

OPTICAL GAIN AND LASING OF COLLOIDAL SEMICONDUCTOR QUANTUM WELLS INTIMATELY INTEGRATED INTO OPTICAL CAVITIES

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

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ABSTRACT

OPTICAL GAIN AND LASING OF COLLOIDAL
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M.S. in Electrical and Electronics Engineering

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Colloidal semiconductor quantum wells, also known as nanoplatelets (NPLs), attract an increasingly greater deal of interest as a promising material platform for light-generating applications. The superior optical properties of NPLs including their ultra-large absorption cross-sections, purely homogeneous broadening, and suppressed Auger recombination make them highly attractive for solution-processable color convertors, LEDs and lasers. In this thesis, we studied the optical gain properties and performance levels of tailored heterostructures of such NPLs intimately integrated into various optical cavities. To do so, we systematically measured their amplified spontaneous emission under one- and two-photon absorption excitations. Also, with these hetero-NPLs as the gain media, we have proposed and demonstrated a new class of practical whispering gallery mode (WGM) NPL-fiber architecture with high stability and low lasing thresholds enabled by record low waveguide loss coefficients in its class. Moreover, we have developed a single-mode vertical-cavity surface-emitting laser (VCSEL) of these hetero-NPLs closely integrated into the wedge cavity of a pair of distributed Bragg reflectors, leading to a record low lasing threshold in its class. The findings obtained in these WGM NPL-laser and NPL-VCSEL structures indicate that these NPLs are excellent for high-performance colloidal lasing.

Keywords: Semiconductor nanocrystals, colloidal nanoplatelets, optical gain, whispering-gallery-mode laser, vertical-cavity surface-emitting laser.

ÖZET

OPTİK ÇINLAÇLAR İÇİNDE YAKİNE TÖMLEŐTİRİLMİŐ KOLOİDAL YARIİLETKEN KUANTUM KUYULARININ OPTİK KAZANCI VE LAZER EYLEMİ

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Nanolevhalar olarak da adlandırılan koloidal yarıiletken kuantum kuyuları ışık üreten uygulamalar için umut vadeden bir materyal platformu olarak artan miktarda yoğun ilgi görmektedir. Nanolevhaların çok yüksek optik soğurma katsayıları, tamamen homojen optik ışıma genişlemeleri ve bastırılmış Auger eksiton birleşimi gibi üstün optik özellikleri onları çözelti halinde işlenebilir renk dönüőtürücüler, ışık yayan diyotlar ve lazerler için oldukça ilgi geçici yapmaktadır. Bu tez kapsamında, özel olarak tasarlanmış heteroyapıya sahip bu nanolevhaları farklı optik çınlaçlar içerisine yakinen tümleőtirerek optik kazanç özellikleri ve performans seviyeleri üzerine çalıştık. Bu amaç doğrultusunda, nanolevhaların bir- ve iki-foton soğurma uyarımı altında yükseltilmiş kendiliğinden ışımlarını sistematik olarak ölçtük. Ayrıca, bu hetero-nanolevhaları optik kazanç ortamı olarak kullanarak, kendi sınıfında rekor düşüklükte dalga kılavuzu kayıp katsayısı sayesinde yüksek kararlılık ve düşük lazer eőiđi değeriine sahip pratik bir fisıldayan-galeri-kip (FGK) nanolevha-fiber mimarisi önerip ve gösterdik. Buna ek olarak, bu hetero-nanolevhaları bir çift dağıtılmış Bragg yansıtıcılar tabanlı kama çınlaç içinde tümleőtirerek yapılan, sınıfında rekor düşüklükte lazer eőik değeriine sahip tek modlu bir dikey çınlaçlı yüzey ışımalı lazer (DÇYİL) geliőtirdik. Burda FGK lazer ve DÇYİL yapılarından elde edilen bulgular bu nanolevhaların yüksek performanslı koloidal lazer eylemi için mükemmel olduklarını göstermektedir.

Anahtar sözcükler: Yarıiletken nanokristaller, koloidal nanolevhalar, optik kazanç, fisıldayan-galeri-kip lazer, dikey çınlaçlı yüzey ışımalı lazer.

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Chapter 1

Introduction

Semiconductors have dramatically revolutionized daily lives since the invention of the first semiconductor transistor, which was realized on a germanium crystal by Walter Brattain, John Bardeen and William Shockley at Bell Labs in 1947 [1]. In the last half century, semiconductor technologies have altered a wide range of fields including computing, military electronics, communication and healthcare by offering a robust and power efficient systems. Besides, although Einstein theoretically explained the mechanisms behind the light-matter interactions such as optical absorption, spontaneous emission and stimulated emission phenomena in 1917 [2], the first successful demonstration of stimulated emission was achieved in 1955 [3] and the first practical laser (light amplification by stimulated emission of radiation) was built by Theodore H. Maiman in 1960, of which gain medium is made out of ruby [4]. However, one needs to wait until 1962 to see the first presentation of semiconductor laser made of gallium arsenide [5], which has an emission at 850 nm corresponding to the near-infrared region of the electromagnetic spectrum. From this date forward, semiconductors have taken an unsubstituted part in the field of photonics.

Energy band gap of a semiconductor material is defined as the energy difference between the top of fully-occupied valence band and the bottom of unoccupied conduction band.

Thanks to their relatively small energy band gaps, semiconductors are irreplaceable candidates to be used in optoelectronics. The strong and controllable interaction between semiconductors and light (electromagnetic wave) enables the utilization of light-harvesting and light-emitting devices for a broad range of applications including lighting, displays and information technologies. This crucial wide-scale role of semiconductors makes the cost of their growth method more important and impactful commercially. However, traditional semiconductor growth techniques like czochralski method and epitaxial growth require ultra-high vacuum and high temperature conditions, resulting in high-cost fabrication and difficulty in large-scale integration. Hence, the development of low-cost and large-area methods to grow semiconductors presents strategic importance. To this end, colloidal semiconductor nanocrystals have emerged as a promising material platform owing to their solution processable nature and their wet chemistry synthesis, which makes them a cost-effective alternative to conventional thin-film semiconductors.

Besides the cost-related issues, colloidal semiconductor nanocrystals (NCs) have attracted great attention owing to their favorable characteristics. Thanks to the controllable quantum confinement realized in these nanometer-sized semiconductor nanocrystals, their optical and electronic features can be conveniently tuned simply by altering their shape, size and compositions [6], [7]. To date, various shapes of colloidal semiconductor NCs have been synthesized via wet chemistry including zero-dimensional quantum dots [8], [9], one-dimensional nanorods [10], [11] and recently, two-dimensional quantum wells [12], [13]. Also, different heterostructures have been engineered to specifically alter the excitonic features of NCs to obtain desired characteristics [6], [14], [15]. So far, owing to their remarkable photophysical properties, NCs have been used in different light-emitting and light-harvesting applications including photovoltaic cells [16], photodetectors [17], luminescent solar concentrators [18], light-emitting diodes (LEDs) [19] and lasers [20].

Among various classes of nanocrystals, colloidal semiconductor quantum wells (CQWs), the so-called colloidal nanoplatelets (NPLs), stand out as an auspicious member of nanocrystal family owing to their superior electronic and optical properties. Their characteristics such as giant oscillator strength [21], extraordinarily large linear and nonlinear absorption cross-sections [22], ultralarge modal optical gain performances [23]

and purely homogeneous broadening [24] make them great candidates to achieve low-threshold optical gain and high-performance colloidal lasers. In fact, with their color tunability, any laser that operates in visible to infrared regions can be built using them [25].

Today, various shapes of colloidal nanocrystals are utilized as gain media for lasing and optical gain application including quantum dots [20], nanorods [26], quantum wells [27], [28] and perovskite nanocrystals [29], [30]. Nonetheless, the prevalence of nanocrystals lasers is restrained by a dominant process, the nonradiative Auger recombination, which makes them impractical for real-life applications. Auger is a rapid recombination process annihilating the active carriers, limiting their performance of colloidal lasers. For this reason, different heterostructures (core/crown [31], [32] and core/shell [28], [33]) of NPLs have been introduced to tune their excitonic features to overcome this issue, which thus enables highly efficient optical gain performance [34]. Hence, by virtue of heterostructures along with aforementioned characteristics, NPLs offer a high-performance media for optical gain and lasing applications.

The realization of a practical NC laser requires the use of the optical cavities (resonators) to confine the emission of optical gain media and provide optical feedback with the help of amplifying in the gain media for lasing action. Previously, different types of NCs have been utilized in colloidal laser applications in close-packed films or in solution phase integrated to various optical cavities. These include vertical cavity surface-emitting lasers [35], which have been implemented by using specialized Fabry-Perot resonators, whispering gallery mode lasers [36], which utilized by ring resonators. Depending on the specific applications, resonator types can be meticulously designed, and the phase (in solution or solid film) of the NC gain media can be adjusted. Furthermore, the excitation regime of the NC laser (single photon or multi photon) can be chosen to address a unique application such as bioimaging under-skin treatment. Hence, it is crucially essential to systematically investigate the optical gain and lasing performances of various heterostructures of colloidal NPLs coupled to different optical cavities.

To investigate these issues, in this thesis, we have designed, developed and analyzed novel nanocrystal-based lasers integrated to different optical resonators. For this purpose, we

have proposed and synthesized engineered-heterostructures of solution-processed colloidal NPLs including core/crown@gradually-alloyed-shell architecture. Then, we have examined their electronic and optical features to obtain desired characteristics for our optoelectronic devices. Here, we have systematically investigated single- and multi-photon pumped optical gain properties of CdSe/CdS@Cd_{1-x}Zn_xS core/crown@gradually-alloyed-shell (C/C@GAS) NPLs. Furthermore, we have employed this advanced heterostructure to obtain a novel fiber-based whispering gallery mode (WGM) laser and vertical-cavity surface-emitting laser (VCSEL). Our record low waveguide loss coefficients and record low lasing thresholds reveal the true potential of the advanced heterostructures of these NPLs for optical gain and lasing studies. These findings indicate that this new generation of nanocrystals may play a vital role to overcome long-standing challenges of traditional colloidal nanocrystal lasers and maybe even surpass the performances of their conventional epitaxially-grown counterparts.

1.1 Organization of the Thesis

In Chapter 2, we present the scientific background about the colloidal semiconductor nanocrystals including their quantum behavior, synthesis, excitonic and optical properties. We also explained the characteristics and different types of the optical resonators in this chapter.

In Chapter 3, we describe experimental methods that are frequently used throughout the thesis such as steady-state absorption and PL spectroscopy. In addition, optical gain characterization methods covering gain threshold, variable stripe length and waveguide loss coefficient measurements are introduced.

In Chapter 4, we propose, simulate and demonstrate multi-mode lasing behavior of colloidal nanoplatelets in solid film phase enabled by fiber-based whispering-gallery-mode optical cavity. We present record low waveguide loss coefficients. Furthermore, by this study, we unleash the potential of close-pack NPL films to be used for multi-mode lasers.

In Chapter 5, we propose and show vertical-cavity surface-emitting laser based on advanced heterostructures of NPLs. Here we report record low lasing threshold among all colloidal nanocrystals.

In Chapter 6, we conclude our thesis with concluding remarks and future outlook along with a summary of the contributions of this thesis.



Chapter 2

Background

2.1 Colloidal Semiconductor Nanocrystals

In this part, we present the scientific background on the colloidal semiconductor nanocrystals. Before explaining the synthesis methodology of NCs, the quantum confinement effect and the influence of heterostructures on this effect are discussed. Then, we explain size- and composition-dependent excitonic and optical characteristics of NCs. Finally, we conclude this part by reviewing the mechanism behind the optical gain phenomenon among colloidal NCs.

2.1.1 Quantum Confinement

Colloidal semiconductor nanocrystals are nanometer-sized crystalline semiconductors that contain a few hundreds to thousands of atoms. As a result of their nanometer-sized dimensions, generated electrons and holes in NCs can easily feel the boundaries of this nano-structure as potential barriers. Before going into details about quantum confinement phenomenon, it is essential to explain the Bohr radius and the formation of the exciton within nanocrystals.

The exciton Bohr radius of a material can be written as follows: [37]

$$a_B = \epsilon a_0 \frac{m_e}{m^*} \quad (2.1)$$

where ϵ is the dielectric constant of the medium, a_0 is the Bohr radius of hydrogen atom, m_e is the rest mass of the electron and m^* is the electron-hole reduced mass. As a result of this material-dependent behavior, exciton Bohr radius depends on the material choice. Exciton Bohr radii of frequently used semiconductors in this thesis are provided in Table 2.1 [38].

Table 2.1 Exciton Bohr radii of II-VI semiconductors that are frequently used in this thesis.

Semiconductor Type	Exciton Bohr Radius
CdTe	7.3 nm
CdSe	5.6 nm
CdS	2.9 nm
ZnS	2.5 nm

If the size of nanocrystal is comparable to or smaller than its exciton Bohr radius, quantum confinement effect will be observed. Due to this strong confinement in a truly small volume, Coulombic attraction between electron and hole bounds them to form an exciton. Moreover, quantum confinement regime of NCs defines their photophysical behavior, resulting in atomic-like discrete energy levels. In the literature, 3D-confined nanocrystals are called as quantum dots, where 2D- and 1D-confined ones are named as nanorods and nanoplatelets, respectively. For instance, in an 1D-confined nanoplatelet, only the thickness of this NC is smaller than the exciton Bohr radius and excitons can freely move in the lateral directions. In addition, owing to discrete energy levels of these quantum-confined NCs, their band gaps can be decreased by increasing their size, resulting a red

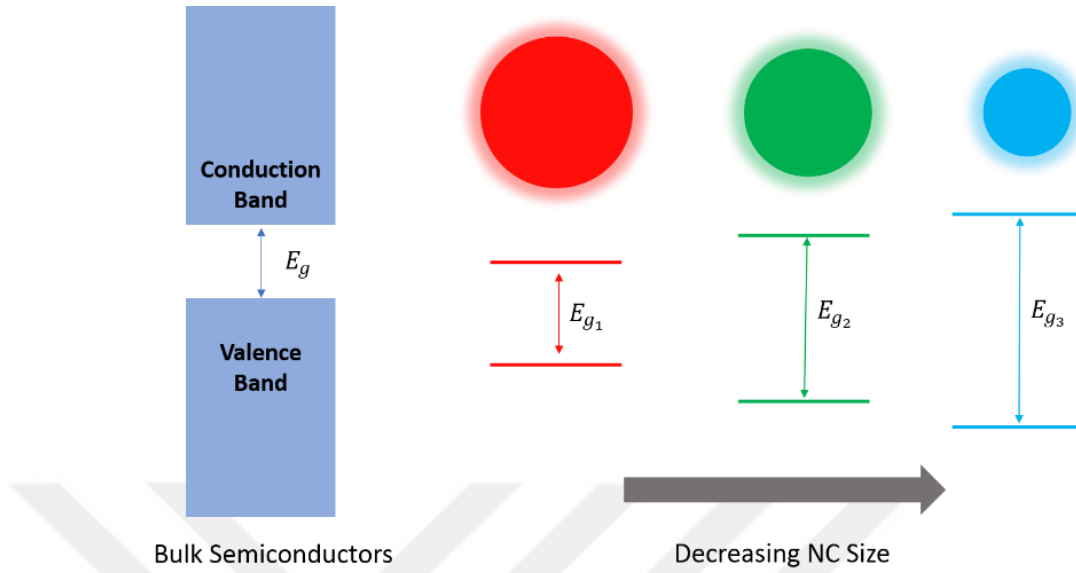


Figure 2.1: Schematic illustration showing the continuous bands of bulk semiconductors along with the effect of size among nanocrystals on energy band gap. Decreasing NC size effectively increases the energy band gap.

shift in their PL emission spectrum. Hence, the band gap of NCs can be simply tuned by changing their size along the way of quantum confinement by using the same material composition (Figure 2.1). The band gap of a nanocrystal is expressed by:

$$E_g(NC) = E_g(bulk) + E_{conf} + E_{exc} \quad (2.2)$$

where the confinement energy and the exciton energy are given as:

$$E_{conf} = \frac{\hbar\pi}{2r^2} \left(\frac{1}{m_h} + \frac{1}{m_e} \right) \quad (2.3)$$

$$E_{exc} = \frac{-1.8e^2}{4\pi\epsilon r} \quad (2.4)$$

Here $\hbar$ is the reduced Plank constant, r is the radius of nanocrystal, m_h is the effective mass of hole, m_e is the effective mass of electron, and ϵ is the dielectric constant. As given above, the band gap of NCs is strongly size-dependent. The exciton energy is inversely proportional to radius r while the confinement energy is inversely proportional to r^2 . Thus, the confinement energy plays a more critical role to determine the band gap of NCs if the particle is strongly confined.

2.1.2 Synthesis of Colloidal Semiconductor Nanocrystals

The successful demonstration of semiconductor nanocrystals was reported in early 1980s in a dielectric matrix where size-dependent absorption features have been observed [39]. Within a half-decade, electrical and optical properties of various nanometer-sized semiconductors were explored [40]. However, the first uniform and nearly monodisperse nanocrystals of semiconductors including CdS, CdTe, and CdSe were reported by Bawendi Group in early 1990s [8]. From then on, great efforts have been made to synthesize different colloidal NCs. The process of colloidal synthesis requires three main factors: ligands, solvents and precursors. Solvent creates the suitable environment for colloidal synthesis. In high temperature environment, precursors are dissolved into monomers and form the NCs by nucleation. Ligands such as oleic acid and oleylamine are used to control the final size as well as to obtain stable, monodisperse and uniform NCs [41], [42].

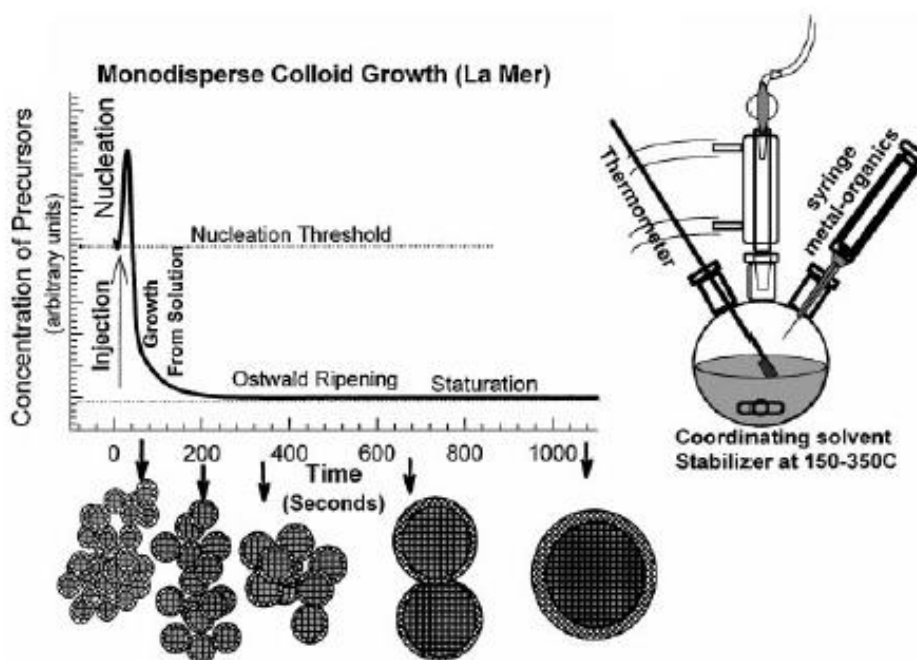


Figure 2.2: The nucleation and growth model of nanocrystals. Reprinted with permission from [41].

