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COLLOIDAL QUANTUM DOT LASING FOR LIGHTING AND DISPLAYS

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Abstract

Semiconductor light-emitting diodes (LEDs) enable artificial lighting with an unprecedented level of efficiency. However, “efficiency droop” occurs in LEDs under high power injection density, practically limiting the feasible efficiency levels at high output powers. To address this problem, the concept of laser lighting has been proposed. Also, the current liquid crystal displays (LCDs) suffer the problems of low energy efficiency and small colour gamut, which can be addressed by employing the polarized white backlighting and saturated primary colours. Lasers with colloidal quantum dots (CQDs) as a gain medium can provide solutions to these limitations of current lighting and display technologies. Thus, the target of my Ph.D. thesis work is to develop and demonstrate low threshold colloidal quantum dot lasing with high linear polarization.

In Chapter 2 of this thesis, unique properties of CQDs, including size dependent bandgap and discrete energy levels, which result from quantum confinement effect, are discussed. Here by adjusting the size, structure and chemical composition, CQDs that emit at various targeted wavelengths were synthesized. The resulting optical and structural characterizations are also presented. In Chapter 3, a brief review of the optical gain from CQDs is given, and the means that can be adopted to abate Auger recombination are discussed. In experimental part, CQD lasing of red, green, and blue CQDs was demonstrated. Moreover, a FRET-assisted indirect pumping scheme for CQD green lasing with standard pumping source was developed. In Chapter 4 and Chapter 5, highly polarized lasing from CQDs was demonstrated by utilization of the optical cavity effect and adoption of the polarized gain medium, respectively. The CQD DFB laser with mechanically flexible substrate was shown and analysed in Chapter 4. However, for a cylindrical optical cavity of a large diameter, which has low selectivity of TE and TM mode, the polarized gain medium that was fabricated by aligned nanorods was employed for realizing highly polarized Whispering Gallery mode lasing. These results

indicate that highly polarized CQD lasing can find important uses in future lighting and displays.

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Abbreviations

1D	One dimensional
AFM	Atomic force microscopy
ASE	Amplified spontaneous emission
CQD	Colloidal quantum dot
DFB	Distributive feedback
DR	Dot-in-rod
EDX	Energy-dispersive X-ray spectroscopy
EL	Electroluminescence
FRET	Föster energy transfer
FSR	Free spectral range
FWHM	Full width at half maximum
HRTEM	High-resolution transmission electron microscopy
LCD	Liquid-crystal display
LD	Laser diode
LED	Light-emitting diode
Nd:YAG	Neodymium-doped yttrium aluminium garnet
NPL	Nanoplatelet
PID	Proportional-integral-derivative
PL	Photoluminescence
PLE	Photoluminescence excitation
PLQY	Photoluminescence quantum yield
QDTV	Quantum dots television
QLED	Quantum dots light-emitting diode
RGB	Red, green, blue

RL	Random lasing
SEM	Scanning electron microscopy
SILAR	Successive ion layer adsorption
TE	Transverse electric
TEM	Transmission electron microscopy
TM	Transverse magnetic
WGM	Whispering-gallery mode
XRD	X-ray Diffraction

Chapter 1 Lasers for Primary Colours in Lighting and Displays

1.1 Introduction

In this chapter, the motivation of my Ph.D. thesis work will be introduced. The limitation of current light-emitting diodes (LED) and liquid-crystal displays (LCDs) will be discussed in the introduction part. Lasers can be one option that can address these problems of modern lighting and displays. Here, regarding the ultra-narrow spectral range, which is not feasible in other conventional light sources, the human eyes' response to such spiky white light that is mixed by emission from lasers is also discussed.

1.1.1 Lasers as More Economic Photon Sources

Nowadays, blue emitting GaN-based LED, which is integrated with rare earth element based phosphors for colour conversion to generate white light, is the light source of the highest energy efficiency compared to conventional light sources, including incandescence bulb, fluorescent tube, and compact fluorescent lamp (CFL).[1] However, such extremely high energy efficiency is generally obtained under low driven power, and therefore, only a small amount of luminous flux is produced by a single LED device. This is a well-known fundamental problem of current III-V LEDs, so called the efficiency droop, which causes a major drop in energy efficiency under high input power.[2] To generate more luminous flux from an LED device, the LED should be working at a higher input power, which will be at the expense of losing energy efficiency, as indicated by the blue curve in Figure 1.1.[3] To resolve this fundamental problem that affects the performance of LED lighting, an alternative device that can be adopted to produce blue emission is a blue laser diode (LD).[3-5] The emission from an LD is originated from the stimulated emission rather than the spontaneous

emission like in LEDs. In principle, the efficiency of an LD can be higher than that of an LED at high input power density, considering the much higher transition rate of stimulated emission that can compete with the nonradiative channel that gives rise to the efficiency droop, as indicated by the red curve in Figure 1.1.[2] With the development of LDs, they become a more economical source of photons.[3]

Figure 1.1 Evolution of power conversion efficiency of a cutting-edge surface-emitting blue LED and an edge-emitting laser diode as a function of input power density. The efficiency of the LED device drops rapidly with increasing input power density, but the efficiency of the LD increases during the initial stage and reaches a plateau at a high input power density. The intersection point of these two curves indicates the “valley of droop”. This figure is adopted from [3].

1.1.2 Human Eye Response of Spectrally Ultra-narrow Emission

However, if the lasers are employed for lighting applications, how good will the performance of the white light source that is made of laser be? Colour rendering index (CRI) is an important parameter for characterizing the capability of a light source to reproduce the colours of

an object under a perfect blackbody-radiation-based light source, e.g., the sun, incandescent lamp.[6] Research has shown that CRI is not sensitive to narrow linewidth, which is characteristics of the emission of lasers, but to the number and the wavelength spread of the component colours.[7] In this sense, although the linewidth of lasers is ultra-narrow, high CRI still can be achieved as long as enough colour components are employed (e.g., four lasers including blue, green, yellow, and red colours).[5, 7] In addition, the human eyes response to red colour drops very rapidly at the long wavelength range,[8] and if the spectrum of the red component of a white light becomes narrower, this prevents the optical energy from falling into the spectral range where retina is not sensitive, and the luminous efficacy (defined by Equation (1-1), for quantifying the efficiency of a light source to generate a visual sensation [8]) can increase.[7] And, the overall luminous efficacy has a 0.15%/nm increment with shrinking linewidth of the red component.[7]

$$\eta = \left[682 \frac{lm}{W} \int V(\lambda) P(\lambda) d\lambda \right] / \int P(\lambda) d\lambda \quad (1-1)$$

Here $V(\lambda)$ is the eye sensitivity function, and $P(\lambda)$ is the spectral power distribution of the light source.

