Canimkurbey, A. T. Isik, F. Shabani, S. Delikanli, S. Shendre, O. Erdem, **F. Isik**, H. V. Demir, "Highly-Directional, Highly-Efficient Solution-Processed Light-Emitting Diodes of All-Face-Down Oriented Colloidal Quantum Well Self-Assembly," **Small**, 2023, 19, 2206582, 11, 2202407 [152]
9. D. A. Tatarinov, S. S. Anoshkin, I. A. Tsibizov, V. Sheremet, **F. Isik**, A. Y. Zhizhchenko, A. B. Cherepakhin, A. A. Kuchmizhak, A. P. Pushkarev, H. V. Demir, S. V. Makarov, "High-Quality CsPbBr₃ Perovskite Films with Modal Gain above 10,000 cm⁻¹ at Room Temperature," **Advanced Optical Materials**, 2023 [153]
10. A. T. Isik, F. Shabani, **F. Isik**, S. Kumar, S. Delikanli, H. V. Demir, "Simultaneous Dual-Color Amplified Spontaneous Emission and Lasing from Colloidal Quantum Well Gain Media in their Own Layered Waveguide and Cavity," **Laser & Photonics Reviews**, 2023, 7, 2300091 [154]
11. E. G. Durmusoglu, S. Hu, P. L. Hernandez-Martinez, M. Izmir, F. Shabani, M. Guo, H. Gao, **F. Isik**, S. Delikanli, V. Kumar Sharma, B. Liu, H. V. Demir, "High External Quantum Efficiency Light-Emitting Diodes Enabled by Advanced Heterostructures of Type-II Nanoplatelets," **ACS Nano**, 2023, 17, 7636-7644 [155]
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 15. K. Onbasli, G. Demirci, **F. Isik**, E. G. Durmusoglu, H. V. Demir, H. Y. Acar, “Aqueous Colloidal Nanoplatelets for Imaging and Improved ALA-Based Photodynamic Therapy of Prostate Cancer Cells,” **Chemical Communications**, 2023, 59, 10512-10515 [159]
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7.3 Future Outlook

There is still a large room for improvement in the field of CSNCs, particularly for their optical gain properties, to achieve electrically-driven all-colloidal lasers. Long-term stability under working device conditions is an issue to be addressed, especially for the CSNCs emitting in blue and green colors. In these regions of the spectrum, the growth of large shells, which helps increase the stability of the particles, cannot be a solution since such large shells relax the confinement. This constraint also limits the improvement in Auger suppression, directly affecting the gain threshold, lifetime, and coefficients.

Alloying the core@shell interface of CQW heterostructures is yet to be matured especially when compared to QDs. This is mainly due to the challenge of maintaining the anisotropic shape during the growth of the shell. For instance, the synthesis of CQW heterostructures with CdSe shells having decent emissive properties is still lacking. This problem is reflected in the growth of a shell with a smooth transition from CdSe core to CdS shell that requires a region with gradient $\text{CdSe}_x\text{S}_{1-x}$ composition. This condition limits the suppression of Auger recombination processes, hampering the optical gain performance.

Another challenge is the crown growth on thicker CQWs which has not been reported to date. This would have boosted the optical gain performance and provided more degree of freedom in the tunability of optical properties. This is mainly due to the energetics of the growth synthesis on thick CQWs, which complicates the feasibility to sustain the anisotropic shape. However, this can possibly be tackled with surface energy modifications implementing novel ligand systems and precursors, which benefitted the achievement in the synthesis of thicker CQWs.

The weakly confined regime in colloidal semiconductors is a recent field of study, which resulted in surprising levels of optoelectronic performance in initial reports. In line with this trend, the optoelectronic properties of the synthesized cubic quantum shells in this thesis will further be investigated in detail via making use of advanced spectrophysical measurement tools, where we anticipate new phenomena that will favor next-generation all-colloidal devices.

We firmly believe that CSNCs, particularly CQWs, hold significant potential to revolutionize photonics technology due to their aforementioned superiorities. Realizing this advancement requires addressing these challenges, primarily through advanced synthetic developments.



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