According to the nucleation and growth model of nanocrystals, which are introduced by La Mer and Dinegar [43], nucleation and growth steps should be separated to synthesize highly monodisperse NCs. A rapid injection of precursors into the hot solution that generates supersaturated solution initiates the nucleation of precursor monomers, resulting in nanometer-sized crystals. This fast nucleation depletes the concentration of the precursors and pulls it down to a level lower than the nucleation threshold, restraining the formation of new nuclei as given in Figure 2.2. After that, previously formed NCs start to grow with small variations in their size. The growth time is a deterministic factor to control the size of NCs. As a result of the-so-called Ostwald ripening, NCs with bigger sizes start to grow and smaller ones dissolve as the growth time increases. Hence, with the control over Ostwald ripening and the growth time, it is possible to determine the size of NCs effectively. Nowadays, considering this relatively basic approach, various shapes of NCs can be synthesized. Since all NCs used throughout this thesis are the atomically flat ones, commonly known as colloidal quantum wells, we will mostly focus on them.

2.1.3 Colloidal Semiconductor Quantum Wells

The first synthesis of colloidal semiconductor quantum wells was reported by Ithurria and Dubertret in 2008 [12]. Since the shape of these atomically-thin NCs seems like platelets, they are alternatively coined as colloidal nanoplatelets (NPLs). One of the characteristic features of NPLs is their vertical thickness, which can be precisely controlled with slight changes in their synthesis procedure. Illustration of a 4 monolayer (ML) thick CdSe NPL is given in Figure 2.3a, where 4 layers of Se atoms are sandwiched within 5 consecutive layers of Cd atoms. High-angle annular dark field transmission electron microscopy (HAADF-TEM) images of 4 ML and 5 ML CdSe NPLs are shown in Figures 2.3b and 2.3c, respectively [44]. Since the quantum confinement effect occurs in the vertical direction, controlling the number of monolayers significantly affects the absorption and photoluminescence (PL) spectra of the resulting NPLs. By increasing the number of MLs, quantum confinement of the carriers becomes more relaxed, causing a red shift in the emission and absorption spectra, which can be also interpreted from Equation 2.3 (see

Figure 2.4). Moreover, the emerging step-like absorption behavior of NPLs indicates their quantum-well-like density of states.

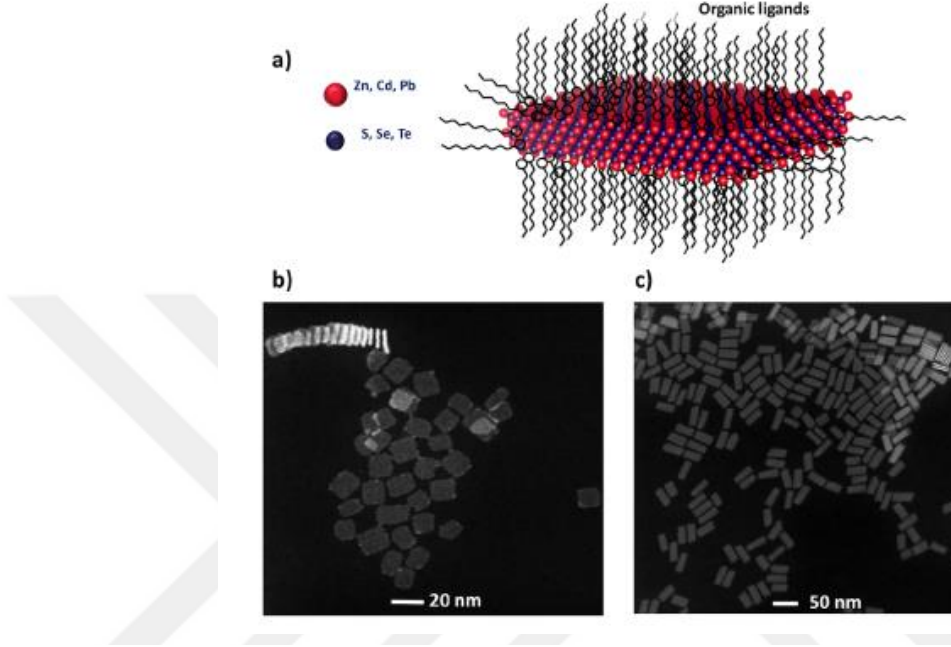


Figure 2.3: (a) Illustration of 4 ML CdSe NPLs, (b) HAADF-TEM image showing 4 ML CdSe NPLs, (c) HAADF-TEM image showing 5 ML CdSe NPLs [44].

For the 4 ML case, the first excitonic peak appears at 510 nm, which corresponds to the upward transition from heavy-hole of the valence band to the conduction band, and the second peak at 484 nm corresponds to the one that belongs to the light-hole. NPLs exhibit strong quantum confinement in only one dimension since their magic-sized thicknesses are significantly smaller than their exciton Bohr radius, while their lateral thicknesses are much larger [21]. Different than other classes of NCs, high monodispersity of NPLs allows to suppress the inhomogeneous broadening, and they thus exhibit purely homogenous broadening [24]. This results in a very sharp PL line with a full-width-at-half-maximum (FWHM) typically narrower than 10 nm.

Even though monodispersity and high control on thickness is achieved, only CdSe NPLs in a simple core architecture yield photoluminescence quantum efficiency (PL-QY) around 25% due to the quenching of photogenerated carriers via nonradiative decay processes or surface traps. To improve and tune their optical and electronic properties,

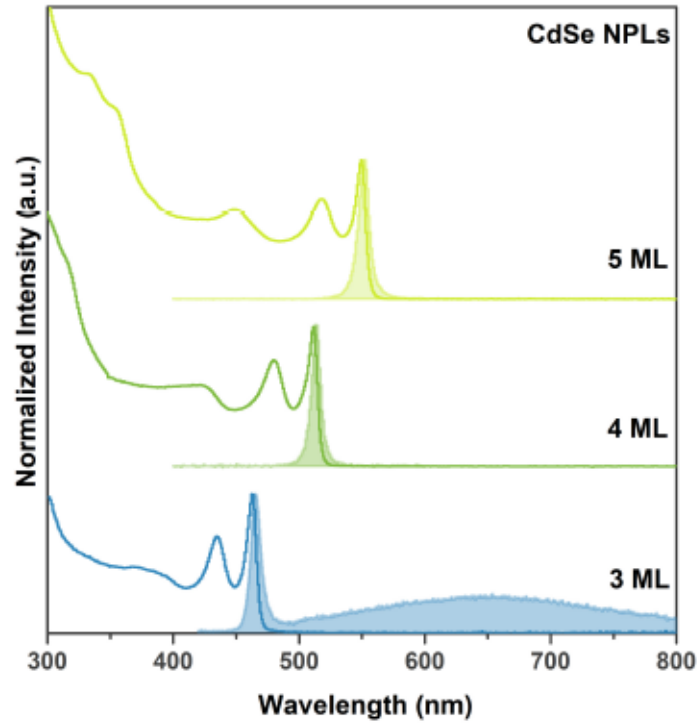


Figure 2.4: PL and absorption spectra of CdSe NPLs with 3, 4 and 5 ML thicknesses [44].

various heterostructures of NCs have been developed. Growing a crown around the core of an NPL only in the lateral direction without changing its vertical thickness was previously used to improve their stability and PL-QY [32]. Moreover, coating a shell around the core was used to control the quantum-confinement and the localization of the hole and electron in the NC [45]. Finally, advanced heterostructures like core/crown@shell was used to further engineer the core NPLs [46]. The schematic illustrations of core/crown, core/shell and core/crown@shell are depicted in Figure 2.5.

With proper choices of semiconductor materials in the heterostructures, Type-I, Type-II or quasi Type-II band alignment can be achieved in NPLs. For Type-I band alignment, both electron and hole wavefunctions are confined in the core region of the NPL. Since the band gap of ZnS is wider than CdSe, CdSe/ZnS core/shell heterostructure of NPL, Type-I can be achieved with them [47]. Besides, in Type-II band alignment, electron and hole confined in different regions of the NC. This delocalization of electron and hole reduces the overlap of their wavefunctions, resulting in stronger suppression of nonradiative Auger recombination. CdSe/CdTe core/crown NPLs reported by Dubertret

group is a good example of this band alignment type [48]. Finally, in quasi type-II alignment, one of the carriers is relaxed through the whole NC while the other one is confined in a region, typically the core, as in the case of CdSe/CdS core/crown NPLs.

2.1.4 Optical Gain of Colloidal Semiconductor Nanocrystals

In this part, we will discuss the light-matter interactions and fundamentals of optical gain in atomic systems to explain the lasing behavior among semiconductor nanocrystals.

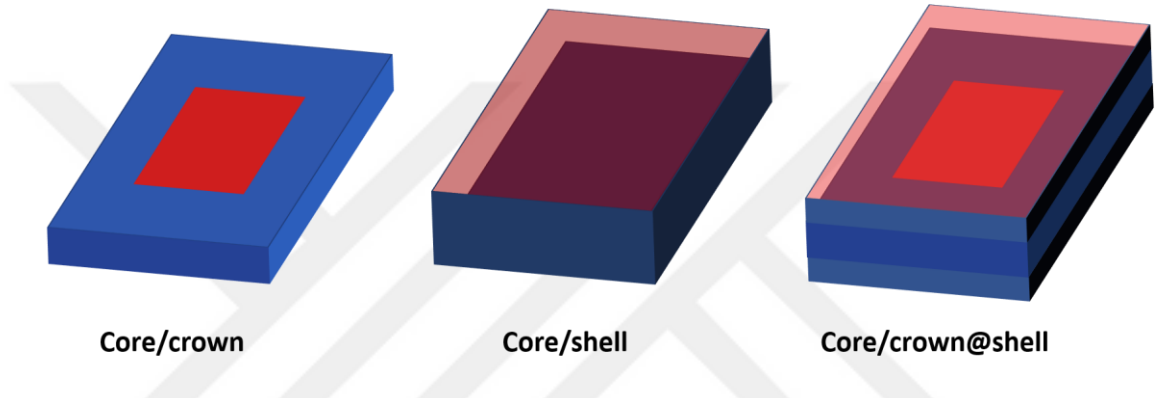


Figure 2.5: Schematic illustration of core/crown, core/shell core/crown@shell heterostructures of NPLs.

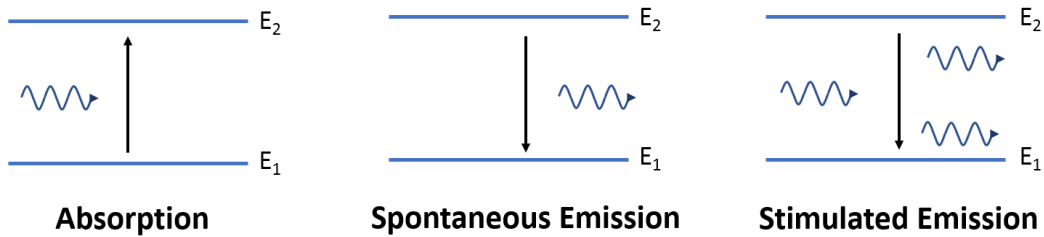


Figure 2.6: Schematics of the basic light-matter interactions for a two-level atomic system.

Three basic light-matter interactions might occur in an atomic system. Let's consider a two-level atomic system. If the system is excited by a photon with an energy larger than the energy difference between two states (correspondingly, the bandgap in semiconductors), atom will be excited to the upper state. This process is called upward transitions, leading to absorption (see Figure 2.6). Then, the excited atom in the upper state relaxes and turns back to the lower state. This relaxation (or recombination in semiconductors) can be radiative or nonradiative. In the radiative case, a photon will be emitted, and this process is known as spontaneous emission. However, this type of

emission is not coherent, which means that each of the emitted photons has a different direction and a different phase even though it has the same energy. On the contrary, in the stimulated emission case, if the emission is triggered with a photon having $h\nu_0$ energy, more than one photon with the same phase, direction and energy are emitted. This phenomenon is essential for achieving lasing action.

Now, let's elaborate these processes using the rate equations. The rate of change in the population of excited atoms in a two-level system is:

$$N_2' = -\frac{N_2}{\tau_{21}} \quad (2.5)$$

where N_2 is the number of excited atoms in the second level, N_2' is its time derivative and τ_{21} is the lifetime of this transition. In fact, this decay might be radiative or nonradiative. Thus, τ_{21} has both radiative and nonradiative components, and can be expressed as:

$$\frac{1}{\tau_{21}} = \frac{1}{t_{sp}} + \frac{1}{\tau_{nr}} \quad (2.6)$$

Here, t_{sp} is the spontaneous emission lifetime and τ_{nr} is the nonradiative emission lifetime. If we only consider the radiative part of the relaxation, we can rewrite Equation 2.6 for spontaneous emission case as:

$$(N_2')_{sp} = -\frac{N_2}{t_{sp}} \quad (2.7)$$

and the solution of this differential equation can be expressed as:

$$N_2(t) = N_2(0)e^{-\frac{t}{t_{sp}}} \quad (2.8)$$

Moreover, the spontaneous emission rate (P_{sp}) can be written as:

$$P_{sp} = \frac{1}{t_{sp}} = \frac{c}{V} \sigma_{21}(\nu) \quad (2.9)$$

where V is the volume of the optical resonator, c is the speed of light and $\sigma_{21}(\nu)$ is the transition cross-section. On the other hand, stimulated emission (absorption rate) is given as:

$$P_{st} (or P_{abs}) = n \frac{c}{V} \sigma_{21}(\nu) (or \sigma_{12}(\nu)) = \phi \sigma_{21}(\nu) (or \sigma_{12}(\nu)) \quad (2.10)$$

Here n is the number of photons, c is the speed of light, $\sigma_{21}(\nu)$ ($\sigma_{12}(\nu)$) is the stimulated emission (absorption) cross-section, and ϕ is the photon flux density. This expression is called as the rate of induced transition (W_i). In addition, these cross-sections can be related as follows:

$$\sigma_{12(21)}(\nu) = S_{12(21)} g_{12(21)}(\nu) \quad (2.11)$$

Here $S_{12(21)}$ is the transition strength and $g_{12(21)}(\nu)$ is frequency-dependent Lorentzian lineshape function.

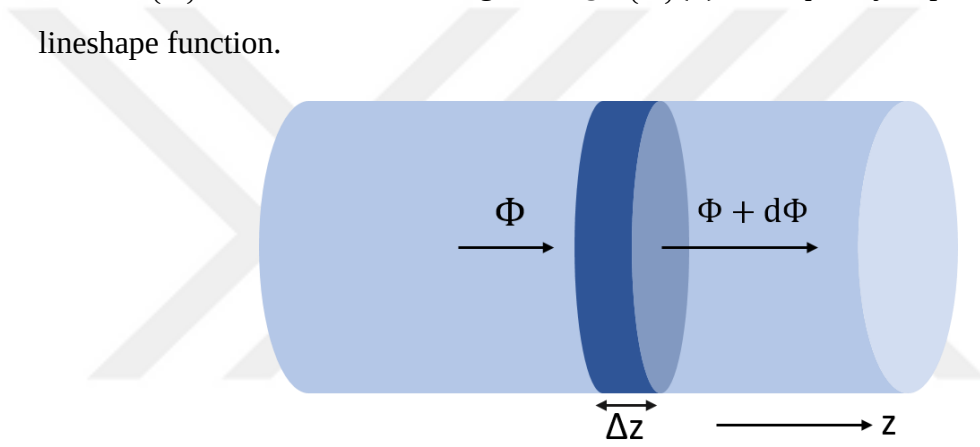


Figure 2.7: Photon flux in a medium along +z axis. Change in the flux in a volume with an infinitesimal length is defined as $d\Phi$.

Now let's consider a medium with a flux input of Φ as depicted in Figure 2.7. Depending on the states of atoms in the medium, the flux changes. In the case of optical absorption, flux will decrease along the way of propagation through the medium and $d\phi$ will be negative. If the absorption and stimulated emission rate are equal, no change happens in the flux, which is called as the transparency condition. Finally, the flux may be amplified through the propagation meaning the population of the excited atoms is larger than the population of ground state atoms. To quantify this net gain behavior, we can express the photon flux change along the z -axis as:

$$\frac{d\Phi}{dz} = (N_2 - N_1)\Phi\sigma(\nu) = N\Phi\sigma(\nu) \quad (2.12)$$

Here N is defined as the population difference between level-2 atoms (N_2) and level-1 atoms (N_1). Positive N ($N_2 - N_1$) means that the population inversion condition is satisfied, and the medium induces net optical gain. Solution of Equation 2.12 gives space depending behavior of the photon flux as:

$$\Phi(z) = \Phi(0)e^{N\sigma(\nu)z} = \Phi(0)e^{g_{mat}(\nu)z} \quad (2.13)$$

where $N\sigma(\nu)$ expression is defined as the gain coefficient of material ($g_{mat}(\nu)$). However, for most of the cases, spatial distribution of the flux does not entirely fall inside the gain medium within the cavity. To take into account incomplete overlap, the material gain coefficient requires a correction factor for the fractional confinement leakage as:

$$g_{modal}(\nu) = \Gamma g_{mat}(\nu) \quad (2.14)$$

Here g_{modal} is the measurable modal gain coefficient of medium and Γ is the confinement factor of the optical mode inside the cavity, which is defined as:

$$\Gamma = \frac{\int_{-V}^{+V} |\bar{E}|^2 d\nu}{\int_{-\infty}^{\infty} |\bar{E}|^2 d\nu} \quad (2.15)$$

where V is the volume of the cavity. It is worth noting that Γ can only take values between 0 and 1.