Moreover, a comprehensive study was carried out to investigate human feelings towards a white light source that is formed by mixing red, yellow, green and blue lasers, as illustrated in Figure 1.2a.[5] The relative intensity of these four lasers is tuned to mimic the four reference light sources, *i.e.*, incandescent lamp, neutral white LED, cold white LED, and warm white LED.[5] The comparison results are summarized in Figure 1.2b, and as can be seen, participants were statistically neutral to the laser white light.[5] Therefore, according to the experimental results, the four-colour-laser-based white light is almost indistinguishable for human's visual perception compared to the conventional white light sources.[5] Although this conclusion seems contrary to intuition, it can be explained as follows. There are three types of cone cells in human eyes, mainly corresponding to red, green, and blue colour sensation.[8] A

person cannot tell the changes of wavelength by just exciting one sort of cone cells, and only via the comparison among the excitation degree of these three types of cone cells, a human can sense a light of particular wavelength.[9] Hence, as long as the photo-pigment in each type of cone cells can be excited, regardless of the spectral distribution of the excitation light, visual perception of a particular colour can be constructed.

Figure 1.2 (a) Schematic illustration of laser illumination with red, yellow, green and blue lasers. The light from these four lasers goes through beam splitters, beam combiners, and diffusers, and finally shines on the objects for the test. (b) The left figures show the

spectral distribution of power of four different sorts of the light source (white curves) and the intensity of the four colour lasers that mimic the conventional light source (black spiky curves). The figures on the right are the results of the comparison between the laser white source and the conventional white sources. This figure is adopted from [5].

1.1.3 Problems of Current Liquid-crystal Display Technology

For the current mainstream LCD screens, white LED backlighting with continuously distributed spectrum and broad red, green, blue (RGB) colour filters are employed as shown in Figure 1.3. Hence, the red, green and blue component for colour mixing is spectrally broad. The colour gamut of such LCD screen with less saturated primary colours can only display around 70% colour of the television colour standard gamut by National Television System Committee (NTSC), which was developed in 1953 for the colour space of broadcasted video.[10, 11] Therefore, in order to achieve a display with a bigger colour gamut, more saturated primary colours should be adopted. If laser emission, which is very narrow in spectrum, is employed to work as the primary colours, the boundary of the colour gamut of such display can be pushed to the spectral locus corresponding to the monochromatic colours in CIE 1931 colour space, the amount of colour that can be reproduced is much increased, and the colour quality can be much improved.

Figure 1.3 The standard white LED backlighting spectrum with RGB colour filters.[12]

On the other hand, the backlighting of current LCD is nonpolarized, and as a result, more than half of the initial energy of the backlighting would be lost when passing through the polarizer in an LCD unit.[13] Thus, it is critical to use polarized backlighting to reduce the energy consumption of an LCD screen. Emission of a laser is usually highly polarized because of the optical feedback process from the cavity structure.[14] Therefore, the utilization of laser for liquid crystal displays can address both problems of small colour gamut and low energy inefficiency of current mainstream LCDs.

1.2 Enlarged Colour Gamut with CQD Lasers as Primary Colours for Displays

To justify the argument that the utilization of saturated primary colours can increase the colour gamut of a display, the locus of colours corresponding to the emission of the same full width at half maximum (FWHM) is plotted in Figure 1.4. The emission spectra are assumed to be Gaussian function like. The curves are plotted with MATLAB. As can be noticed from the plot, with the FWHM of the spectrum increasing, the area that is enveloped by the locus that corresponds to the colours with the equal spectral width becomes smaller. Therefore, if

the spectral width of the primary colours becomes larger, the colour gamut will shrink, and fewer colours can be displayed.

In this work, the lasing emission from CQDs is adopted to demonstrate the spectrally ultra-narrow RGB light, as shown in Figure 1.5. The detailed discussion about CQD lasing will be presented in the following chapters. The blue, green, and red CQD lasing is from CdZnS/ZnS nanodots, CdSeS/CdZnS/ZnS giant nanodots, and CdSeS/ZnS nanodots, respectively. All the RGB lasing spectra were measured with CQDs in a capillary tube with a diameter of 300 μm , which leads to very dense optical modes and where almost every mode within the gain profile of CQD occurs. Therefore, the lasing peaks look a bit broader (~ 3 nm in FWHM) than a single mode laser. The coordinates of the RGB CQD lasing emission are plotted in CIE 1931 colour space, and the corresponding points are in the vicinity of the boundary, where the monochromatic colours are represented. If these three CQD lasing emission is adopted as primary colours for a display, the triangle of colour gamut can be 124% compared to the NTSC 1953 standard colour gamut, and almost twice of the colour gamut of a conventional LCD.

Figure 1.4 Plot of the locus of the colours of Gaussian-like spectral shape with the same FWHM in CIE 1931 colour space.

Figure 1.5 CQD lasing peaks emerge on PL spectra of red, green, and blue CQDs. The red, green and blue lasing was achieved by optically pumped CdSeS/ZnS nanodots, CdSeS/ZnSeS/ZnS giant nanodots, and CdZnS/ZnS nanodots, respectively.

1.3 Summary

In this chapter, the motivation of my Ph.D. thesis work is discussed. Nowadays, the efficiency droop at high input density is a fundamental limitation for current GaN-based high power LED devices. Laser can be an alternative to address this problem, which is an efficiency photon source with high power density. Moreover, the ultra-narrow emission of lasers can increase the luminous efficacy if they are employed to generate white illumination. Furthermore, lasers are usually polarized, which can be utilized for displays or reduction of glare from reflective surfaces for lighting.[5] Also, the spatial coherence (low divergence) property of lasers facilitates a better photon management, such as focusing, directing, and mixing, compared to conventional light sources.[5] In addition, greater modulation bandwidth compares with LED make lasers very promising for visible light communication.[15]

Meanwhile, the white light that is mixed by four colour lasers is not distinguishable by human eyes when it was compared to other conventional white light sources.

As to the display technology, laser is a good option to resolve the problems of current LCD screens, including small colour gamut and less energy efficiency, by means of its ultra-narrow emission and the polarization properties introduced by the well-designed optical cavity. Moreover, polarized emission, which can be easily achieved by a laser, is also widely employed for three-dimensional displays.[16]

Therefore, to address the limitations of current lighting and display technologies as discussed above, it is critical to realize semiconductor lasers that cover the full visible spectral range with high efficiency and linear polarization. I adopt colloidal quantum dots to demonstrate RGB lasing with high polarization to pave the way for the development of novel lighting and displays of greater energy efficiency and colour quality.

Figure 1.6 The colour gamut (within the yellow boundary triangle) of a display with the RGB CQD lasing as primary colours in CIE 1931 colour space. The triangle with magenta boundary represents the NTSC 1953 gamut.