Upon optical excitation, semiconductors generate electron and hole pairs instead of excited atoms. On the other hand, for quantum confined semiconductor NCs, electron and hole form bounded pairs known as excitons. In fact, NCs are highly promising for optical gain studies due to their spectral tunability ranging from ultraviolet to infrared spectrum [7]. However, their optical gain performance is critically limited by the dominant nonradiative Auger recombination [49]. This very rapid process (typically with a lifetime of ~ 100 ps) annihilates the biexcitons (see Figure 2.8). Instead of emitting a photon, the energy of recombination is transferred to a third (hole or electron) carrier to generate a hot carrier. Then, this hot carrier relaxes via carrier-phonon interactions. Thus, it is

significantly important to suppress this Auger recombination to achieve high-performance optical gain behavior among NCs.

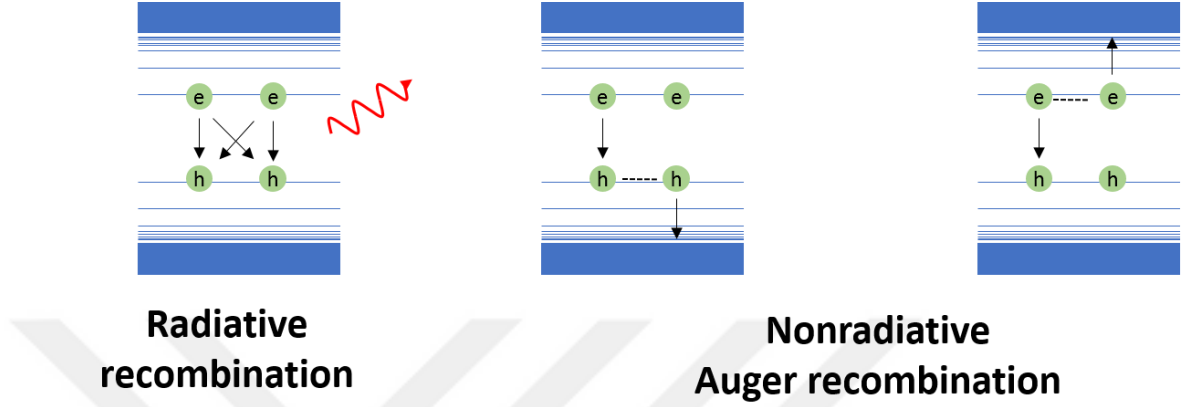


Figure 2.8: Radiative recombination and nonradiative Auger recombination of biexcitons. In the latter case, the exciton energy is transferred to a third carrier, and then is lost through lattice vibrations.

2.2 Optical Resonators

In this section, we will briefly discuss the basics of the optical resonators including Fabry-Perot and ring resonators. In addition, we will explain the physics behind some specialized resonators, which were used throughout in this thesis study. Optical resonators are the optical analogues of electronic resonating circuit. They store and confine the electromagnetic radiation, by reflecting it back and forth at specific frequencies. Owing to the configurability of their resonance frequencies, they might be used as optical filters as well. Optical resonators are essential components of the lasers since they provide optical feedback for stimulated emission.

2.2.1 Fabry-Perot Resonator

An ideal Fabry-Perot resonator consists of two reflecting parallel mirrors, which are placed as depicted in Figure 2.9. Electromagnetic wave (light) bouncing back and forth from these partial mirrors determines the resonant frequencies of the standing wave along with its spatial distribution within the cavity.

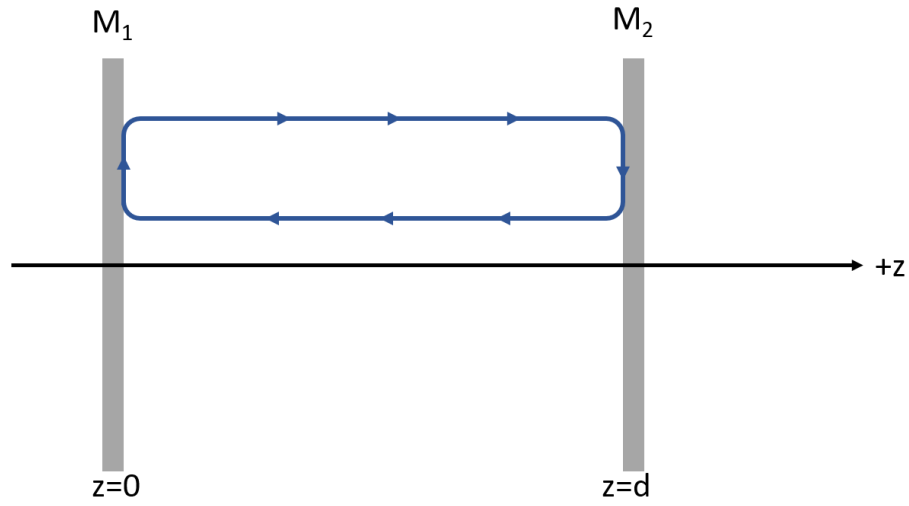


Figure 2.9: Schematic illustration of a Fabry-Perot resonator with two reflecting flat mirrors.

In fact, the reflecting surfaces do not have to be planar. They can be spherical (concave or convex) to support specific modes (*e.g.*, Gaussian beams). To comprehend the nature of a Fabry-Perot resonator, let's analyze the behavior of the circulating light within it. Since light is an electromagnetic wave, its nature is governed by Maxwell equations. Here let us consider the following wave equation as a simplified version of Maxwell's equation:

$$\nabla^2 u - \frac{1}{c^2} \frac{\partial^2 u}{\partial t^2} = 0 \quad (2.16)$$

Here u is a scalar wavefunction, c is the speed of light and ∇^2 is the Laplacian operator. A possible solution of Equation 2.16 is a sinusoidal wave given as follows:

$$u(z, t) = A(z) \cos(2\pi\nu t + \phi) \quad (2.17)$$

Since there is no nonlinear component within the system, we can express u in its phasor domain as:

$$u(z, t) = \text{Re}\{U(z)e^{j2\pi\nu t}\} \quad (2.18)$$

Substituting Equation 2.18 into 2.17 yields the time independent Helmholtz equation as follows:

$$\left(\nabla^2 + \left(\frac{2\pi\nu}{c}\right)^2\right) U(z) = 0 \quad (2.19)$$

Solution of this equation can take the following form:

$$U(z) = A_1 \sin(\alpha z) + A_2 \cos(\alpha z) \quad (2.20)$$

Replacing this expression to Helmholtz equation yields $\alpha = \frac{2\pi\nu}{c}$. Moreover, the solution should satisfy the boundary conditions of $U(z = 0) = 0$ and $U(z = d) = 0$. Hence, these boundary conditions yield $A_2 = 0$ and, U must satisfy:

$$U(z = d) = A_1 \sin(\alpha d) = 0 \quad (2.21)$$

To satisfy both Equation 2.21 and Helmholtz equation, α should be:

$$\alpha = \frac{\pi q}{d} = \frac{2\pi\nu}{c} \quad (2.22)$$

where q is an integer number. Equation 2.22 gives us the allowed modes of a Fabry-Perot cavity as:

$$\nu_q = \frac{c}{2d} q \quad (2.23)$$

Hence, a Fabry-Perot resonator can only support the discrete frequencies that satisfy Equation 2.23 by forming standing wave patterns within the cavity mirrors. It is worth noting that it is required to overlap the spectral band of the gain medium with the supported modes of the Fabry-Perot cavity to possibly construct a laser from it.

The reflectivity of the mirrors is significantly important for the quality a Fabry-Perot cavity. Most of the daily mirrors use aluminum or silver coating to create the reflection. However, those metal layers are highly lossy in the visible regime, decreasing the quality factor (Q-factor) of the resulting cavity. Thus, it is required to construct a low-loss mirrors to use in Fabry-Perot cavities. Distributed Bragg reflectors (DBRs) are excellent candidates for this purpose. Alternating layers of dielectrics are coated to fabricate DBRs. The illustration of a 3-bilayer DBR is depicted in Figure 2.10. For convenience, quarter-wave dielectrics are usually chosen to fabricate DBRs.

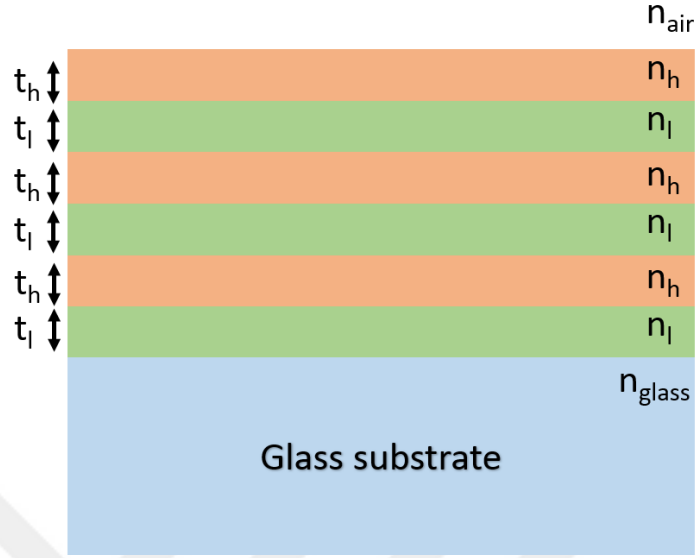


Figure 2.10: Structure of a 3-bilayer distributed bragg reflector (DBR) fabricated over a glass-substrate.

The thickness of high (n_h) and low (n_l) refractive index medium may be chosen to be quarter-wavelength within that medium. Quantitatively, their thicknesses are then set to $t_h = \frac{\lambda_0}{4n_h}$ and $t_l = \frac{\lambda_0}{4n_h}$. Here n_h is the high dielectric medium, n_l is the low-index dielectric medium and λ_0 is the desired operating wavelength. Through the back and forth propagation in $\lambda/4$ thicknesses, wave accumulates π phase. In addition to that, each reflection from low to high index adds π phase too. Hence, the reflections from each interface constructively interfere and collectively a high reflection from the overall structure can be achieved. The reflection of an m-bilayer DBR can be calculated as: [50]

$$R = \left[\frac{n_{air}(n_2)^{2N} - n_{glass}(n_1)^{2N}}{n_{air}(n_2)^{2N} + n_{glass}(n_1)^{2N}} \right]^2 \quad (2.24)$$

The experimental reflection result of a fabricated DBR, at 645 nm, on a quartz substrate is shown in Figure 2.11, where 11-bilayer of SiO₂ (n=1.46) and Si₃N₄ (n=2.04) are deposited.

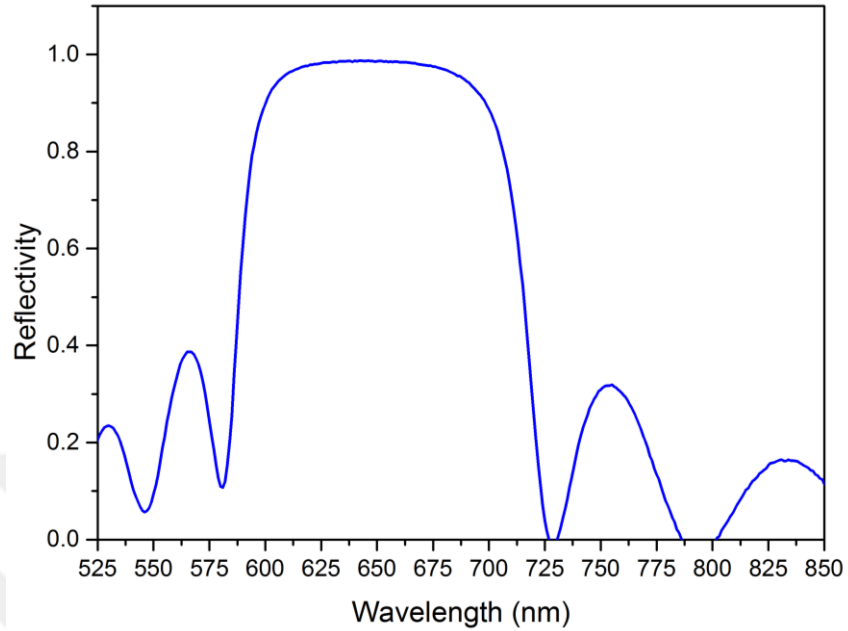


Figure 2.11: Reflectivity of 11-bilayer $\text{SiO}_2\text{-Si}_3\text{N}_4$ distributed bragg reflector (DBR) fabricated over a quartz substrate.

2.2.2 Ring Resonator

Ring resonators confine the light by waveguiding or reflecting it through their structures. Apart from Fabry-Perot cavities, optical isolators can be placed within them to inhibit one component of the standing waves. This prevents the formation of standing waves, and they can be designed to support only traveling waves. For that reason, they are also called as travelling-wave resonators.

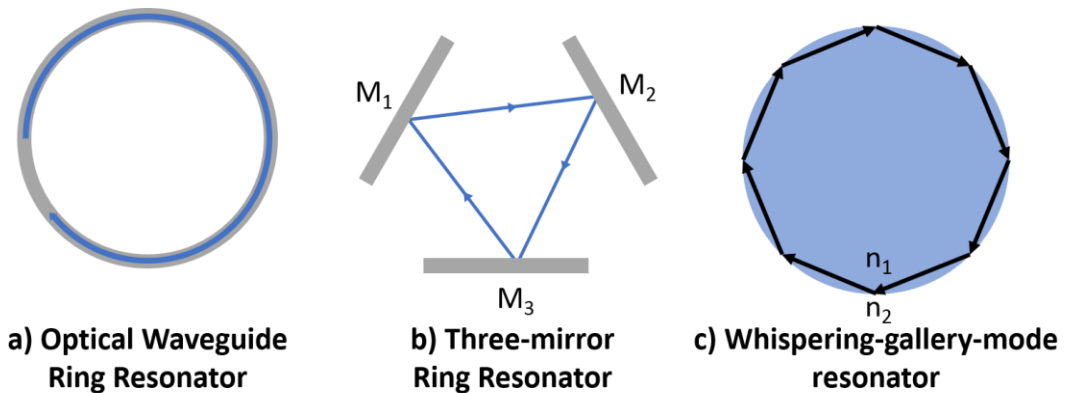


Figure 2.12: Schematics of a) an optical waveguide resonator, b) a three-mirror ring resonator, c) a whispering-gallery-mode (WGM) resonator.

Various types of ring resonators can be constructed. Three common examples, which are in the forms of an optical waveguide ring resonator, a three-mirror ring resonator and a whispering-gallery-mode (WGM) resonator, are provided in Figure 2.12. Since they support only their resonant frequencies, they may be used as optical filters (*e.g.*, by coupling them to nearby optical fibers).

The allowed wavelengths of a ring resonator are directly related to the optical path that light takes in one round around the cavity. For example, for an optical waveguide ring resonator, the resonant wavelengths can be calculated as:

$$m\lambda_m = 2\pi nR \quad (2.25)$$

Here m is the mode number, λ_m is the wavelength of the m^{th} mode, n is the refractive index, and R is the radius of the cavity.

WGM resonators make a special type of ring resonators that can support whispering gallery modes. The first discussions on WGMs date back to early 1900s, where the propagation of sound waves was examined on a curved gallery of a cathedral [51]. In the last decades, WGM-based resonators have attracted great attention in photonics for their low loss and high-Q natures. In order to support WGMs, the electromagnetic wave should be able to perform total internal reflection at the outer interface of the cavity. Thus, the refractive index of the cavity medium should be higher than the outer media. Since they follow the physics of ring resonators, their resonance frequencies can be calculated *via* Equation 2.25. Schematic illustration of a typical WGM resonator is given in Figure 2.12c, where the refractive index of cavity (n_1) is higher than outer medium (n_2). Owing to their superior optical properties, WGM resonators have been used in various applications including biosensors [52], optofluidic lasers [53] and opto-electronic oscillators [54].

Chapter 3

Experimental Methods

In this chapter, we will explain the characterization techniques that are used to study optical and structural properties of colloidal NPLs.

3.1 Steady-State Absorption Spectroscopy

Steady-state absorption spectroscopy is a powerful technique to characterize the thickness and structure of NPLs. Figure 3.1a illustrates the working principle behind the absorption spectroscopy. A broadband source (white light) is used along with a rotating diffraction grating to excite samples at the desired wavelength. Moreover, a small slit is placed to select only a specific wavelength. The whole system acts as a monochromator that sweeps the excitation wavelength from UV to visible region of electromagnetic spectrum by rotating the diffraction grating. Then, the light is transmitted through our sample inside the quartz cuvette, which is dissolved in a suitable solvent (*e.g.*, hexane, toluene, water). Some portion of the light is absorbed, and transmitted light is collected *via* a photodetector.

To analyze the data, the collected transmitted light is compared with a reference, which is obtained by a cuvette filled by solvent without any nanocrystals. An important point to

note that if the NC dispersion is concentrated, absorption and transmission are not the only possible interactions. Scattering and reflection might occur as well. To neglect these effects, the solution of NCs should be diluted enough. Hence, throughout the system, the measured change in the optical transmission is attributed to absorption with the following equation:

$$\Phi_{tr}(\lambda) = \Phi_{exc}(\lambda)10^{-A(\lambda)} \quad (3.1)$$

Here Φ_{tr} is the transmitted light, Φ_{exc} is the excitation light and $A(\lambda)$ is the absorbance. In addition to that, according to the Beer-Lambert Law, absorbance can be expressed as:

$$A = \varepsilon cL \quad (3.2)$$

where ε is the molar extinction coefficient (L/mol cm), c is the concentration of NCs (mol/L) and L is the width of our cuvette (cm). An exemplary absorbance data of 4 ML CdSe NPLs is depicted in Figure 3.1b.

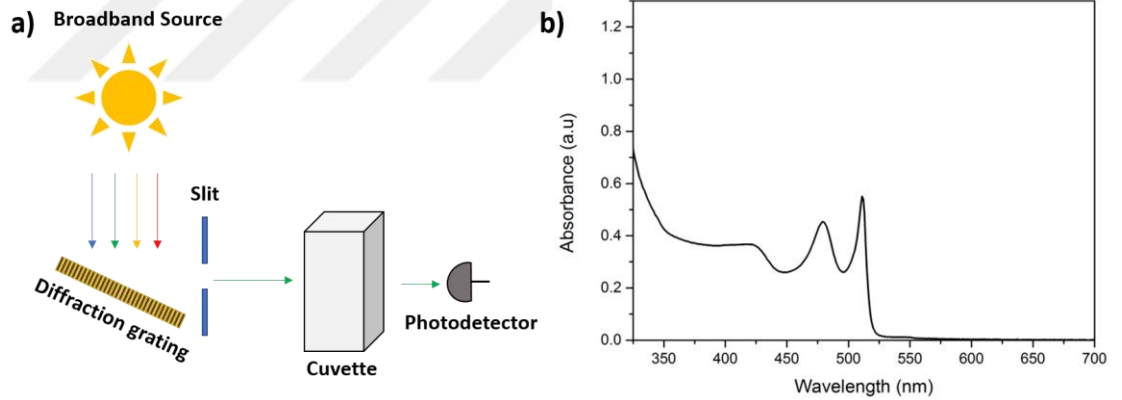


Figure 3.1: a) Schematic of the experimental setup behind steady-state absorption spectroscopy. b) An exemplary absorbance spectrum of 4 ML thick CdSe core NPL dissolved in hexane.

Since optical properties of NPLs are strongly size-dependent, absorption spectroscopy is used to determine the thickness of NPLs after their synthesis. Moreover, formation of heterostructures can be also verified by this method. For instance, it is expected to observe a red-shift in the excitonic features of the absorption spectrum if CdS shell is coated around a CdSe core. Hence, the absorption spectrum helps us to understand and estimate the formation and thickness of the heterostructures.

3.2 Steady-State Photoluminescence Spectroscopy

Complementing absorption spectroscopy, steady-state photoluminescence (PL) spectroscopy is also an important characterization technique for colloidal NCs. Its setup typically consists of two monochromators. Similar to absorption spectroscopy, the first one is used for excitation purpose. Following the optical excitation, spontaneous emission of the NCs is collected *via* the second monochromator. The schematic showing the experimental setup of photoluminescence spectroscopy is given in Figure 3.2a. Spontaneous emission of the NPLs exhibits thickness dependent characteristics. 5 ML thick CdSe core has a photoluminescence emission peak centered at ~553 nm, while 4 ML and 3 ML thick CdSe cores have photoluminescence emission at ~513 and ~465 nm, respectively. Thus, by examining the photoluminescence spectrum of an NPL solution, the thickness of the NCs can be determined. An example case showing the photoluminescence spectrum of 4 ML thick CdSe core NPLs is shown in Figure 3.2b.

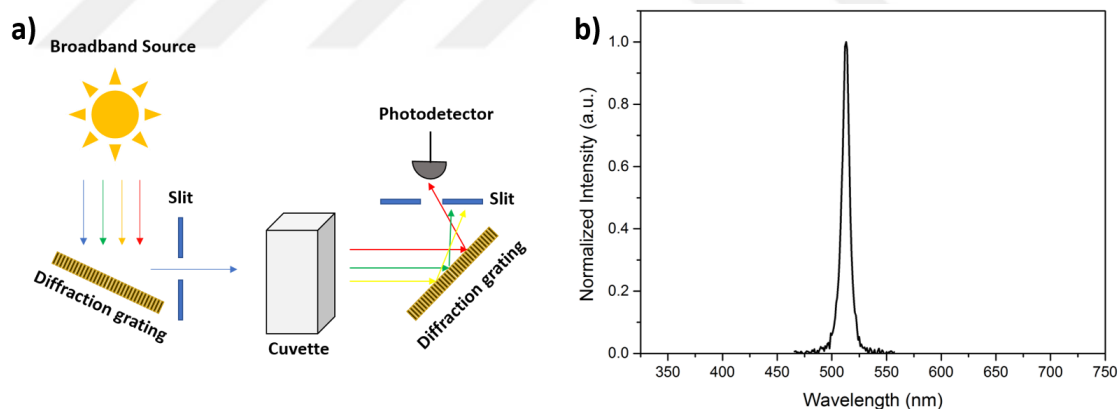


Figure 3.2: a) Schematic of the experimental setup behind steady-state photoluminescence spectroscopy. b) An exemplary photoluminescence spectrum of 4 ML thick CdSe core NPL dissolved in hexane.

3.3 Electron Microscopies

Although optical microscopy is a robust and reliable imaging technique, its resolution is limited by the optical diffraction. Considering a visible light at 400 nm, the resolution (R) of an optical microscope can be at most 200 nm by using the rough relation of $R=\lambda/2$. Hence, to resolve features smaller than this limit, electron beams are utilized. Electrons

accelerated under high voltage can have De-Broglie wavelength around a few nanometers and thus can be used to image nanocrystals.

Scanning electron microscopy (SEM) is a strong method that is used to image in μ -meter range. A highly focused electron beam is used to scan the surface. Backscattered and secondary electrons are collected to obtain the material information and to construct the image. An example SEM image of a bare fiber with 250 μ m diameter is given in Figure 3.3a. Transmission electron microscopy (TEM) is also a powerful tool to characterize shape, structure and size of nanocrystals. Moreover, TEM can be used to determine the crystalline structure of NCs. In this thesis, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was commonly used to image our 10-40 nm NPLs. An exemplary HAADF-STEM image of core/crown@shell NPLs is shown in Figure 3.3b.

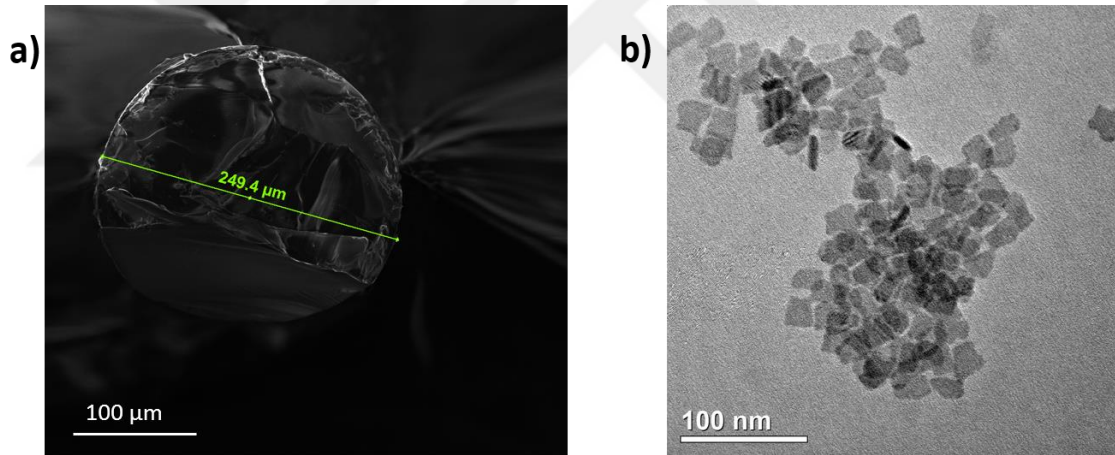


Figure 3.3: a) SEM image of a SiO₂ fiber with 250 μ m diameter. b) HAADF-STEM image of CdSe/CdS@Cd_{1-x}Zn_xS core/crown shell NPLs.

3.4 Optical Gain Measurements

3.4.1 Optical Gain Threshold Measurement

Amplified spontaneous emission (ASE) can be observed in colloidal NCs when they are excited with a pulsed laser with high enough pump fluences. ASE occurs when the population inversion condition in the semiconductor material is satisfied, meaning that optical gain threshold is exceeded. Hence, the presence of ASE is a must to achieve lasing

in nanocrystals, and the ASE performance is directly related to the lasing performance of a gain medium. Schematic illustration of the experimental setup for ASE measurement is shown in Figure 3.4

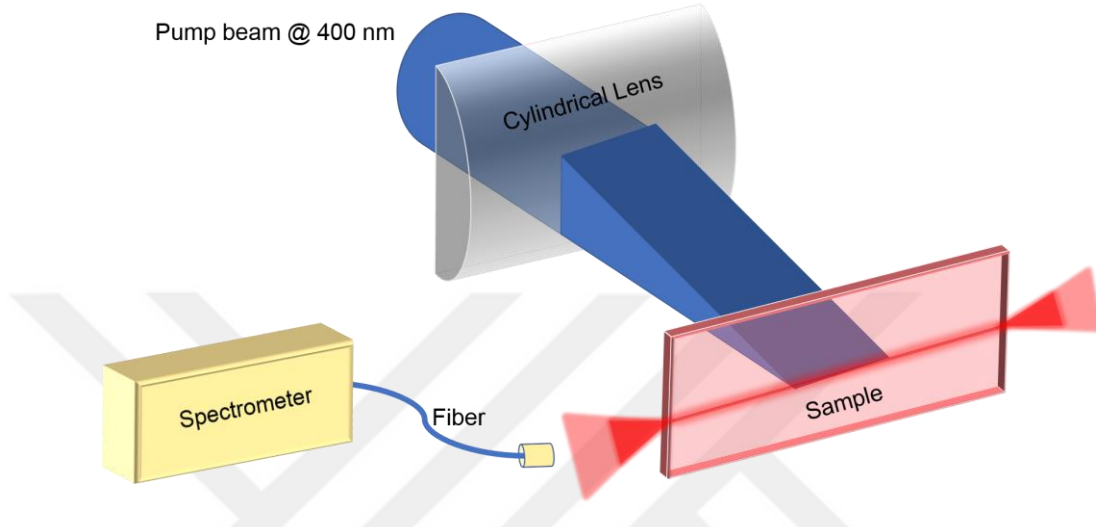


Figure 3.4: Schematic of experimental setup to measure ASE spectrum of NCs.

To characterize the ASE performance, NPLs are usually drop-casted or spin-coated on a quartz substrate. Then, the samples are excited with a stripe-shaped pulsed laser beam. As a result of the internal reflection between the NPL film and upper surface of the quartz substrate, waveguiding effect occurs, which guides the emission to the edge of the sample. This emission is then collected with a fiber connected to a spectrometer.

As previously mentioned, nonradiative Auger recombination is the rapid process that annihilates biexcitons. Hence, it is required to generate biexcitons before Auger recombination takes place. To ensure this, we use Spectra Physics (Spitfire Pro XP) laser with 120 fs pulse width and 1 kHz repetition rate at 800 nm as an optical pumping source. For one-photon absorption (1PA) regime, frequency is doubled via a BBO (beta barium borate) crystal and the remaining of 800-nm beam is filtered out by employing a bandpass filter. To adjust the amplitude of pump fluences, a rotatable ND (neutral density) filter is placed right before the BBO crystal. Finally, the stripe shape is achieved by using a cylindrical lens. Emission of the sample is collected by using Maya2000 Pro spectrometer. Photograph of the experimental setup used for our ASE measurements is given in Figure 3.5.

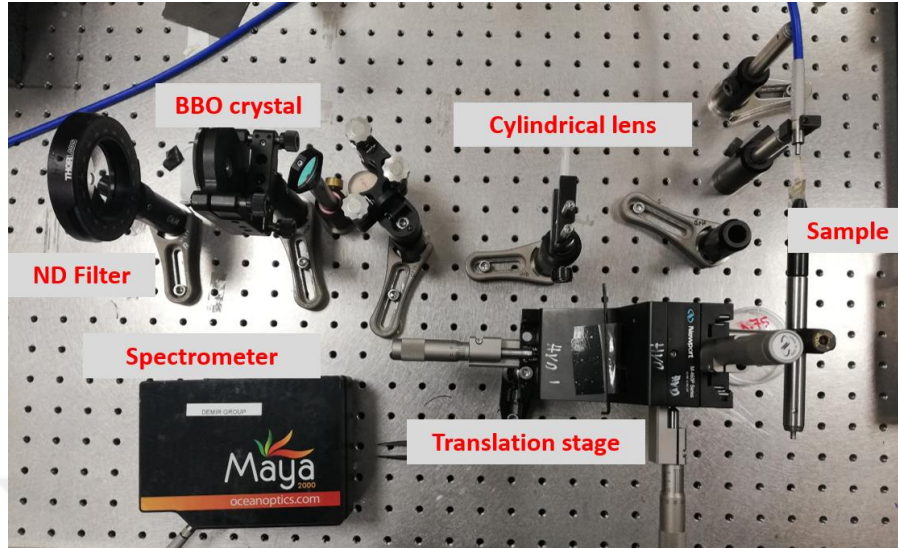


Figure 3.5: Experimental optical setup for ASE measurement under one-photon absorption.

Figure 3.6a depicts exemplary emission spectra of CdSe/Cd_{0.25}Zn_{0.75}S core/shell NPLs under one-photon absorption. As pump intensity is increased, a transition from spontaneous emission to ASE occurs with a narrow red-shifted emission after the optical gain threshold. To quantify the exact threshold, integrated intensity of the emission is plotted as a function of the pump intensity as given in Figure 3.6b. After the optical gain threshold (2.45 $\mu\text{J}/\text{cm}^2$ in this case), ASE starts to dominate overall emission with a super linear increase in the integrated intensity.

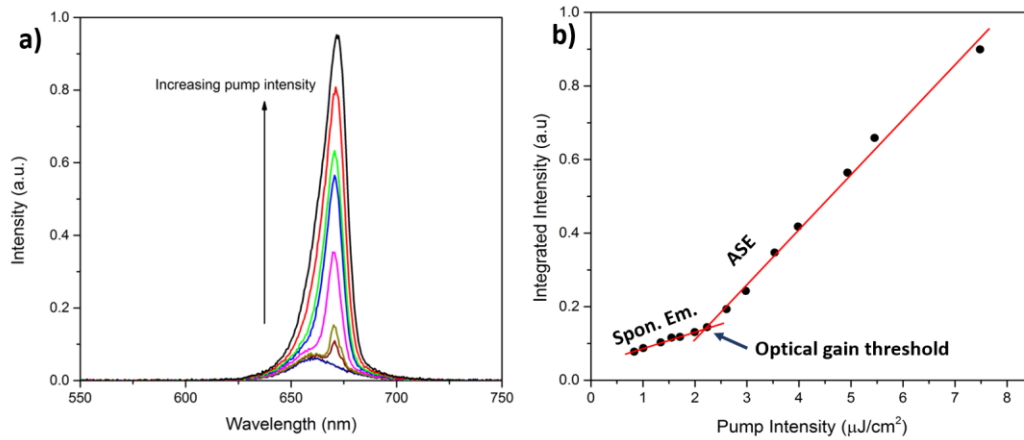


Figure 3.6: a) Exemplary emission spectra of CdSe/Cd_{0.25}Zn_{0.75}S core/shell NPLs under one-photon absorption. b) Exemplary integrated intensity of CdSe/Cd_{0.25}Zn_{0.75}S core/shell NPLs showing the optical gain threshold.

3.4.2 Variable Stripe Length Measurement

We employed variable stripe length (VSL) measurement to characterize the net peak modal gain coefficients of colloidal NPLs. Similar to the optical gain threshold characterization technique, we excite our samples with a stripe-shaped femtosecond laser beam with a pump intensity larger than ASE threshold. However, in this case, an adjustable slit is placed right before our samples as can be seen in Figure 3.7a. By increasing the length of the excitation stripe, emission spectra of an NPL-coated quartz sample are collected. After a certain stripe length, ASE peak starts to appear, resulting in an exponential increase in the integrated intensity data. An exemplary VSL measurement data is plotted in Figure 3.7b.

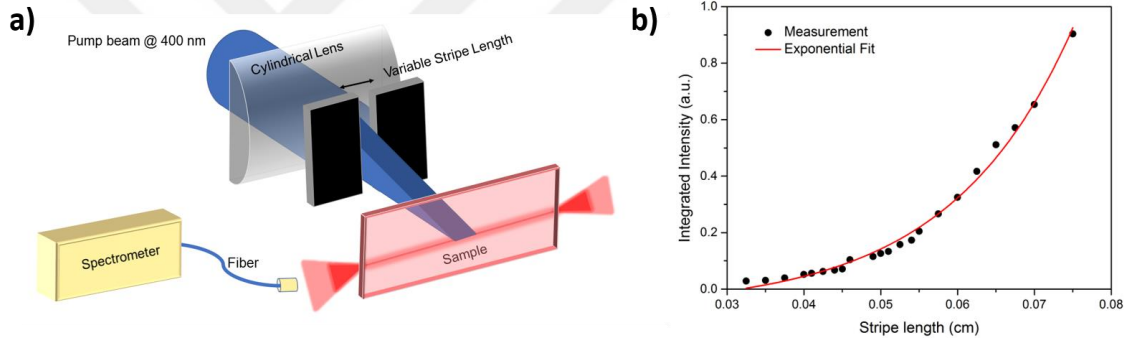


Figure 3.7: a) Schematic of the experimental setup of variable strip length measurement. b) Exemplary VSL data after measurement showing the exponential fit.

Then, to quantify net modal gain coefficients, empirical data is fitted to the following equation:

$$I(l) = \frac{I_s}{G} (e^{Gl} - 1) \quad (3.3)$$

where $I(l)$ is the integrated intensity, G is the net modal gain coefficient, l is the stripe length and I_s is a constant. By this fit, one G value for a specific pump intensity can be obtained. Later, this measurement is repeated for various pump intensities and multiple G values are obtained. Finally, G is plotted as a function of the pump intensity. As the pump intensity is increased, G increases as well. However, a saturation of the net modal gain of the NPLs is observed as the pump intensity is further increased. Such gain saturation is a typical characteristic seen in all gain materials.

3.4.3 Waveguide Loss Coefficient Measurement

Measurement of waveguide loss coefficients is frequently used for optical gain characterization. Since amplified spontaneous emission is waveguided through the edge of the sample, a waveguiding loss (α) attenuates this emission during the propagation. To measure this coefficient, the sample along with fiber is connected to a high precision translation stage. Then, the sample and the fiber are moved together on an axis perpendicular to the optical excitation axis. Hence, the distance between the edge of the sample and the stripe is changed. After a certain distance, an unexcited part on the sample is revealed, where ASE intensity is attenuated *via* waveguide loss. This intensity is collected from the edge and plotted as a function of the distance from the edge of the sample. The schematic showing this measurement is given in Figure 3.8.

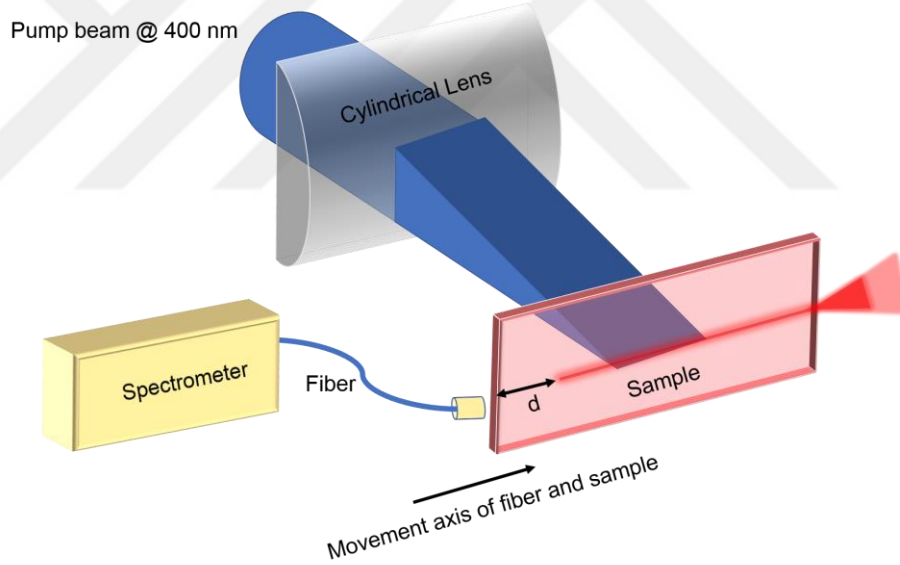


Figure 3.8: Schematic of the experimental setup to measure waveguide loss coefficient.