Chapter 2 Synthesis and Basic Characterization of Colloidal Quantum Dots

2.1 Introduction

The advent of semiconductor nanocrystals, also known as colloidal quantum dots (CQDs), can be dated back to about 30 years ago in the former Soviet Union.[17, 18] Since then, intense researches have been carried out worldwide theoretically and experimentally to understand and utilize the unique properties of this sort of nanomaterial.[19] Nowadays the family of semiconductor nanocrystals has been very big, and they have been applied to various usage, including biolabelling [20], LEDs [21, 22], solar cells [23, 24], water splitting [25], lasers [26, 27], and so forth [28, 29]. In this chapter, the basic properties and synthetic methodologies of CQDs are reviewed. The CQDs synthesized during my Ph.D. program will be presented, and the corresponding optical and structural characterizations of CQDs will also be shown. Meanwhile, regarding the concern about the potential adverse effects of CQDs' utilization, the discussion of their environmental and human health impact is briefed. Good understandings of the fundamental properties of CQDs and a firm grasp of the synthetic methods together with the characterization techniques of CQDs are prerequisites for the further study and application of CQDs. Thus, this chapter is the foundation for following chapters.

2.2 Properties of Colloidal Quantum Dots

Energy gap that separates continuous conduction band and valence band are intrinsic to a particular sort of bulk semiconductor.[30, 31] However, as to nanoscale crystalline or nanocrystals (NCs), the particle boundary starts to impact their electronic structure[31, 32], and the modified electronic structure can be schematically illustrated in Figure 2.1.[33, 34]

The phenomenon of the size-dependent electronic structure is quantum confinement effect, and the corresponding additional energy is called quantum confinement energy.[31-33] The simplest way to describe the electronic structure of a CQD is to employ the so-called “quantum box” model: for a CQD with core only, the bandgap energy can be written as

$$E_g(CQD) = E_g(bulk) + \frac{\hbar^2 \pi^2}{2m_{eh} R^2} \quad (2-1)$$

where m_{eh} is the reduced mass of an electron and hole pair, R is the radius of a CQD.[33]

More precise and complete treatments of the electronic structure can be found in [34]. The dimension of a CQD should be comparable with the Bohr radius of exciton [33], and the Bohr radius of the exciton in CdSe, ZnS, and CdTe is 3.0 nm, 2.2 nm, and 7.5 nm, respectively.[35]

The strong confinement regime corresponds to the Bohr radius of electrons, holes, and excitons is greater than that of quantum dots, where electrons, holes, and excitons are strongly confined by quantum dots boundary.[34] And, weak confinement regimes refer to the radius of a CQD is larger than Bohr radius of electron and hole but smaller than that of the exciton, and the intermediate confinement regimes is that the radius of a CQD is greater than the Bohr radius of the hole but smaller than that of electron and exciton.[34] In light of Equation (2-1), as the size of a CQD shrinks, the bandgap becomes larger accordingly, as illustrated in Figure 2.2a. Therefore, by just changing the size of CQDs, the emission can be tuned continuously, which is shown in Figure 2.2a.

Aside from the size-dependent energy gap, leading to tunable emission wavelength, another important property of quantum dot is the discretely distributed energy levels, as illustrated in Figure 2.1.[33] Such atomic-like electronic structure of a CQD is resulted from its finite size, which gives rise to the quantized energy levels.[33]

Figure 2.1 Comparison of band structure between the bulk semiconductor and semiconductor nanocrystal. Band gap separates continuous valence and the conduction band of the bulk semiconductor, but band gap of semiconductor nanocrystal is size-dependent and energy levels are discretely distributed. This figure is adopted from [33].

Another way to synthesize a sort of CQD with particular emission wavelength or optical properties is to adopt the heterostructure of CQDs. By manipulating the band alignment between the core/shell structures, as shown in Figure 2.2b, the distribution of wave function of the hole and electron will be tailored.[36] As a consequence, the energy of the exciton that accounts for emission will be changed. If the dimension, structure, and chemical composition (Figure 2.2c) is well designed, almost the emission of any wavelength can be realized with a decent quantum yield.[37]

Besides the tunable emission wavelength, other aspects that make CQDs very attractive material for photonic applications are rare earth element free [38] and solution processability [39], which can reduce the cost of the device fabrication significantly.

Figure 2.2 (a) Schematic illustration of the evolution of the electronic levels of CQDs with different sizes, which is resulted from quantum confinement effect. The lower panel is the corresponding image of the CQD solution under UV illumination. (b) Schematic illustration of three types of band alignment in CQD heterostructures. Via tuning the relative position of the energy band of the core/shell heterostructures, the distribution of electron and hole wave functions can be manipulated. (c) The relative position of the conduction band (CB) and valence band (VB) with respect to the vacuum level of various sorts of semiconductors. This figure is adopted from [36].

2.3 Environmental Impact of Cadmium-based CQDs' Usage

Since the increasing popularity of the products that contains Cd based CQDs in the market, the potential adverse effects of this type of CQDs to the environment and human health should be seriously evaluated and considered.[40] The cadmium and selenium content, which are the most common constituent elements of CQDs, can give rise to both acute and chronic intoxication [41, 42], and have aroused dramatic public concerns regarding their consequent detriments to human health and the environment.

At the beginning of this year (2015), the European Commission issued a directive regarding an exemption for cadmium usage for lighting and display applications. It reads in the directive:

“The evaluation showed that the use of quantum dots in displays has indeed a positive overall impact due to their low energy consumption. Quantum dots are a new technology that will replace older colour converting designs in many applications in the near future. The

elimination of quantum dots via design changes is technically impracticable, as they are a new and superior technology. Although it would be desirable to substitute cadmium in quantum dots, Cd-free quantum dots (using e.g. indium phosphide) are still in the scientific research stage and years away from production.”

EU COMMISSION DELEGATED DIRECTIVE of 30.1.2015

Moreover, actually, the amount of Cd in one current display device with Cd based CQDs is tiny, *i.e.* less than 0.01 g, which is around 1/500 of the amount of Cd that is contained in a standard AA nickel-cadmium battery.[12] Therefore, although the Cd content in CQDs cast a debatable future of this type of nanomaterial, Cd based CQD is still a very promising candidate for next generation lighting and displays, regarding its outstanding optical performances and their controllable potential hazards.