Then, the obtained data is fitted to the following expression to quantify α :

$$I(l) = I_p e^{-\alpha d} \quad (3.4)$$

where I_p is the peak ASE intensity, α is the waveguide loss coefficient, and d is the distance between the edge of the sample and the end of excitation beam.

Chapter 4

Whispering-gallery-mode Laser Colloidal Nanoplatelets

This chapter is based on our manuscript **M. Sak**, N. Taghipour, S. Delikanli, S. Shendre, I. Tanriover, Y. Gao, J. Yu, Z. Yanyan, S. Yoo, C. Dang, H. V. Demir, in submission (2019).

4.1 Motivation

Colloidal semiconductor nanocrystals recognized as promising candidates for optical gain studies [26], [55], [56] owing to their cost-effective synthesis and solution processable nature. Moreover, they can be spectrally tuned by modifying their size, shape and composition [57]. Up to now, different classes of NCs including colloidal quantum dots [55], colloidal quantum wells [35] and nanorods [58] have been studied for optical gain and lasing applications. Colloidal quantum wells, or semiconductor nanoplatelets (NPLs), earn an incomparable spot among these NCs thanks to their large absorption cross-sections [22], fully homogeneous broadening [24], huge oscillator strength [21], and large optical gain coefficients [23]. Moreover, by utilizing heterostructures including core/shell [28], [33] and core/crown [31], [32], the excitonic properties of NPLs can be adjusted to achieve

high performance in optical gain. To date, different heterostructures of NPLs used as gain medium coupled to various optical resonators including photonic-crystal nanobeam cavities [59], vertical-cavity surface-emitting lasers [35], and multiphoton-pump Fabry-Pérot cavities [60].

Lately, whispering-gallery-mode resonators have emerged as a promising optical resonator thanks to their very low optical losses [36]. As a result of cutting-edge nanofabrication technologies, various forms of WGM cavities were made including micro rings [61], micro disks [62] and micro spheres [63]. As a practical WGM resonator, fiber-based structures have been utilized for lasing in the solution phase of various materials such as nanorods [36], colloidal quantum dots [53] and dyes [64]. Nonetheless, the performances of these structures are mostly limited as a result of the low packing-density of the gain media. This causes poor lasing stability, high optical gain and lasing thresholds. To address these issues, close-packed films of nanocrystals can be used in fiber-based WGM resonators as a gain medium.

Here, we propose and demonstrate a fiber-based WGM laser made of close-packed NPLs films which addresses the issues of instability and large lasing thresholds by the first WGM-NPL lasing structure. We show ASE and lasing from close-packed films of core/crown/gradually-alloyed-shell (CCGAS) NPLs coated around fibers under one-photon- (1PA) and two-photon-absorption (2PA) regimes. The laser cavity is made of a unique fiber-based WGM resonator. To do so, we integrated bare glass fibers with close-packed CCGAS NPLs films by utilizing adhesion. Then we systematically investigated their 1PA and 2PA ASE performances using two different fiber diameters (125 μm and 250 μm). A record low waveguide loss coefficient ($\sim 7.1 \text{ cm}^{-1}$) and high net modal gain coefficient ($\sim 485 \text{ cm}^{-1}$) were achieved by this novel structure, resulting in low ASE thresholds of $\sim 90 \text{ }\mu\text{J}/\text{cm}^2$ and $\sim 3.0 \text{ mJ}/\text{cm}^2$ for 1PA and 2PA regimes, respectively. Moreover, we demonstrated an NPL-WGM laser with $\sim 190 \text{ }\mu\text{J}/\text{cm}^2$ lasing threshold under 1PA pumping with a linearly polarized emission that has a stable emission under 150 minutes of optical excitation.

4.2 Experiments

4.2.1 Precursor Preparation

Cadmium precursor (cadmium myristate) was synthesized according to a previous article [32]. 3.13 g of Na myristate and 1.23 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 250 and 40 mL methanol, respectively. After that, the solution was stirred for three hours. Then, the white powder was collected and washed by methanol to wipe out the remaining unreacted precursors. After three consecutive washing process, the powder was left in vacuum for twelve hours to dry.

4.2.2 Colloidal Synthesis of 4 ML CdSe NPLs

To synthesize 4 ML thick CdSe core NPLs, a recipe from a previous publication was followed with some slight changes [32]. Inside a three-neck glass flask, 28 mL of octadecene, 26 mg of Se and 340 mg of cadmium myristate was placed. Then, this mixture was kept under vacuum for 30 minutes at room temperature. After that, the solution was heated up to 240 °C within inert gas environment. At 200 °C, 140 mg of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was injected to this solution. After reaching the temperature of 240 °C, the solution was kept at this temperature for 180 seconds. Then, 1 mL of oleic acid was injected to the solution and the temperature is decreased to room temperature. Finally, ethanol and hexane were added to precipitate CdSe NPLs, which were then dissolved and kept within the hexane.

4.2.3 Preparation of CdS Crown Growth Solution

To prepare the growth solution, we followed a slightly changed recipe from a previous publication [32]. 8 mL of octadecene, 680 µL of oleic acid and 960 mg of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were put into a glass beaker. Then, this solution was sonicated for 60 minutes. After that, the temperature was raised to 180 °C and frequently sonicated while stirring to obtain a whitish gel. Finally, 6 mL of 0.1 M S-octadecene was added to cadmium precursor for the crown growth.

4.2.4 CdSe/CdS Core/Crown NPL Synthesis

To synthesize CdSe/CdS core/crown NPLs, a recipe from previously published article was followed after some slight changes [32]. 15 mL of octadecene and 4 mL thick CdSe NPLs dissolved in hexane were placed into a glass flask. Then, this solution was left under vacuum at a temperature of 80 °C to evaporate hexane. Under inert atmosphere, the solution was heated up to 240 °C and anisotropic growth mixture was injected with a rate of 10 mL/h. After that, we waited for NPLs to reach the desired crown size and we decreased the temperature to room temperature. As-synthesized core/crown NPLs were centrifuged for precipitation after adding ethanol. Finally, by using methanol and ethanol, NPLs were washed three times to eliminate excess precursors and obtained NPLs were dissolved in hexane.

4.2.5 CdSe/CdS@Cd_{1-x}Zn_xS Core/Crown/Shell NPL Synthesis

For this, a published recipe was followed with some slight modifications [33]. 0.4 M of Cd(NO₃)₂·4H₂O and 0.4 M of Zn(NO₃)₂·6H₂O solutions were prepared in N-methyl formamide. For S precursor, 40-48 wt% water-based solution of (NH₄)₂S was used. 40 µL of (NH₄)₂S was injected to 4 mL of N-methyl formamide along with 1 mL of CdSe/CdS core/crown NPLs under stirring. After 120 seconds, acetonitrile and toluene were added and NPLs were centrifuged. After that, NPLs were dissolved in N-methyl formamide (NMF) and this cleaning process was performed two more times to eliminate excess S precursors. Then, NPLs were dispersed in 4 mL of NMF. 1 mL solution of X% Cd(NO₃)₂ and (100-X)% of Zn(NO₃)₂ within NMF was added to these NPLs for cation deposition. Under ambient conditions, the solution was stirred for 45 minutes. Then, by adding acetonitrile and toluene, NPLs were precipitated. This cleaning process was undertaken two more times to separate unreacted cation precursors. This growth steps were then repeated to obtain desired number of shells. For the first Cd_{1-x}Zn_xS shell layer X value was selected as 50, while for the second and the third ones they were selected as 10 and 5, respectively. Finally, CCGAS NPLs were dissolved and kept in hexane.

4.2.6 Sample Preparation

We prepared highly concentrated solution of CCGAS ($\text{CdSe/CdS/Cd}_{1-x}\text{Zn}_x\text{S}$) NPLs in hexane to form close-pack high density films of these NPLs around glass bare fibers. 125- and 250- μm -diameter fibers were dipped into this concentrated solution. Afterwards, they were left there for 20-30 minutes. By the virtue of adhesion, NPLs were coated around both parts of the fibers, the part within the solution and the upper part remained above the solution.

4.2.7 Simulation Methodology

The full electromagnetic solution of the NPL-WGM resonator was conducted via a commercial FDTD software package (Lumerical Inc.). To model glass fiber, built-in SiO_2 in the software was used. Moreover, NPL film was modeled by a lossless dielectric medium with a refractive index of 1.8, which was obtained *via* ellipsometry. The modeled cavity was excited by a dipole source with an arbitrary phase and location inside the NPL region. The field and spectrum of the cavity were collected via 2D frequency-domain field and power monitors.

4.3 Results and Discussion

In this part of the thesis, by utilizing colloidal atomic layer deposition, 3 MLs of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ shells were grown onto 4 ML thick CdSe/CdS core/crown NPLs to realize $\text{CdSe/CdS/Cd}_{1-x}\text{Zn}_x\text{S}$ CCGAS NPLs [33]. Owing to this specially designed advanced hetero-NPLs, the electron wavefunction in the conduction band was subjected to a soft potential confinement in the shell direction, although the hole wavefunction in the valence band was confined in the CdSe core part. This delocalization of the carriers helps us build a quasi-type-II electronic band alignment as formerly shown in dot-in-rod nanocrystals [58]. Furthermore, it has been theoretically [65] and experimentally [66] demonstrated that the formation of soft potential confinement can be used to help suppress nonradiative Auger recombination. Thus, as a result of the smoothened potential barrier of our advanced NPLs, we further may effectively suppress the Auger recombination.

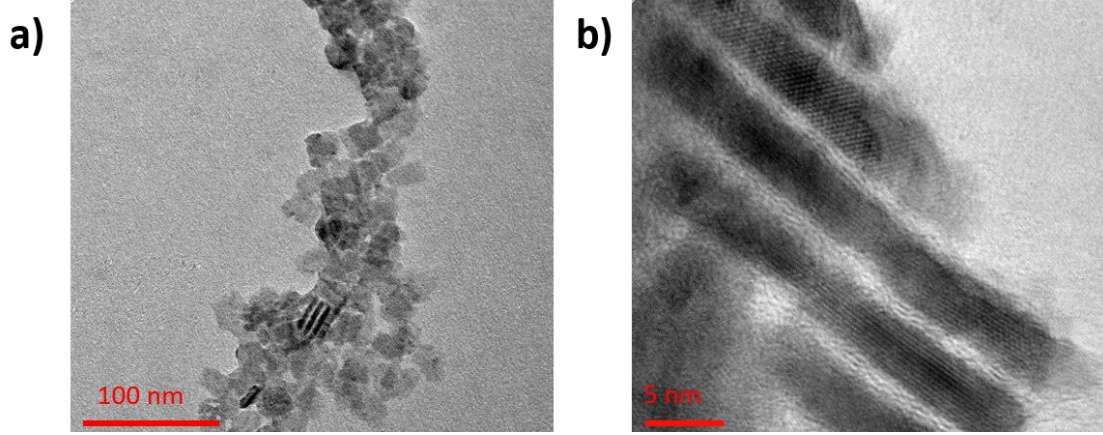


Figure 4.1: HAADF-STEM images of CCGAS NPLs with 3 monolayers of gradient alloy shell showing a) their lateral sizes and b) their vertical thicknesses.

HAADF-STEM (high-angle annual dark-field scanning transmission electron microscopy) images of our CCGAS NPLs are shown in Figure 4.1. Lateral size of our NPLs was $\sim 20\text{-}30$ nm, while their thicknesses were ~ 3.5 nm. In Figure 4.1b, formation of shells around the core can be seen.

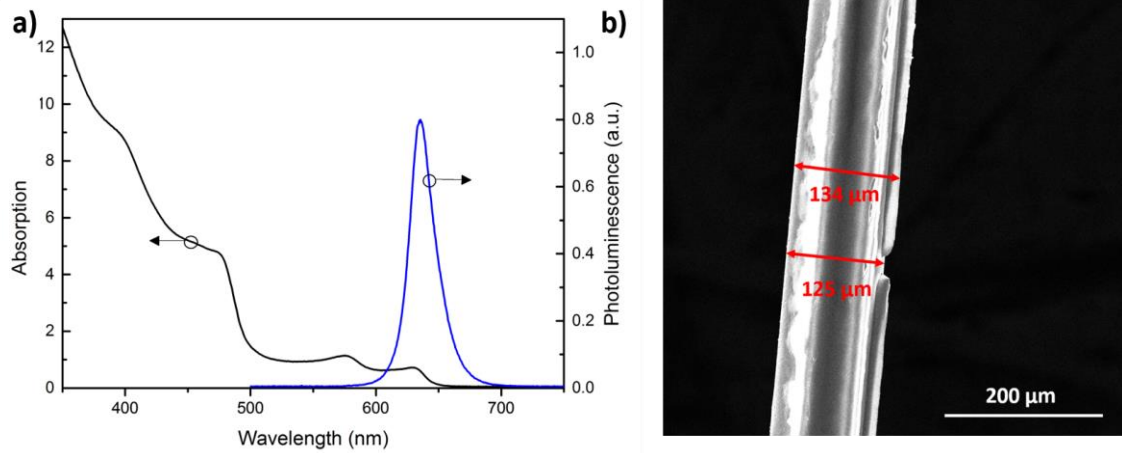


Figure 4.2: a) Absorption and PL spectra of our CCGAS NPLs. b) SEM image of the fiber showing the coating of NPLs with the film thickness.

For optical characterization of our hetero-NPLs, absorption and photoluminescence (PL) spectroscopies were used. Figure 4.2a shows the PL spectrum of the $\text{CdSe/CdS/Cd}_{1-x}\text{Zn}_x\text{S}$ CCGAS NPLs, which is centered at ~ 640 nm with a full-width-at-half-maximum (FWHM) of ~ 25 nm. The excitonic peaks appearing at 630 nm and 575 nm correspond to the upward heavy-hole and light-hole transitions, respectively, as given in absorption spectrum of Figure 4.2a.

To study the optical gain performance of our NPLs, we formed high-density close-packed films of our NPLs over two different sized fibers with diameters of 125 and 250 μm . To do so, tips of the bare fibers were plunged into high concentration hexane solution (60-70 mg/mL) of our NPL. Then, through adhesion, NPLs were coated around the fibers. Thanks to this simple and convenient technique, fiber-based NPL-WGM resonators were constructed. SEM image of the fiber with 125 μm diameter illustrates the film formation of NPLs with a thickness of ~ 9 μm as depicted in Figure 4.2b. Then, we studied ASE performance of these fibers under 1PA and 2PA pumping. For the optical excitation, a Ti:Sapphire mode-locked laser at 800 nm (1 kHz repetition rate, 120 fs pulse width) was used for 2PA-pumped analysis. However, for 1PA study, A BBO crystal was utilized for frequency doubling to obtain 400 nm optical excitation.

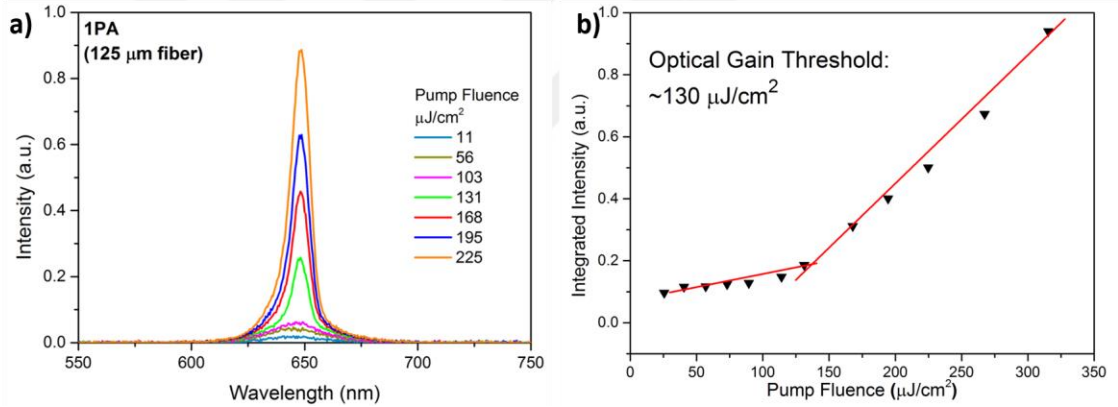


Figure 4.3: : For NPL-coated fiber with 125 μm diameter, a) emission spectra at various pump fluences, b) integrated intensity as a function of the pump fluence under one-photon absorption excitation.

Figure 4.3a illustrates the emission intensity of NPL-coated fiber with 125 μm diameter under 1PA pumping. As the pump fluence increases an abrupt increase in the spectrum can be observed, corresponding to an increase in the slope of integrated intensity vs. pump fluence, as can be seen in Figure 4.3b. The pump fluence where the ASE peak appears is called as ASE threshold. Hence, for 125 μm fiber, the ASE threshold was measured as ~ 130 $\mu\text{J}/\text{cm}^2$ under one-photon absorption regime. After this threshold, a narrowing in the PL spectrum can be observed.

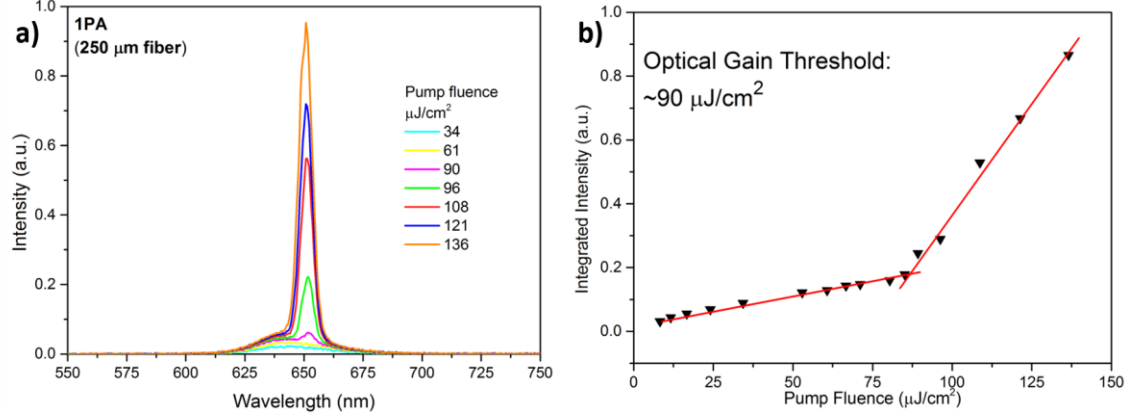


Figure 4.4: For NPL-coated fiber with 250 μm diameter, a) emission spectra at various pump fluences, b) integrated intensity as a function of the pump fluence under one-photon absorption excitation.

A similar analysis was also performed for the 250-μm-diameter fiber, similar to the previous one. After the ASE threshold a narrow peak emerged with a full-width-half-maximum (FWHM) of ~7 nm. For this case, optical gain threshold, where the population inversion condition is satisfied, was measured as ~90 μJ/cm², as can be seen in Figure 4.4.

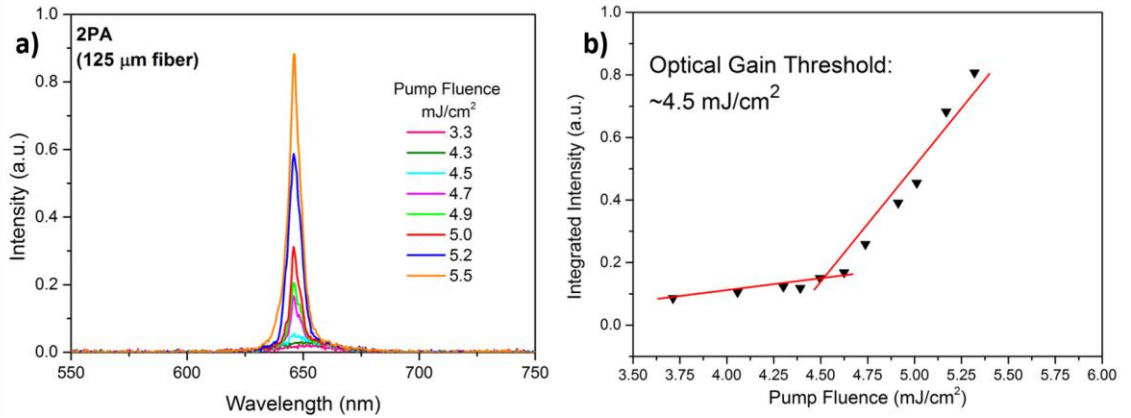


Figure 4.5: For NPL-coated fiber with 125 μm diameter, a) emission spectra at various pump fluences, b) integrated intensity as a function of the pump fluence under two-photon absorption excitation.

Furthermore, two-photon absorption (2PA) excited ASE performance of our NPL-coated fibers was investigated at 800 nm pumping. Figure 4.5a displays the luminescence spectra of the NPL-coated fiber with 125 μm diameter, where a spectral narrowing can be observed at elevated pump values. 2PA-pumped ASE threshold for this fiber was found as 4.5 mJ/cm², as can be seen in Figure 4.5b. It can be observed that below the ASE

threshold luminescence spectra consist of only spontaneous emission. However, after the ASE threshold, stimulated emission starts to overweigh in the spectrum. Finally, this ASE measurement was performed on a 250- μm -fiber under 2PA pumping. Figures 4.6a and 4.6b present the emission spectra for different pump fluences and the integrated intensity as a function of the pump fluences, respectively. The ASE threshold for the 250- μm -fiber under 2PA pumping was found as $\sim 3.0 \text{ mJ/cm}^2$. It can be observed that, as the diameter of the fiber increases, ASE threshold decreases for both 1PA and 2PA excitation. We attributed this improvement in the optical gain performance to the waveguide loss coefficients. Later in this chapter, we will analyze this behavior.

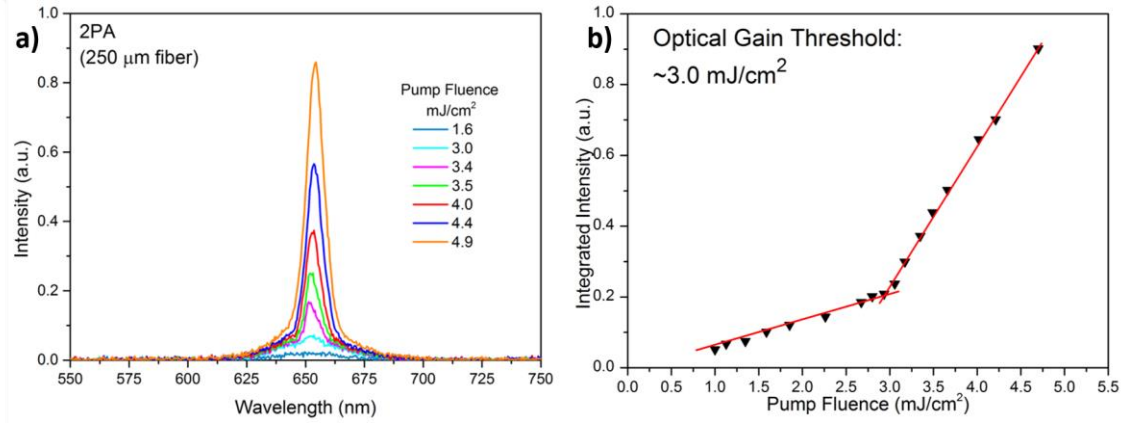


Figure 4.6: For NPL-coated fiber with 250 μm diameter, a) emission spectra at various pump fluences, b) integrated intensity as a function of the pump fluence under two-photon absorption excitation.

Furthermore, we performed variable stripe length (VSL) analysis to characterize net modal gain coefficients of our CCGAS NPLs. For this purpose, we recorded PL spectra of NPL-coated fiber with 250 μm diameter for different stripe lengths at an operating pump fluence larger than ASE threshold. Then, this measurement was repeated for various pump fluences. Figure 4.7 shows the integrated intensities as a function of the stripe lengths. After that, to quantify the net modal gain coefficients at a specific pump fluence, each of these exponentials is fitted to the expression given in Equation 4.1.

$$I(l) = \frac{I_{sp}}{G} (e^{Gl} - 1) \quad (4.1)$$

where $I(l)$ is the collected integrated intensity, I_{sp} is spontaneous-emission-related constant, G is the net modal gain coefficient, and l is the length of the excitation stripe.

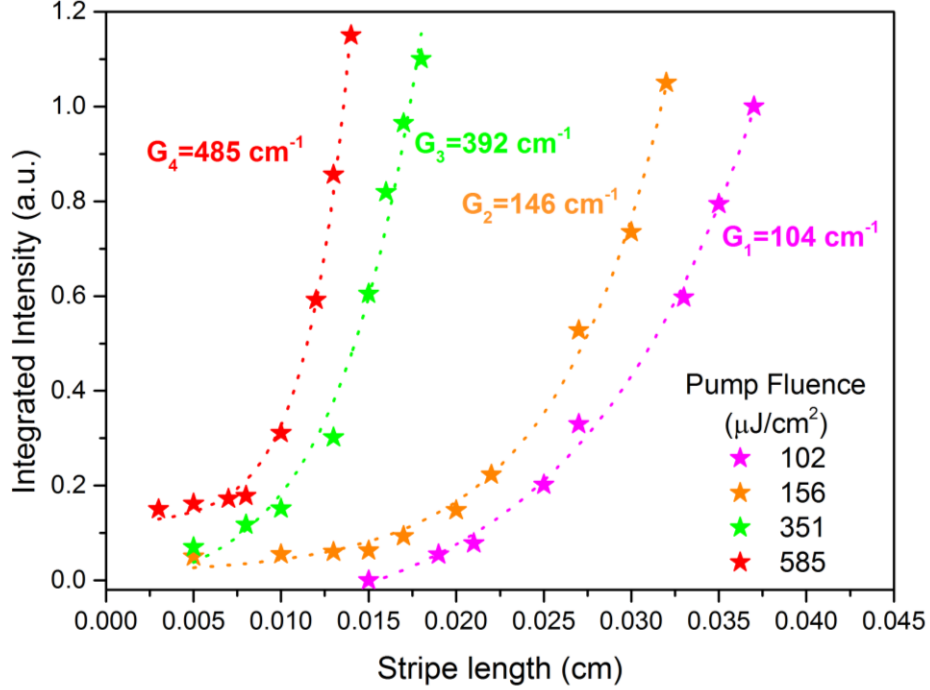


Figure 4.7: Variable stripe length (VSL) measurement of our NPL-coated fiber with 250 μm core diameter at various excitation fluences.

Afterwards, the obtained G values were plotted as a function of the pump fluence to determine the saturation pump fluence as given in Figure 4.8. For that, the experimental G values were numerically fitted to the following expression:

$$G = g - \alpha = \Gamma \sigma_{st} \frac{\Phi_{pump}}{\frac{\Phi_{pump}}{\Phi_{sat}} + 1} \quad (4.2)$$

Here G is the net modal gain coefficient, g is the peak modal gain coefficient, α is the loss of the overall structure, Γ is the optical confinement factor, σ_{st} is the absorption cross-section for stimulated emission, Φ_{sat} is the saturation pump intensity, and Φ_{pump} is the peak pump intensity. As given in Figure 4.8, the highest experimental G value was found as $\sim 485 \text{ cm}^{-1}$. Moreover, after the numerical fitting, Φ_{sat} was determined as $\sim 900 \mu\text{J}/\text{cm}^2$.

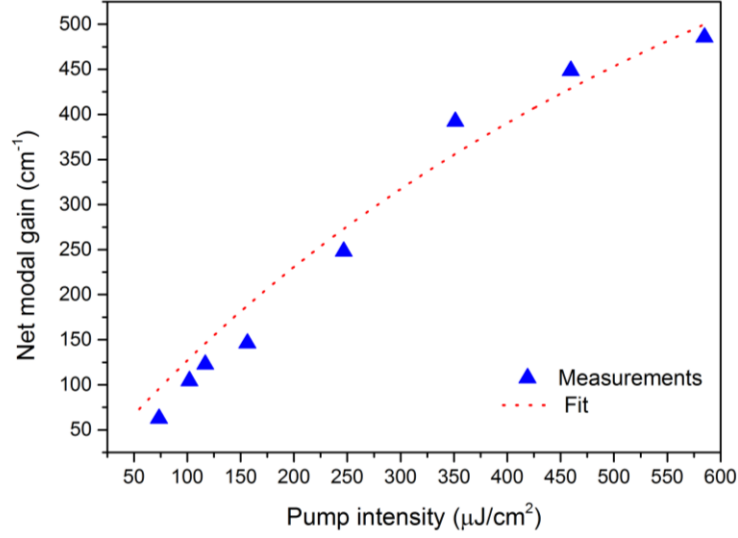


Figure 4.8: Net modal gain coefficient as a function of the pump fluence along with the numerical fitting.

Furthermore, to understand the improvement in the ASE performance with the increase in the fiber diameter, we investigated the waveguide loss coefficients of our NPL-coated fibers. To do so, we excited our fibers with a pump fluence larger than ASE threshold, then we collected ASE intensity by changing the distance between the edge of sample and the end of the excitation beam. Afterwards, we fitted the empirical data to the following exponential equation:

$$I(l) = I_0 e^{-\alpha l} \quad (4.3)$$

Here $I(l)$ is the ASE intensity, I_0 is the peak ASE intensity, α is the waveguide loss coefficient, and l is the distance from the end of the excitation beam. Figure 4.9 shows the experimental results and exponential fits for both 125- and 250-μm NPL-fibers. After the fitting, waveguide loss coefficient values were found as 12.3 and 7.1 cm⁻¹ for 125- and 250-μm NPL-fibers, respectively. To the best of our knowledge, our results for waveguide loss coefficients are the record low values compared to previous report among solution-processed materials [34], [67], [68].

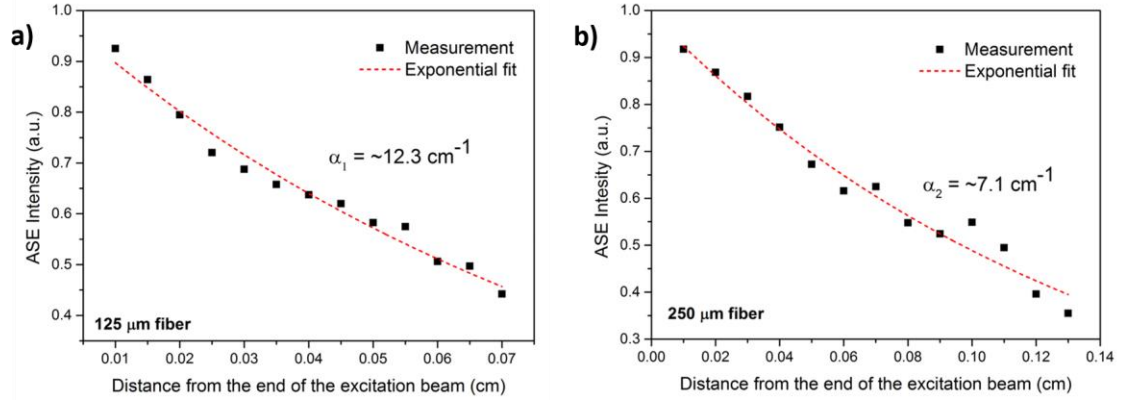


Figure 4.9: Waveguide loss coefficient measurement along with exponential fits for a) 125 μm NPL-fiber, b) 250 μm NPL-fiber.

In our NPL-fiber resonator, since the refractive index of the NPL films is larger than the air medium ($n_{\text{air}}=1$) and SiO₂ fiber ($n_{\text{fib}}=1.46$), the total internal reflection occurs at the air-NPL and SiO₂-NPL interfaces. Hence, our NPL-fiber can support whispering gallery modes and acts as a novel NPL-WGM resonator. Herein, we demonstrate WGM lasing in our NPL-WGM resonator by optically exciting it with a spot-shaped laser on the fiber with the diameter of 250 μm. Schematic illustration of the cross-section of our NPL-WGM resonator is depicted in Figure 4.10a, where the film formation of our NPLs on the fiber surface is not necessarily very uniform, which results in an effective refractive index. Figure 4.10b shows the laser emission of our NPL-WGM resonator along with the spatially-defined laser spot.

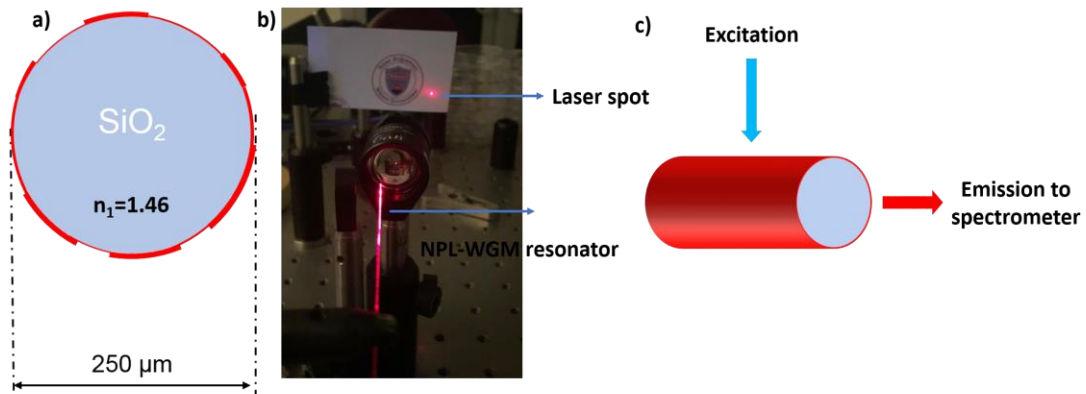


Figure 4.10: a) Illustration of the cross-section of NPL-WGM resonator. b) Image of the NPL-WGM under optical excitation with the resulting laser emission. c) Illustration of experimental setup

It is worth mentioning that we excited our NPL-fibers perpendicular to fiber axis and collected our lasing emission along the fiber axis as show in Figure 4.10c. We coupled the omnidirectional emission of WGM to the waveguiding modes of the fibers. This allow us to effectively guide and collect the laser emission along the fiber .

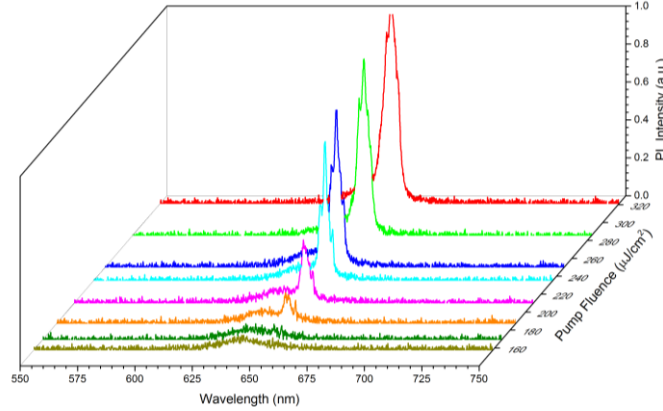


Figure 4.11: PL spectra of 250-μm fiber acts as an NPL-WGM resonator under 1PA excitation.

The emission spectra of the NPL-WGM resonator under 1PA excitation are presented in Figure 4.11. It can be seen that, after a certain pump fluence, multi-mode lasing emerges with a FWHM of ~ 1.4 nm, which conforms to the allowed modes of the WGM resonator. Pump-dependent emission of WGM laser is shown in Figure 4.12, where the 1PA-pumped lasing threshold of $\sim 190 \mu\text{J}/\text{cm}^2$ can be seen. After the lasing threshold, PL intensity exponentially increases, then a gradual saturation damps this increase at higher pump fluences.

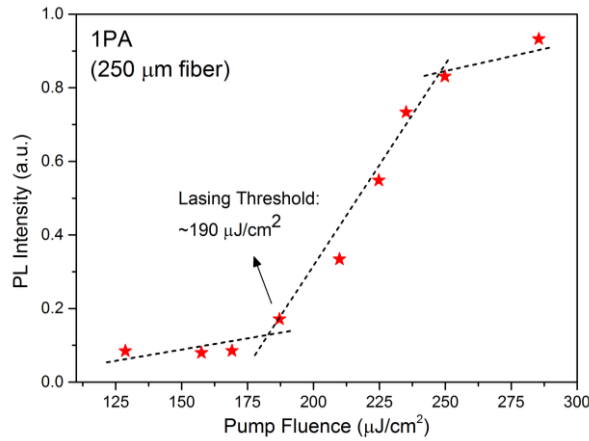


Figure 4.12: PL intensity of NPL-WGM resonator at various pump fluences under 1PA pumping.