2.4 Synthesis of Colloidal Quantum Dots

Colloidal quantum dots are synthesized in a solution that is dissolved with the precursors. It is relatively easy to grow a flawless crystal in such small length scales, where defects do not have enough time to be introduced, but it becomes quite challenging to control the properties of CQDs' size and surface.[43] Murray and et al. reported the method that is based on high-temperature pyrolysis of organometallic precursors, which is a milestone in controlling the size of CQDs.[44] However, in their synthesis protocol dimethyl cadmium ($\text{CH}_3\text{-Cd-CH}_3$) was adopted as the precursor of Cd, and this reagent is very toxic, highly pyrophoric, and quickly degraded. In 2001, Peng and his coworkers reported a greener methodology of the synthesis of Cd-based CQDs, which replaced dimethyl cadmium with cadmium oxide (CdO).[45] Generally, four steps are involved in the synthesis of CQDs: preparing precursor solutions, nucleation and nuclei growth, terminating crystal growth, and post-preparation.[46] For a better passivation of the surface of CQDs, which remove the surface defects and increases the quantum yield, a core/shell structure was developed.[43, 47]

The process of colloidal particle nucleation can generally be understood with La Mer and Dinegar's study, as shown in Figure 2.3a.[34, 48] Discrete nucleation takes place after rapid injection of precursors, which decomposes and forms oversaturated monomer solution in the reaction vessel.[34, 48] As growth proceeding, monomer keeps adding to nuclei, and the concentration of monomer decrease to a level that the formation of new nuclei stops.[34] Then, Ostwald ripening stage follows, which is not desirable because it broadens the size distribution of the nuclei.

2.4.1 Synthesis Setup

The basic setup for CQDs synthesis is shown in Figure 2.3b: three-neck flask is the reaction vessel that connects to Schlenk line for switching between vacuum and inert gas atmosphere; temperature probe communicates with a temperature controller, and the precursors can be injected through the rubber turnover using syringes. The synthesis setup that is used in Luminous! is shown in Figure 2.3c. The temperature probe with glass protector is connected to a temperature controller, and the output power of the heating mantle is determined by proportional-integral-derivative (PID) feedback mechanism in the temperature controller to control and maintain the temperature in the reaction flask stable.

Figure 2.3 (a) Schematic illustration of different stages of the growth of monodisperse CQDs. (b) Sketch of the typical apparatus that are employed for CQDs synthesis. (a) and (b) are adopted from [34]. (c) Synthesis setup of CQD synthesis in Luminous!. Schlenk

line is used to switch the atmosphere in the reaction vessel between vacuum and Ar. Cooling water from a chiller circulates in the condenser. The temperature probe is covered with a glass shield and touches the reaction solution. The temperature controller is connected to the temperature probe and controls the power of the heating mantle via PID feedback mechanism. The synthesis reaction takes place in a three-neck flask, and a stir bar is put in the flask for solution blending.

2.4.2 Synthesis of Cadmium-based Colloidal Quantum Dots

One of the most attractive properties of CQDs is their tunable emitting wavelength realized by adjusting their shape, composition, dimension and structure.[37, 49] There are two classes of the mainstream synthetic method of CQDs, one is the one-pot [45, 50, 51], and the other one is the successive ion layer adsorption and reaction (SILAR) [52-54]. The former approach is easier, but the latter one allows a more precise control of shell thickness and emission wavelength. I synthesized CQDs that emit blue, blue green, yellow green, yellow, red and infrared light according to the recipes that are published in [35], [55], [55], [53], [56], and [57-59] with the methods of precursors pyrolysis. The absorption spectra and photoluminescence (PL) spectra are shown in Figure 2.4a and b, respectively. First absorption peak can be well resolved, and the PL peaks are narrow, which indicates an excellent monodispersity of the as-synthesized CQDs.

Figure 2.4 (a) Absorption spectra (b) PL spectra of different CQDs as-synthesized dissolved in toluene. From left to right: the blue curves corresponding to CdZnS nanodots [35], the blue green, yellow green, and yellow curves corresponding to CdSeS/ZnSeS nanodots [55], the red curves corresponding to CdSeS/ZnS nanodots [56], and the magenta curves corresponding to CdTe/CdSe nanodots [57-59].

2.4.3 Synthesis of Indium-based Colloidal Quantum Dots

Employment of InP-based CQDs is an alternative to the utilization of Cd-based CQDs. Indium phosphide (InP) nanocrystals were synthesized with no epitaxial shell at the early stage, which required long reaction time, up to several days, and post treatment with diluted hydrogen fluoride (HF).[60, 61] However, this sort of nanocrystals with bare InP core demonstrated a broad size distribution, substantial defect emission, and low photoluminescence quantum yield (PLQY). To make the surface InP nanocrystal better passivated, a zinc sulfide (ZnS) shell was introduced.[51, 62] With ZnS shell, PLQY was increased up to 60%, and meanwhile, the full width at half maximum (FWHM) was around 60 nm.[3, 4] What's more, these protocols shortened the synthesis time to hours.[51, 62] On the other hand, the lattice constant and band structure mismatch between InP and ZnS is big, which leads to carrier trapping defects and enhancement of Auger process in nanocrystals.[63] As the development of nanocrystal shell engineering, InP-based multishell nanocrystals were synthesized.[64-66] Compared with InP/ZnS nanocrystals, the nanocrystals with ZnSe/ZnS multishell showed higher stability, higher PLQY, and better monodispersity.[64-66] Considering the precursor of phosphorus, *i.e.* tris(trimethylsilyl)phosphine, depletes very fast after the nucleation, and the InP CQDs enters to the stage of ripening, which is detrimental to the monodispersity of InP CQDs.[67] Here, I developed a new protocol that injects bis(trimethylsilyl)sulfide immediately after the injection of tris(trimethylsilyl)phosphine to

passivate the as formed InP CQD with ZnS shell, which prevents the ripening process of InP cores and improves their monodispersity. The synthesis protocols are described as follows:

Materials: Indium acetate ($\text{In}(\text{Ac})_3$, Sigma-Aldrich, 99.99%), Zinc acetate ($\text{Zn}(\text{Ac})_2$, Sigma-Aldrich, 99.99%), Palmitic acid (PA, Sigma-Aldrich, 99%), 1-octadecene (1-ODE, Sigma-Aldrich, 90%), Tris(trimethylsilyl)phosphine ($(\text{TMS})_3\text{P}$, Sigma-Aldrich, 95%), Bis(trimethylsilyl)sulfide ($(\text{TMS})_2\text{S}$, Sigma-Aldrich, synthesis grade), 1-dodecanethiol (1-DDT, Sinoreagent), Oleic acid (OA, Sigma-Aldrich, 99%).

0.08 mmol $\text{Zn}(\text{Ac})_2$, 0.08 mmol $\text{In}(\text{Ac})_3$, 0.24 mmol palmitic acid in 4 ml 1-octadecene were added in a 25 ml three neck flask. The mixture was heated to 110 °C and kept under vacuum for 2 hours to remove water. After degassing, 0.04 mmol $(\text{TMS})_3\text{P}$ in 1 ml 1-ODE was injected into the reaction vessel at 150 °C rapidly. After three minutes, 0.04 mmol $(\text{TMS})_2\text{S}$ in 1 ml 1-ODE was injected slowly, and then the temperature was increased to 230 °C and kept for 1 hour. After that, 0.12 mmol $\text{Zn}(\text{Ac})_2$ was added at room temperature and heat the reaction vessel to 230 °C for 1 hour. Then, 80 μl 1-DDT in 1 ml 1-ODE was loaded into a syringe and injected slowly at 230 °C and held at 230 °C for 2 hours.