Next, we characterized the lasing performance of our NPL-WGM resonator under 2PA pumping to explore its possible applications in up-converted lasers [69] and biosensing [70]. Luminescence spectra of our structure under 2PA pumping is shown in Figure 4.12, where very narrow lasing peaks appear after the lasing threshold. Finally, pump-fluence-dependent PL spectra under 2PA pumping are given in Figure 4.13, where the lasing threshold for 2PA pumping is found as $\sim 1.40 \mu\text{J}/\text{cm}^2$. Both Figures 4.12 and 4.14 indicate the characteristic S-like curve behavior of lasing.

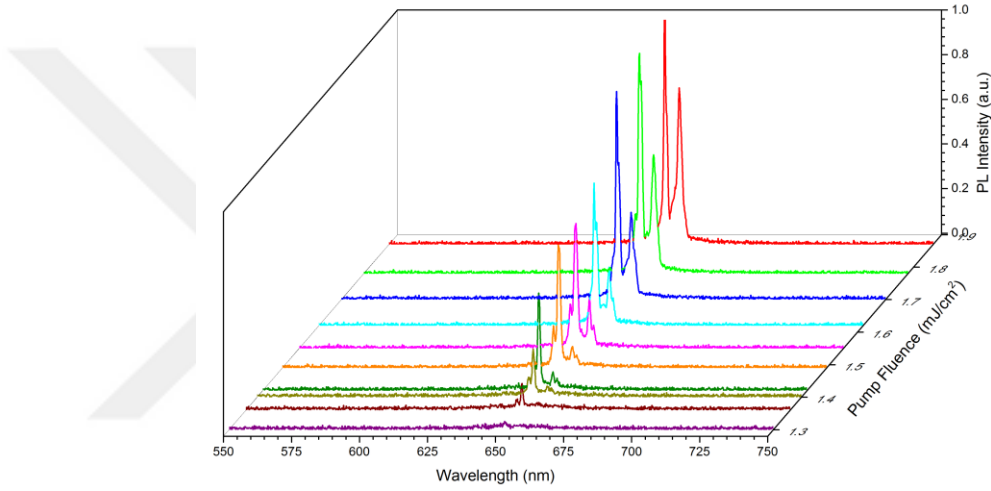


Figure 4.13: PL spectra of 250- μm NPL-coated fiber, which acts as an NPL-WGM resonator under 2PA excitation.

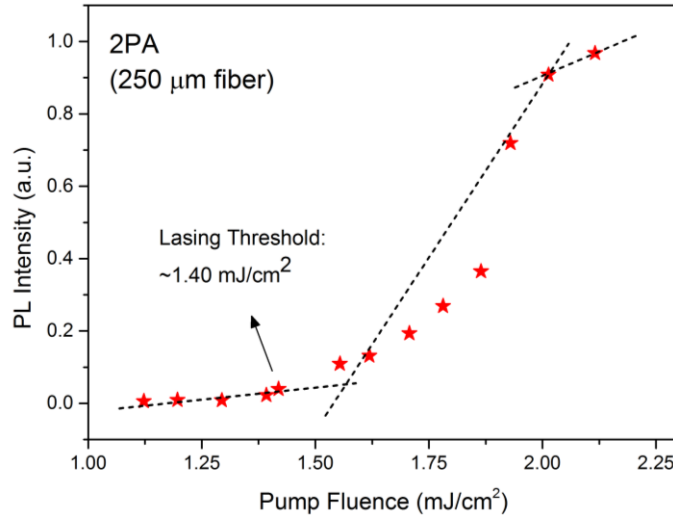


Figure 4.14: PL intensity of NPL-WGM resonator at various pump fluences under 2PA pumping.

The performance results of our NPL-WGM resonator are better than the previous reports of WGM lasers based on colloidal NCs including nanorod-based ones [36], quantum dot based ones [71]–[73], and NPL-based ones [60]. Since our structure relies on the close-pack film formation of NPLs, we have achieved superior performance results while the all previous ones are based on the solution phase of NCs [53]. Additionally, as a result of the suppressed scattering losses of our NPL-WGM resonator, which yields record low waveguide loss coefficients, together with high net modal coefficients of our NPLs, we obtained low thresholds in our NPL-WGM structure.

To further analyze the WGM lasing behavior of our structure, we investigated its response via a commercial FDTD software (Lumerical FDTD Solution). In our model, we used an NPL gain medium (n_{gain}) with a refractive index of 1.80, which was experimentally obtained by ellipsometer measurement. Figure 4.15 presents the simulation results showing a strong electric field (E-field) localization in the NPL region of the structures owing to the dominant total internal reflections at the interfaces. This effective confinement in the gain medium indicates the optical cavity behavior of this structure for lasing applications.

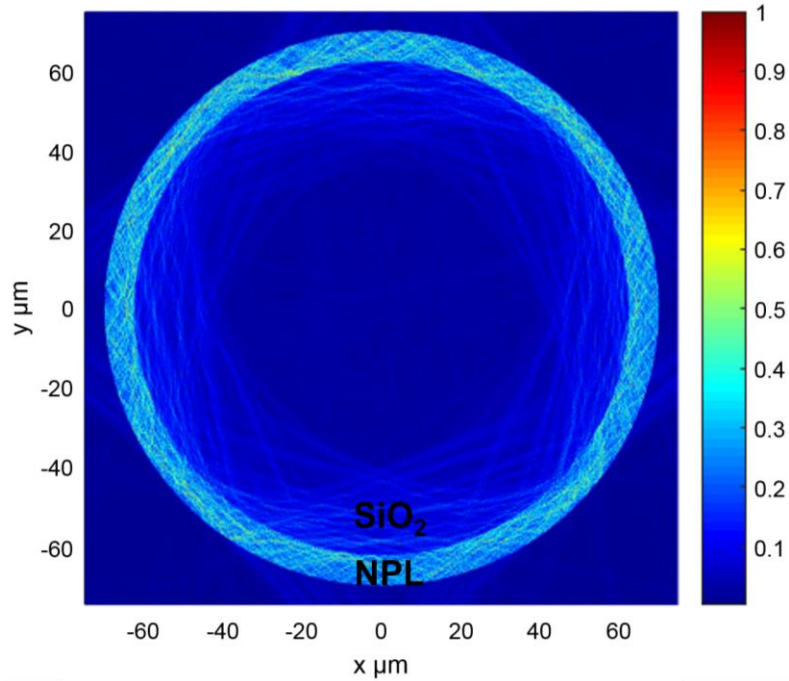


Figure 4.15: E-field distribution of NPL-WGM resonator with 125 μm diameter fiber.

Additionally, to determine the angular mode numbers of our WGM lasing, we utilized the following equation:

$$q\lambda_q = D\pi n_{eff} \quad (4.4)$$

Here q is the angular mode number, λ_q is the wavelength of the q^{th} mode, D is the diameter of the cavity, and n_{eff} is the effective refractive index of the NPL film [74]. Then, we calculated n_{eff} by assuming that the consecutive modes of the WGM resonator conforms to the lasing peaks of our experimental results. Then, the effective refractive index of the medium was found as ~ 1.13 . This means that the effective refractive index of our structure is lower than the refractive index of our NPLs, implying that the guided modes leak to lower refractive regions to some extent (silica and air) and thus the NPL film is not necessarily all the same thickness (*i.e.*, it might be thinner locally on parts of the coating).

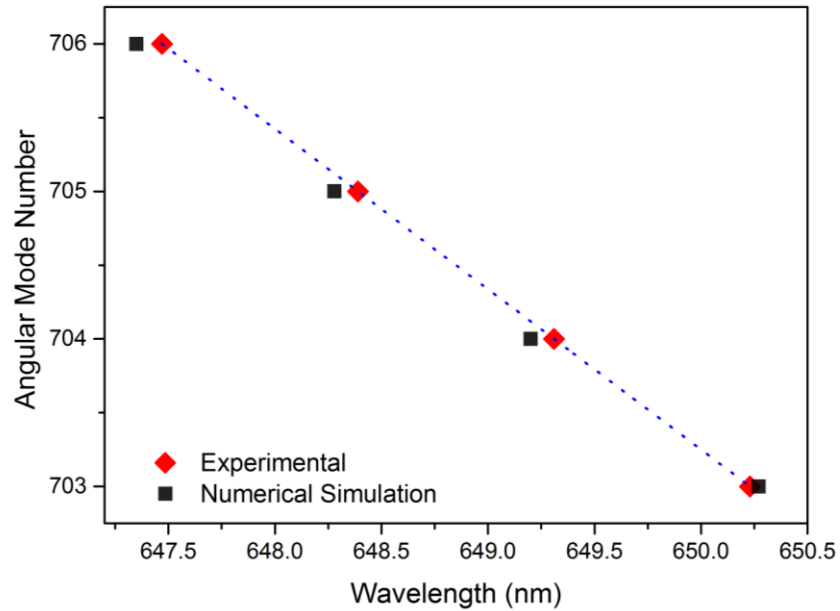


Figure 4.16: Lasing peaks of the NPL-WGM resonator with 125 μm diameter, where experimental and numerical peak locations spectrally overlap.

Figure 4.16 shows the experimental lasing peaks and the corresponding theoretical mode numbers along with the spectral response of the numerical simulation. It can be seen here that peak locations of the experimental measurements almost perfectly overlap with the simulation results using a fixed effective refractive index.

Furthermore, to investigate polarization state of our NPL-WGM laser, we placed a linear polarizer filter between the WGM cavity and the collection fiber of the spectrometer. We excited our structure at a fixed pump fluence larger than the lasing threshold. Then, by rotating the angle of the linear polarizer filter, we recorded the lasing spectra of our structure. Figure 4.17 shows the PL intensity of the laser output as a function of the analyzer angle along with its $\cos(\theta)^2$ fit. Moreover, to quantify the polarization state, we calculated R using the following expression [75]:

$$R = \frac{1 - \frac{I_{\perp}}{I_{\parallel}}}{1 + \frac{I_{\perp}}{I_{\parallel}}} \quad (4.5)$$

where $I_{\perp}$ and $I_{\parallel}$ are the laser intensities perpendicular and parallel to the emission axes of our NPL-WGM structure. R was found to be ~ 0.70 showing a strongly-linearly-polarized laser emission of our structure.

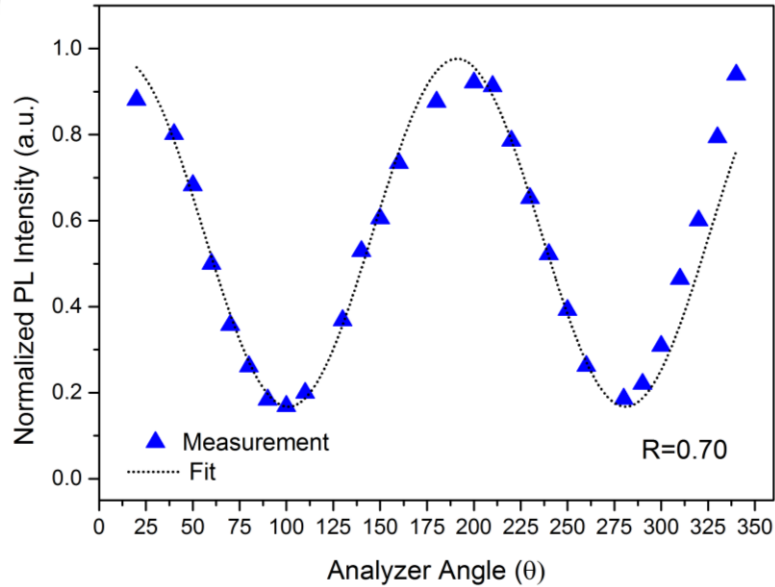


Figure 4.17: Normalized PL intensity of our laser as a function of the polarizer angle and fitted quadratic cosine function.

Finally, we investigated the stability of our NPL-WGM lasing by exciting our structure at a pump fluence 4-times larger than the lasing threshold. Our laser output was stable nearly up to 150 minutes by maintaining an intensity larger than half of its peak. Figure 4.18 shows this measurement. It is worth noting that the lasing intensity starts to increase in

the first 30 minutes of the excitation. This effect was attributed to the effective annealing of the NPLs, which was previously reported to generate a healing effect [46]. Our stability reports outperform the previous quantum-dot-based WGM lasers [53], [76] thanks to the solid film formation of our NPLs around the fiber.

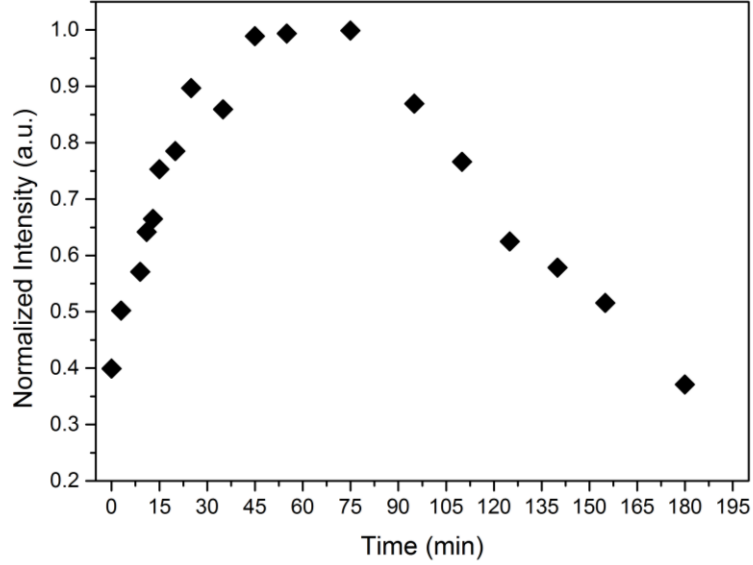


Figure 4.18: Normalized laser intensity our NPL-WGM resonator under a fixed pumping for stability measurement.

4.4 Summary

In summary, we proposed and developed a fiber-based NPL-WGM resonator empowered by the high-density films of CCGAS NPLs using a convenient coating method. Large net modal gain of $\sim 485 \text{ cm}^{-1}$ and low waveguide loss coefficient of $\sim 7.1 \text{ cm}^{-1}$ allowed us to obtain very low ASE thresholds of $\sim 90 \text{ } \mu\text{J}/\text{cm}^2$ and $\sim 3.0 \text{ mJ}/\text{cm}^2$ for 1PA and 2PA excitation regimes, respectively. Furthermore, 1PA- and 2PA-excited WGM lasing of the proposed NPL-fiber structure was demonstrated with low lasing thresholds of $\sim 190 \text{ } \mu\text{J}/\text{cm}^2$ and $\sim 1.40 \text{ mJ}/\text{cm}^2$ under 1PA and 2PA pumping, respectively. Also, a highly linearly polarized emission along with high stability was achieved. These promising results indicate motivation for possible interesting applications of this structure in the fields of the biophotonics and biosensing.

Chapter 5

Vertical-cavity Surface-emitting Laser of Colloidal Nanoplatelets

This chapter is partially based on the manuscript “Sub-single exciton optical gain threshold in colloidal semiconductor quantum wells with gradient alloy shelling,” N. Taghipour, S. Delikanli, S. Shendre, **M. Sak**, M. Li, F. Isik, I. Tanriover, B. Guzelturk, T. C. Sum, H. V. Demir, under review (2019).

5.1 Motivation

The first demonstration of vertical-cavity surface-emitting lasers (VCSELs) dates back to 1978, where heterostructures of epitaxially-growth semiconductor were utilized as a gain cavity structure [81]. Later, they have been subjects of active research and development considering their advantages including wafer-level testing and silicon-compatible fabrication techniques [82]. Within the last decade, colloidal semiconductor materials have been utilized as active gain media for the realization of VCSELs [25], [35]. However, achieving the performance of epitaxially-grown VCSELs is still a challenge with the current use of colloidal semiconductor materials.

In this chapter, we proposed and developed a vertical-cavity surface-emitting laser of colloidal nanocrystals by utilizing CdSe/CdS/Cd_{1-x}Zn_xS core/crown/gradually-alloyed-shell (CCGAS) NPLs as active gain media coupled to an optical cavity of two distributed Bragg reflectors (DBRs). Owing to the suppressed Auger recombination and large optical gain coefficients of our advanced NPLs, we achieved a record low lasing threshold of $\sim 7.5 \mu\text{J}/\text{cm}^2$ under one-photon-absorption (1PA) pumping. These leading results from NPLs may play an important role to bring colloidal light-amplification optoelectronic devices on par with their epitaxially-growth counterparts.

5.2 Experiments

5.2.1 Colloidal Synthesis

Experiments conducted for NPLs synthesis including precursor preparation, 4 ML CdSe NPL synthesis, CdSe/CdS core/crown NPL synthesis, and CdSe/CdS/Cd_{1-x}Zn_xS CCGAS NPL synthesis are the same as Chapter 4.2. Thus, the same procedures are followed to synthesize NPLs used in this chapter and the only difference is the number of shell monolayers. In this chapter we have utilized NPLs with 4 ML thick alloyed-shells of Cd_{1-x}Zn_xS, while in the previous one we have used 3 MLs of Cd_{1-x}Zn_xS alloyed-shells.

5.2.2 Sample Preparation

To construct the VCSEL structure, previously fabricated DBRs, which are on a $2 \text{ cm} \times 2 \text{ cm}$ quartz, were used. 300 μm thick Kapton tape was stuck on one edge of the first DBR, and then the second DBR was placed on top of the first one with a small overlap such that tape-stick region becomes partially exposed. After that, three remaining edges of the DBRs were glued with epoxy to form a closed structure. After 30 minutes, Kapton tape was removed to obtain wedge cavity. Since the presence of Kapton tape creates an obstacle for the two DBRs, preventing them from fully sticking to each other, this structure forms a wedge after the epoxy glue is dried. Thus, the thickness of the cavity changes along the vertical direction.

After the construction of the wedge cavity, it was filled with a highly-concentration solution of our CCGAS NPLs ($\sim 70 \text{ mg/mL}$). To fill the cavity, a few μL of our

concentrated solution was poured inside via micropipette and then the cavity was left for 15 minutes to dry. This process was repeated around 20 times to fill the wedge cavity with our NPLs.