The absorption and PL spectra of the toluene solution of InP/ZnS CQDs are shown in Figure 2.5. The FWHM of the emission from the CQD solution is 49 nm, which is very narrow for InP-based CQDs. The InP/ZnS CQD solution was dropped cast on a glass slide to form a thin film, and the emission spectrum is shown in Figure 2.5. As can be seen, the emission peak of the dried CQD film is red shifted compared to that of the CQD solution, and the spectrum is broadened to 56 nm in width. The red shift of colloidal quantum dot (CQD) film is because reabsorption process and energy transfer between CQDs becomes very significant in a film, especially for InP CQDs with big size distribution.

Figure 2.5 Absorption (blue curve) of green InP/ZnS CQD solution and PL spectra of green InP/ZnS CQDs in solution (red curve, the excitation wavelength is 355 nm) and InP/ZnS CQD film (black curve, the excitation wavelength is 450 nm).

Recently a new sort of InP-based nanocrystals with GaP/ZnS multishell was synthesized.[68] The band gap of GaP lies between that of InP and ZnS, giving rising to a gradient band alignment. Moreover, GaP layer abates the lattice mismatch between InP core and outmost ZnS shell. We adopted the protocol developed by S. Kim and et al. for the InP/GaP/ZnS nanocrystal synthesis.[68]

The experiment is described as follows. 0.24 mmol indium acetate ($\text{In}(\text{Ac})_3$), 0.8 mmol $\text{Zn}(\text{Ac})_2$, 0.72 mmol PA, and 8 mL 1-ODE was loaded in a 25 mL three-neck flask. The mixture was heated to 110 °C and put under vacuum for 2 hours. Then, 0.12 mmol $(\text{TMS})_3\text{P}$ in 1 mL 1-ODE was injected into the mixture at 300 °C. The mixture was kept at 230 °C for 2 hours. The dose for GaP shell growth was prepared by mixing 8 mg GaCl_3 and 0.1 mmol oleic acid (OA) in 2 mL 1-ODE and injected slowly at 200 °C. The solution was held at 230 °C for 1 hour. 0.3 mmol $\text{Zn}(\text{Ac})_2$ was added to the flask at room temperature and the

solution was degassed again and kept at 230 °C for 4 hours. 0.5 mmol 1-DDT was slowly injected, and the solution was kept at 230 °C for 2 hours.

Figure 2.6 shows the absorption and emission spectra of our as synthesized InP/GaP/ZnS nanocrystals. As compared with standard fluorescence dye Rhodamine 6G, the PLQY was determined as 68.9% (details of the measurement will be shown in Section 2.5). The PL peak was at 551 nm, and it was near the wavelength range where the human eye is most sensitive, *i.e.* 555 nm.[8]

Figure 2.6 Absorption and PL spectra of InP/GaP/ZnS CQDs in toluene solution. The absorption spectrum is magnified by 25 times, and the first excitonic peak can be resolved.

2.5 Fluorescence Quantum Yield Measurement of CQDs

The fluorescence quantum yield (Φ_f) of CQDs is an important measure to estimate their quality and characterize their optical properties, and it is defined as the ratio of the number of photons that are emitted ($N_{em}(\lambda_{ex})$) to the number of photons that are absorbed ($N_{abs}(\lambda_{ex})$) at a particular excitation wavelength (λ_{ex}), which can be written as [69]:

$$\Phi_f = \frac{N_{em}(\lambda_{ex})}{N_{abs}(\lambda_{ex})} \quad (2-2)$$

The methods for determination of the fluorescence quantum yield of CQDs can be classified into two categories; one is the absolute method [70], the other one is the relative method [69].

- The absolute measurement of fluorescence quantum yield

In my experiment, the absolute fluorescence quantum yield (QY) analysis was carried out with an integrating sphere that is equipped with a laser diode (405 nm) and a portable spectrometer (Ocean Optics USB2000). The intensity of the excitation laser without sample ($I_{ex,reference}$) and the background intensity in the emission wavelength range of the sample ($I_{em,reference}$) is first measured, then the sample is placed in the integrating sphere and measure the intensity of the excitation laser ($I_{em,sample}$) and the emission intensity of the sample ($I_{em,sample}$). And, the fluorescence quantum yield is calculated according to the Equation (2-2).[70]

$$\Phi_f = \frac{N_{em}(\lambda_{ex})}{N_{abs}(\lambda_{ex})} = \frac{\int \frac{\lambda}{hc_0} [I_{em,sample}(\lambda) - I_{em,reference}(\lambda)] d\lambda}{\int \frac{\lambda}{hc_0} [I_{ex,reference}(\lambda) - I_{ex,sample}(\lambda)] d\lambda} \quad (2-3)$$

- The relative measurement of fluorescence quantum yield

The relative method for fluorescence quantum yield measurement was carried out with comparison with standard dyes.[69] The fluorescence quantum yield measurement can be obtained with the Equation (2-4) by virtue of the absorption and emission measurements of the CQD solution of interest and the solution of the standard dye.[69]

$$\Phi_{f,x} = \Phi_{f,st} \frac{F_x}{F_{st}} \cdot \frac{f_{st}(\lambda_{ex})}{f_x(\lambda_{ex})} \cdot \frac{n_x^2}{n_{st}^2} \quad (2-4)$$

where,

$$F = \frac{1}{hc_0} \int_{\lambda_1}^{\lambda_2} I_c(\lambda_{ex}, \lambda_{em}) \lambda_{em} d\lambda_{ex} \quad (2-5)$$

$$f(\lambda_{ex}) = 1 - T(\lambda_{ex}) \quad (2-6)$$

And, $\Phi_{f,st}$ is the fluorescence QY of the reference dye, “ x ” and “ st ” denote the CQD solution of interest and standard dye, respectively. An example is shown in Figure 2.7; the fluorescence QY for CdSeS/ZnSeS CQDs, the absorption spectra of CQD solution and standard dye solution were measured first. Then, the PL spectra for the sample and the standard dye solution were measured with the excitation wavelength where they had the same absorption, and the fluorescence QY was 0.903, which was calculated according to Equation (2-4).

For the comparative method of QY measurement, the emission wavelength of CQDs and that of the standard dyes should be matched so that the effect of wavelength dependent sensitivity of the spectrometer can be removed.[69] And, for a precise measurement, the concentration of the CQD solution should be small to minimize the reabsorption.[69]

Figure 2.7 Fluorescence QY measurement of CdSeS/ZnSeS CQDs in solution in comparison with 2',7'-dichlorofluorescein. Absorption (a) and fluorescence (b) spectra of CQD solution and 2',7'-dichlorofluorescein solution.