5.3 Results and Discussion

In this chapter, we have grown 4 ML of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ gradually-alloyed-shell on top of 4 ML thick CdSe/CdS core/crown NPLs by employing colloidal atomic layer deposition (c-ALD) technique to obtain CdSe/CdS/ $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ core/crown/gradually-alloyed-shell (CCGAS) NPLs [33]. As a result of the gradual shell, electron wavefunction feels a smoothened barrier and delocalizes through the shell portion of the structure. Absorption and photoluminescence (PL) spectra of our NPLs are given in Figure 5.1a. The excitonic peaks at 572 and 630 nm correspond to the upward transitions from the light-hole and heavy-hole to the conduction band, respectively, and photoluminescence spectrum of these NPLs appears at ~ 640 nm with a FWHM of 20 nm. High-angle annular dark-field scanning transmission electron microscopy image of our NPLs is depicted in Figure 5.1b, where a lateral size of ~ 13 nm was measured.

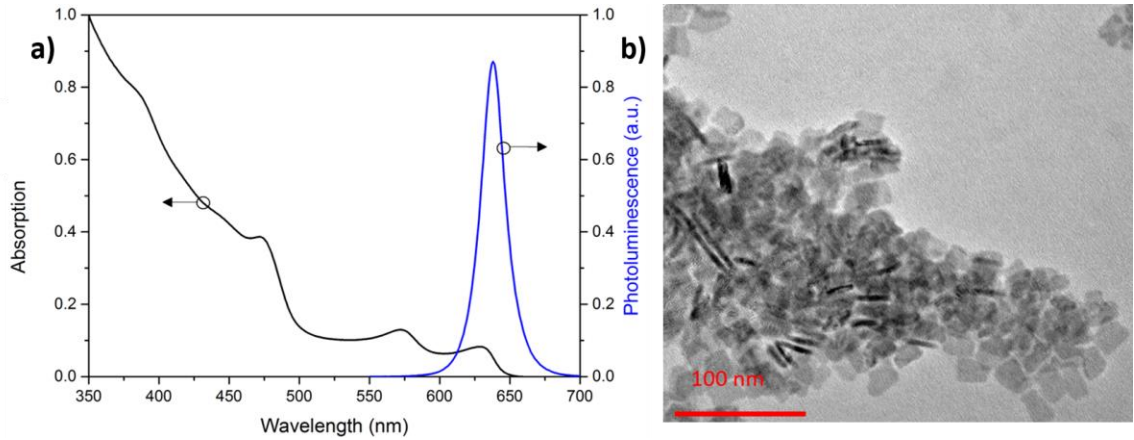


Figure 5.1: a) Absorption and PL spectra of our CCGAS NPLs. b) HAADF-STEM images of CCGAS NPLs with 4 monolayers of gradient alloyed shell.

To achieve high reflectivity in the emission region of our NPLs, 6-bilayers of SiO_2 and TiO_2 are deposited on quartz substrate. The reflectivity of the resulting DBR is shown in

Figure 5.2. It is essential to note that these DBRs are specially designed such that their highly reflective regions cover the gain spectrum of our NPLs.

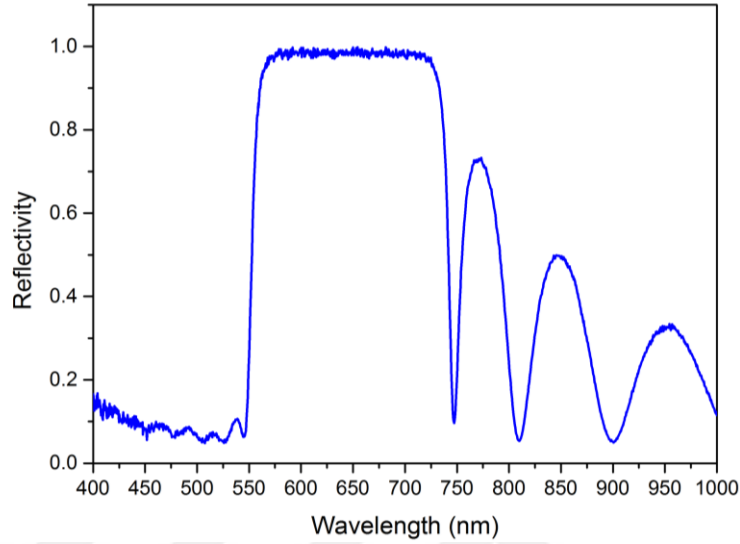


Figure 5.2: Reflectivity of the fabricated DBR, where near perfect reflection was achieved in 580-700 nm range covering the gain spectrum of our NPLs.

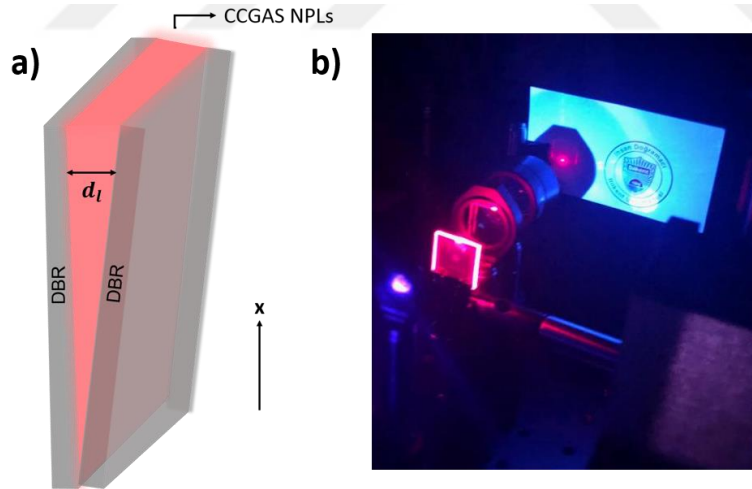


Figure 5.3: a) Schematic illustration of our wedge VCSEL cavity. b) Image of our NPL-VCSEL cavity pumped with a pump fluence above lasing threshold with the resulting lasing spot on the paper. covering the photoluminescence spectra of our NPLs.

Two of these DBRs have been attached to each other in order to construct the cavity of the VCSEL structure. Then, this cavity was filled with our NPLs to obtain close-packed solid films of gain media. An essential feature of our cavity is that its optical length was

changing through the structure (see Chapter 5.2.2 for details). This allows us to adjust the free spectral range (FSR) of the cavity by simply changing the location of the excitation spot. Thus, this configurability gives us the degree of freedom to spectrally overlap the stimulated emission wavelength of our gain medium with the resonant frequencies of the optical cavity. Figure 5.3a displays the illustration of our wedge VCSEL cavity.

We optically excited our NPL-VCSEL cavity with a mode-lock Ti:Sapphire femtosecond laser (120 fs pulse width, 1 kHz repetition rate, at 400 nm) to induce lasing. The photographic image of NPL-VCSEL cavity with the spot of laser output is shown in Figure 5.3b. The photoluminescence spectra of our NPL-VCSEL were collected via spectrometer at various pump fluences. Figure 5.4 displays a very sharp single-mode lasing of NPL-VCSEL whose FWHM is ~ 0.5 nm. A very narrow single mode lasing was observed at pump fluences larger than $7.50 \mu\text{J}/\text{cm}^2$. Moreover, the quality factor (Q-factor) of our cavity was experimentally calculated as high as $\sim 1,220$.

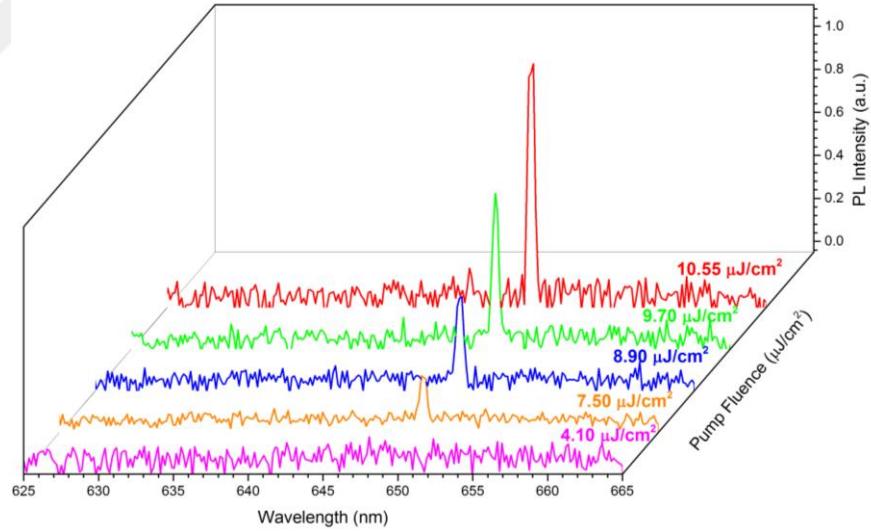


Figure 5.4: PL spectra of NPL-VCSEL under 1PA excitation, demonstrating a single-mode lasing.

The PL intensity of our VCSEL is plotted as a function of the pump fluence to indicate lasing behavior with the corresponding threshold as can be seen in Figure 5.5. With our structure, we obtained the record low lasing threshold of $7.50 \mu\text{J}/\text{cm}^2$ by outperforming among all previously reported NC-based VCSELs [25], [35]. Similar to previous the

chapter, we have observed an exponential increase in the PL spectra of our laser after the lasing threshold followed by saturation at high pump fluences.

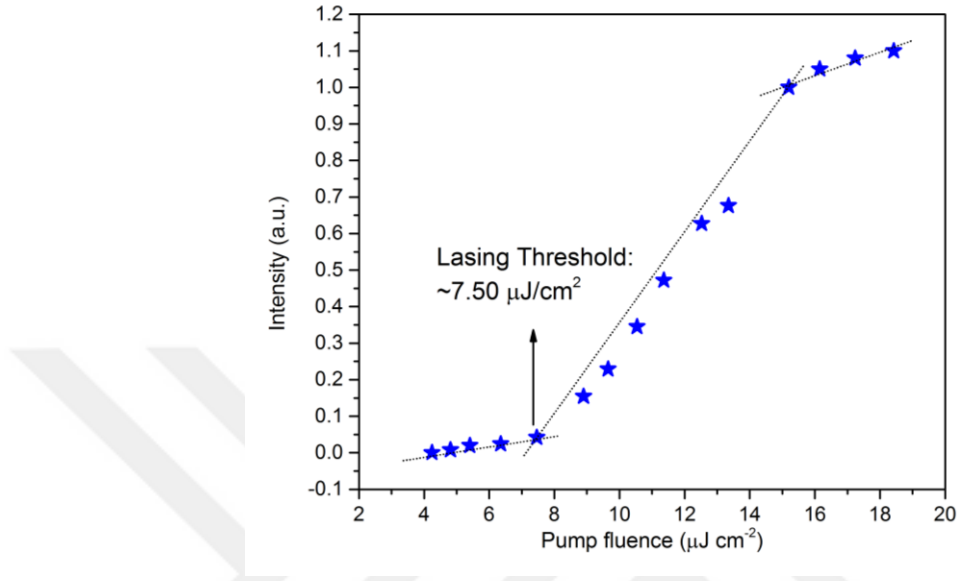


Figure 5.5: Emission intensity of NPL-VCSEL under 1PA excitation as a function of the pump fluences, where the record low lasing threshold and saturation at higher pump can be observed.

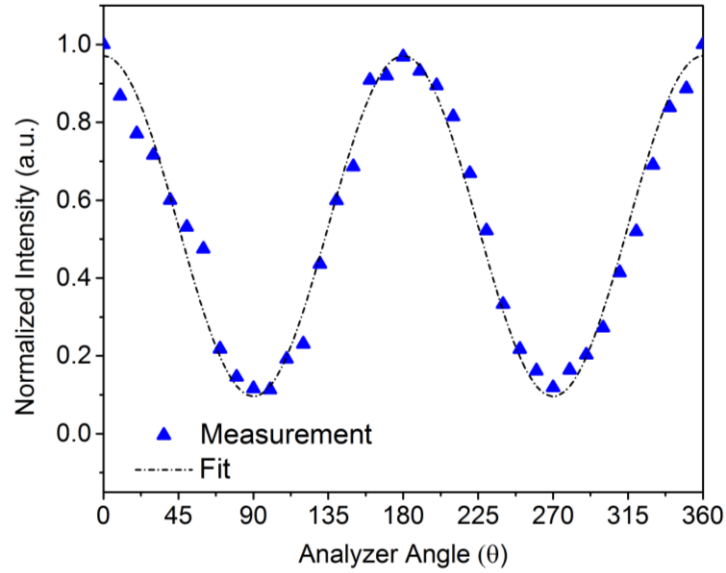


Figure 5.6: Laser output as a function of the analyzer angle and its fit to a quadratic cosine function.

Furthermore, the polarization state of NPL-VCSEL was investigated with the help of a polarizer, which was placed right before collecting the laser output. By varying the analyzer angle, PL intensity was collected and then it was fitted to $\cos^2$ -function. Figure 5.6 shows this measurement along with the fit. To quantify the polarization state, the following equation was used:

$$R = \frac{1 - \frac{I_{\perp}}{I_{\parallel}}}{1 + \frac{I_{\perp}}{I_{\parallel}}} \quad (5.1)$$

where $I_{\parallel}$ and $I_{\perp}$ are the intensities of the laser beam parallel and perpendicular to optical axes, respectively. Then, R was found to be ~ 0.80 , indicating highly linearly polarized emission.

5.4 Summary

In summary, we have proposed and demonstrated CdSe/CdS/Cd_{1-x}Zn_xS CCGAS NPLs based vertical-cavity surface-emitting lasers by utilizing two DBRs as an optical cavity. Owing to the effective suppression of the Auger recombination intrinsic to our NPLs along with our special cavity, we have obtained the record low lasing threshold of $7.50 \mu\text{J}/\text{cm}^2$, which is significantly better than previous colloidal-NC-based lasing reports. High-performance results of our NPL-VCSEL motivate future applications of such auspicious heterostructures of these NPLs for the next-generation of NC-based light-sources.

Chapter 6

Conclusion

6.1 Concluding Remarks

Atomically-thin 2D nanocrystals, the nanoplatelets, show superior optical and electronic properties as a result of their large absorption cross-sections, purely homogeneous broadening, huge optical gain coefficients, and very narrow emission bandwidths. These make them excellent candidates to be used in light-emitting applications. To this end, in this thesis, light-amplification characteristics of NPLs were investigated and their convenience for lasing was shown in two different studies.

In the first one, core/crown/gradually-alloyed-shell CdSe/CdS/ CdSe/CdS/Cd_{1-x}Zn_xS NPLs were coated on fibers. Then, single- and multi-photon-pump optical gain performance of these NPL-fibers was investigated. As a result of high-density close-pack film formation of our NPLs along with their specially engineered band alignment, very low optical gain thresholds were achieved, together with record low waveguide losses. By utilizing refractive index medium difference among the media, a simple and convenient method to construct fiber-based NPL-WGM resonators was demonstrated. Compared to previous reports on various colloidal luminophores, significant performance

improvements were shown in terms of the lasing thresholds and stability with our unique structure.

In the second study, core/crown/gradually-alloyed-shell CdSe/CdS/Cd_{1-x}Zn_xS NPLs were employed as an optical gain medium sandwiched between two distributed Bragg reflectors to achieve vertical-cavity surface-emitting laser structure. Owing to the effective suppression of the Auger recombination in our NPLs with our high-Q optical cavity, record low lasing threshold in its class was achieved. Moreover, the polarization state of our VCSEL was explored.

In conclusion, within the scope of this thesis, we investigated the optical gain properties of colloidal NPLs including their optical gain thresholds and net modal gain coefficients. Then, by integrating advanced heterostructures of these NPLs into different optical cavities, various laser structures were demonstrated including WGM laser and VCSEL. Moreover, spectral behavior of our lasers was examined along with their stability and polarization states. We believe that these promising findings on the optical gain and lasing of such NPLs pave the way for the next-generation of high-performance NPL optoelectronic devices.

6.2 Outlook

Even though we have achieved ultra-high performance results and demonstrated novel approaches to induce optical gain and obtain lasing from colloidal NCs, there are still many challenges that need to be overcome before the successful commercialization of these devices. The realization of optical gain of NCs requires pulsed laser (with ns or fs pulse durations). This creates an obstacle against making practical NC-lasers. Utilization of continuous-wave-pumped (CW-pumped) lasers for optical gain can be solution to this problem. However, this requires high pump intensities (kW/cm²), which will cause heating of the samples. Thus, the synthesis of heat-resistant nanocrystals along with smart engineering of the band-alignment to further reduce thresholds may lead the way to CW-pumped nanocrystal lasers. Moreover, the convenience of our NPL-WGM structure may guide the way to construct multi-color NC-laser within the same device. By regulating the

film formation and nanocrystal types around the fibers, two-color or even white laser can be realized.

6.3 Contributions

In this section, we list our contributions to the literature throughout this thesis study.

- (1) **M. Sak**^{*}, N. Taghipour^{*}, S. Delikanli, S. Shendre, I. Tanriover, Y. Gao, J. Yu, Z. Yanyan, S. Yoo, C. Dang, H. V. Demir, “Highly Stable, Low Threshold Fiber-based Whispering-gallery-mode Laser from Colloidal Nanoplatelets,” in submission (2019). ^{*}Equal contribution.
- (2) N. Taghipour, S. Delikanli, S. Shendre, **M. Sak**, M. Li, F. Isik, I. Tanriover, B. Guzelturk, T. C. Sum, H. V. Demir, “Sub-single exciton optical gain threshold in colloidal semiconductor quantum wells with gradient alloy shelling,” under review (2019).
- (3) Y. Altintas^{*}, K. Gungor^{*}, Y. Gao^{*}, **M. Sak**, U. Quliyeva, G. Bappi, E. Mutlugun, E. Sargent, H.V. Demir, “Giant Alloyed Hot Injection Shells Enable Ultra-Low Optical Gain Threshold in Colloidal Quantum Wells,” under review (2019). ^{*}Equal contribution.
- (4) D. Dede^{*}, N. Taghipour^{*}, U. Quliyeva, **M. Sak**, Y. Kelestemur, K. Gungor, H. V. Demir, “Highly Stable Multicrown Heterostructures of Type-II Nanoplatelets for Ultralow Threshold Optical Gain,” *Chemistry of Materials* (2019). (doi: 10.1021/acs.chemmater.9b00136). ^{*}Equal contribution.
- (5) O. Erdem, K. Gungor, B. Guzelturk, I. Tanriover, **M. Sak**, M. Olutas, D. Dede, Y. Kelestemur, H. V. Demir, “Orientation-controlled nonradiative energy transfer to colloidal nanoplatelets: Engineering dipole orientation factor,” *Nano Letters* (2019), in press (doi: 10.1021/acs.nanolett.9b00681).

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