2.6 Electron Microscopic Characterization of CQDs

Electron microscopy is a powerful tool for the characterization of the morphology and structure of nanomaterials.[71] The high-resolution transmission electron microscopy

(HRTEM) image of CdSe/CdS nanorods that was taken with JEOL 2100F with accelerating voltage of 200 kV (Figure 2.8a), Figure 2.8b shows the HRTEM image of a silver nanoparticle (taken with JEOL 2010 with accelerating voltage of 200 kV). The CdSe/CdS nanorods were synthesized according to [72], and the silver nanoparticles were provided by Prof. Sergey Gaponenko's group at National Academy of Sciences of Belarus. The mechanism of the contrast in HRTEM images, accounting for the atomic level resolution, is phase contrast.[73] Since the CQDs are minuscule, to improve the contrast of HRTEM image, TEM grids coated ultra thin carbon film with lacy holes were used in my experiments.

Scanning electron microscopy (SEM) has a lower resolution compared to TEM, and it can be employed to observe the collective arrangement of nanocrystals. Figure 2.9a shows an SEM image of opal-like self-assembly of silica nanoparticles (the silica nanoparticles were synthesized based on [74]). In Figure 2.9b, the SEM image of a thin layer of CdSe/CdS nanorods on ITO glass is shown, where the nanorods are randomly oriented.

Figure 2.8 HRTEM image of CdSe/CdS nanorods (taken with JEOL 2100F) (a), silver nanoparticle (taken with JEOL 2010) (b). TEM images were taken in Facility for Analysis, Characterisation, Testing and Simulation (FACTS), School of Materials Science & Engineering, NTU.

Figure 2.9 SEM images of a self-assembly of silica nanoparticles (a), and a thin layer of CdSe/CdS nanorods on ITO glass. The images were taken with JEOL JSM 6700F in Division of Physics and Applied Physics, NTU.

2.7 Summary

In this chapter, the unique optical properties of CQDs are introduced. Although the heavy metal element containing of cadmium based CQDs aroused many public concerns about the concomitant detriments to human health and environment, the overall impact of utilizing Cd based CQDs on illumination and display applications is positive. Then, the development of CQD synthesis is reviewed, and the methods for CQD synthesis are discussed for Cd based and InP-based CQDs. Once the CQDs are synthesized, fluorescence quantum yield is measured to characterize the quality and optical properties of the as-synthesized CQDs. And, SEM and TEM are also key technologies for understanding the structure and morphology of CQDs.

A comprehensive training and firm grasp of the synthesis and characterization methods of CQDs lay a solid foundation for the further usage of CQDs. With the fundamental knowledge

of CQDs, I tuned the morphology and chemical composition of CQDs to realize CQDs with particular band alignment and emission wavelength, which facilitates the utilization of the optical gain from CQDs for lighting and display applications.

Chapter 3 Optical Gain from Colloidal Quantum Dots

3.1 Introduction

In Chapter 2, the outstanding optical properties of CQDs have been discussed. If we want to utilize CQD lasing towards novel lighting and display applications, it is critical to understand the mechanism of optical gain in CQDs and realize RGB stimulated emission via optical pumping. In this chapter, firstly, the development of researches of optical gain in CQDs will be reviewed. And then, the Auger process resulting from the multiexciton interaction within a CQD, which is an undesirable competing channel of stimulated emission, will be discussed, and the approaches that have been developed to abate the Auger recombination will be reviewed as well. In Section 3.2, two methods, *i.e.* stripe excitation and random lasing, which have been drawn up to test CQDs and determine their suitability for optical gain applications, are presented. Then, a novel indirect way to pump green CQDs and observe green lasing with standard pump laser is exhibited. The process is assisted by nonradiative energy transfer as a result from the dipole-dipole interaction. In the last section, the whole chapter will be summarized.

3.1.1 Optical Gain from Colloidal Quantum Dots

For traditional semiconductor bulk material for laser applications, there is almost no material system whose emission is capable of covering the full visible spectral range with a decent energy efficiency.[75] In light of the emission colour tunability of CQDs by virtue of adjusting their size, structure, and composition, CQD is a fabulous type of material that can provide optical gain at virtually any wavelengths if it is carefully designed. Meanwhile, the atomic-like energy level of CQDs guarantees that their laser performances are stable and temperature insensitive.[27, 76] Stimulated emission from CQDs was first observed in 1991 from CdSe nanocrystals that were doped in glass, which was optically pumped at liquid

nitrogen temperature.[77] After Klimov demonstrated optical gain from CdSe QDs at room temperature[78], the studies of lasing from QDs are on the rise. Scientists coupled QDs with various types of optical cavity structures to achieve laser action, such as microsphere [79], capillary tube [80, 81], Fabry-Pérot cavity [26, 79], Bragg grating [82, 83], and etc. moreover, random lasing from QDs was also demonstrated by introducing scattering centres in the gain medium made of QDs.[84, 85] Lasing has been not only observed from optically pumped zero-dimensional CdSe nanocrystals but also from one-dimensional nanorods [86] and two-dimensional nanoplatelets [87, 88], as well as nanocrystals with the corresponding epitaxial shells. Recently, C. Dang demonstrated single exciton lasing from red, green, and blue QDs with vertical-cavity-surface-emitting laser (VCSEL) or distributive feedback (DFB) configuration, which shows very low lasing threshold and high beam coherence.[26, 82] Therefore, the development of QD lasers enables their more novel usage in photonic devices.

On the other hand, optical gain was not only observed in cadmium based QDs, but some journal papers have also shown the lasing from InP base QDs, which paved the way to lasing from Cd-free QDs.[89, 90] But from my experimental experiences of InP-based QDs, the lasing threshold of InP-based QDs is extremely high compared to that of Cd-based QDs, given their relevant broader emission spectra, lower PL quantum yield and worse photostability. So a more practical laser with InP-based QDs can be expected only after a quantum leap takes place on the synthesis methodologies of such Cd-free QDs.

3.1.2 Auger Recombination of Multiexciton in QDs

The prerequisite of optical gain in QDs is that absorption bleaching is greater than the absorption of the ground state that accounts for the optical gain, *i.e.* $-\Delta\alpha/\alpha_0 > 1$. [33] Generally, the average number of exciton per QD, $\langle N \rangle$, has to be greater than 1, as illustrated in Figure 3.1a. However, if more than one exciton are optically generated in a QD, Auger

recombination will take place as a fast nonradiative channel to compete with the transition of stimulated emission. In Auger process, other than radiative recombination, one exciton transfers its energy to a third carrier (electron, hole, or exciton) that will be excited into a higher energy level, as illustrated in Figure 3.2. As a consequence, the lifetime of optical gain can be significant reduced, which hinders the lasing action in CQDs.

Figure 3.1 Schematic illustration of single exciton optical gain. (a) When the exciton-exciton interaction is absent, the photon that is generated by exciton recombination would be reabsorbed if the average number of exciton per CQD is 1. So in this case, no optical gain can be observed but the ground state optical transparency. (b) If the state of absorption is higher than the energy of emission, due to Stark Shift that is originated from the local electric field, the as emitted photon would not be reabsorbed, and therefore, light can be amplified in this CQD. This figure is adopted from [91].

Figure 3.2 Schematic illustration of Auger recombination in CQD. E_g is the energy band gap of a CQD. It describes a recombination of an electron (solid blue circle) in the conduction band and a hole (empty red circle) in the valence band, and the energy that is released nonradiatively excites another hole in the valence band into a higher energy state. This figure is adopted from [92].

The development of methodologies to abate the Auger recombination is crucial for the utilisation of CQDs for optical gain applications, and many efforts have been done for suppression of such undesirable nonradiative bypass. Here, some of these methods are briefly reviewed.

- Employment of single exciton gain

As illustrated in Figure 3.1, if the symmetry of the transition of absorption and emission is broken due to the Stark effect in the local electric field, the emitted photon is not reabsorbed, and optical gain can occur with average one exciton per CQD.[91] Single-exciton gain from CQD is considered as a radical approach to remove the effect of Auger recombination, because if there is only one exciton in single CQD, there will be no multiexciton interaction and no Auger process consequently. However, when the CQDs are strongly optically pumped,

the multiexciton generation seems inevitable. And, in some work, single exciton gain is achieved in type-II CQDs, where the electrons and holes are spatially separated in core or shell.[91] However, such employment of type-II CQDs results in a dramatic reduction of the overlap between the wavefunctions of holes and electrons, so the transition rate of emission is also decreased significantly.

- Employment of nanorods

A direct way to mitigate the Auger process is to reduce the columbic interaction between the excitons, so if the volume of a CQD increases the Auger recombination could be abated.[93] Given the fact that the emission wavelength of a CdSe nanorod is mainly determined by its radius but not its length [94], elongating the length of 0D CQDs with the emission of a particular wavelength into 1D nanorods can suppress the Auger process while maintaining the emission wavelength.[95] Comparing nanorods and nanodots with the same diameter, the Auger recombination rate can be reduced significantly and the optical gain lifetime is increased, which makes the nanorod a good material for CQD lasing.[86, 95]

- Employment of CQDs with gradient band alignment

Scientists found that the profile of the confinement potential of the exciton in a CQD has a strong impact on the Auger recombination rate.[63] The process of Auger recombination requires a strict conservation of momentum.[92] For a typical core/shell CQD, the interface between the core and shell of two unlike material gives a rise to an abrupt band energy change at the interface. When an exciton interacts with the step-like interface, as illustrated in the left panel of Figure 3.3, the abrupt band shift with an undefined slope at the interface can provide the momentum of any values and directions to meet the requirement of momentum conservation and facilitate the Auger process of the excitons. In contrast, in the CQDs with a gradually changed energy functions, the conservation of momentum of the Auger process is broken, and therefore, the Auger recombination is mitigated. The suppression of blinking

effect, which is due to the trion configuration from Auger-like process, and prolonged gain lifetime in CQDs with gradient energy band structure was observed.[92, 96]

On the other hand, in the CQDs with gradient shell, the average absorption energy would be higher than that of the emission, which is analogical to the so-called band fluctuation[97], and the absorption mainly happens in the CdS shell, but the emission takes place in the core with lower energy. Therefore, the Stokes shift, the spectral distance between the first excitonic peak and the emission peak of CQDs, becomes larger.[98]

Figure 3.3 Sketch of core/shell CQDs with step-like (left) and gradient (right) energy band. This figure is adopted from [92].

In summary, to lower the lasing threshold from CQDs, the Auger recombination needs to be suppressed by reducing the columbic interaction or breaking the momentum conservation. In addition, to reduce the CQD lasing threshold, the reabsorption of the emission should be minimized. Therefore, a big Stokes shift is very desirable.[26, 99]

3.2 Stripe Excitation and Random Lasing

For accessing whether the as-prepared CQDs could work as a gain medium, before coupling those CQDs with an optical cavity, the neat CQD films were pumped. An observation of amplified spontaneous emission (ASE) or random lasing (RL) in such experiments indicates the suitability of CQDs for lasing applications.

Optical pumping with a stripe-shaped light spot is a very widely used way to characterize the optical gain properties of the sample of interest. The pumping laser stripe can enable the optical gain of light propagating in the waveguide along the laser stripe. Light propagates along the excitation stripe and is amplified, and ASE from CQD film can be measured from the edge of the film, as shown in Figure 3.4a. As can be seen, ASE peak developed at the high energy side of the spontaneous emission peak as the pumping power increased. From Figure 3.4b, an apparent threshold of ASE can be observed, indicating such CdSeS/ZnS CQDs are a suitable sort of CQDs for optical gain experiments.

Another convenient method to examine the optical gain properties of CQDs is random lasing. Random lasing has many applications in bioimaging, and etc.[84] Since my topic is about the CQD lasing in lighting and display applications, I would like to mention an interesting paper that introduces applying RL for illumination as a light source of low spatial coherence but high power.[100]

In my experiment, I scratched a glass slide with a diamond pen to introduce scattering centres on the substrate. And then, a toluene solution of a high concentration of CQD was drop cast on the scratched glass, the upper image of Figure 3.5a. When the sample was optically pumped above the lasing threshold with a microPL setup, random spiky peaks emerged around the spontaneous peak, as shown in Figure 3.5b, and a very bright region can be observed under the microscope, which part was corresponding to the area of RL (the lower image of Figure 3.5a). For optical feedback structures, the wave number, $2\pi/\lambda$, is conjugate to the characteristic optical length of the feedback structure in Fourier transform.[101, 102] The RL spectrum was operated by Fourier transform, and the transformed curve represents the amplitude of optical feedback as a function of the optical path. As can be seen, there is a peak around 70 μm , which corresponds to the dominant optical feedback path.

Figure 3.4 (a) Spectra evolution of edge emission from drop cast CQD film in stripe excitation geometry. (b) The power transfer function of the ASE collected from the edge of the CQD film.

Figure 3.5 (a) The drop cast CQD layer on scratches on a glass slide. The upper image is the sample under white light illumination. The lower image is the sample that was optically pumped above the lasing threshold. The bright region corresponds to the area where random lasing took place. The side length of the images is 300 μm . (b) Spectrum of the random lasing from CQD layer on a scratched glass slide. (c) Fourier transform of the spectrum that is shown in (b), where the optical pathlength is conjugate with $2\pi/\lambda$.

Other than stripe excitation and RL, loading CQDs in a capillary tube is also a good configuration to examine the optical gain from CQDs, which will discuss in detail in Section 3.3 and Chapter 5.

3.3 FRET-assisted Stimulated Emission from Green Emitting CQDs

Given the energy inefficiency of the emission from III-V semiconductor in green regime [75], CQDs with tunable wavelength and high PL quantum yield are expected to be a good material for filling the so-called “green gap”.

The blue and green CQDs were synthesized with one pot method according to published literature.[103-105] Our blue and green emitting CQDs showed a very narrow PL spectrum with FWHM of 22 nm and 18 nm, as presented in Figure 3.6a. The PL quantum yield of the blue and green CQDs in toluene solution was 0.55 and 0.845, which was measured with an integrating sphere at the excitation wavelength of 405 nm. The narrow emission and high quantum yield of the green CQDs imply their high quality. The emission spectrum of the blue CQDs overlaps with the absorption spectrum of the green CQDs, which makes nonradiative energy transfer between blue and green dots possible.[106]

The solution with a high concentration of blue or green CQDs (100 mg/mL) was loaded into a capillary tube, and the CQD solution was dried under reduced pressure to form a densely packed CQD superlattice. The capillary tube with a diameter of hundreds micrometer not only can serve as a container of gain medium but also can act as a cylindrical optical microcavity, which can support multimodes of lasing that covers the full range of the gain profile of CQDs.[80, 107] In addition, only a tiny amount of gain medium solution, less than 10 μL , is needed to be loaded in a capillary tube for lasing characterization in contrast to the quantity that is required to make a thick and uniform film on a glass slide for stripe excitation

measurement. Therefore, gain medium in such a capillary tube is an excellent laser configuration for gain medium characterization of CQDs.

The samples were optically pumped with a pulsed UV Nd: YAG laser at 355 nm (third harmonics of the fundamental wavelength) with a repetition rate of 60 Hz and pulse width of 520 ps. Compared to pulse laser with a pulse duration in the order of femtosecond, pulsed Nd: YAG laser with nanosecond pulse is a more commonly used and a cheaper optical pumping source. In this work, the pulse duration of the optical pumping source is in sub-nanosecond range, which is much larger than the typical time constant of Auger recombination of multiexcitons (sub 100 ps for small cores).[93]

Figure 3.6 (a) Normalized absorption and PL spectra of diluted green (green curves) and blue (blue curves) emitting CQD solution. (b) and (c) are HRTEM images of a single green and blue emitting CQD, respectively. The side length of both (b) and (c) is 15 nm.

When the neat blue CQDs in the capillary tube were optically pumped, a sharp peak emerged at the low energy side of the spontaneous emission, as shown in Figure 3.7a. The Whispering gallery modes (WGMs) cannot be resolved here, because of the resolution of the monochromator that was used, whose resolution is around 0.6 nm, but the free spectral range

of the WGM lasing in this laser configuration is about 0.2 nm. A clear lasing threshold is exhibited in the laser transfer function that is plotted in Figure 3.11a. However, if we replaced the blue CQDs by the green CQDs under the exactly same pumping configuration, the green dots only showed spontaneous emission, Figure 3.7b. As can be seen in Figure 3.11a, the emission intensity of the green CQDs built up quite linearly with increasing pumping fluence during the initial stage of optical pumping, but the rate of the emission intensity increment decelerated under high excitation fluence. The slope of the emission intensity of green CQDs as the function of pump energy decreased by 43.4% when they were pumped under 25 μJ pulses compared to the green CQDs being pumped with low energy pulses. Thus, the PL quantum yield dropped from 0.845 under weak excitation to 0.478 under strong optical pumping. When the green CQDs were strongly optical pumped, multiexcitons would be generated in the CQDs, and as a consequence, Auger recombination, a nonradiative bypass of the radiative emission, would take place, which has a much shorter lifetime ($\sim 100\text{ps}$) than that of spontaneous emission (7.66 ns). Therefore, the PL quantum yield of the green CQDs decreased as increasing the pulse energy of pumping laser. On the other hand, since the photon energy of the excitation source is 3.49 eV (corresponding to 355 nm), the as excited excitons have much higher energy compared to the band gap of the green CQDs, which is 2.34 eV (corresponding to 529 nm). Therefore, the long path of the hot carrier relaxation to the band edge results in a high probability of the exciton trapping in the multishell interface and high energy defects of the green CQDs, which impeded the population inversion at the band gap and increased the threshold extremely high for the green CQDs in our pumping configuration. In contrast, if the same sample of the green CQDs was optically pumped by another pulsed laser with wavelength of 460 nm and pulse width of 5 ns, the sample started to lase under a low pump energy, as shown in Figure 3.8, even though the pulse duration is much longer than the pulsed laser that was used for previous pumping experiments with wavelength of 355 nm and pulse width of 520 ps. For the photon energy of the pumping

source decreased from 3.49 eV to 2.69 eV when the pumping wavelength was tuned from 355 nm to 460 nm, the amount of energy that needed to be released for relaxation to the band edge was much smaller, which made the CQD less heated, and excitons relax faster to the band edge without many trappings from the defects and Auger process.[99] Therefore, optical gain can be observed from the green CQDs under relevant low pump energy with pumping wavelength of 460 nm.

Figure 3.7 Spectra evolution of blue (a) and green (b) emitting CQD layer in a capillary tube with increasing pump power, respectively.

Figure 3.8 (a) Spectral evolution of green CQDs in a capillary tube as the pump energy increased. (b) The laser transfer function of green CQD layer in a capillary tube.

Systematic experiments were conducted with the CQD mixture of different weight ratio of the amount of blue to green CQDs in a capillary tube. The spherical green and blue CQDs that are used in our experiments exhibit a similar diameter (Figure 3.6b and c), and given that the composition of these two sorts of CQDs is both alloy of Cd and Zn chalcogenide, it is valid to assume the molar mass of blue and green CQD is similar. So the mass ratio of these two sorts of CQDs is approximately same as a molar ratio. The capillary tubes were loaded with mixed CQDs in toluene solution with concentration and amount of blue/green CQDs of 83 mg/83 mg per mL (1:1), 83 mg/41.5 mg per mL (2:1), 83 mg/27.6 mg per mL (3:1), respectively. The mixed CQD solution was loaded in capillary tubes with a diameter of 300 μm by capillary action. The CQD solution in capillary tubes was dried under reduced pressure. A closely packed binary CQD layer can be formed attaching to the inner wall of the capillary tube.[108]

To determine the fluorescence lifetime of the blue and green emission from the CQD mixture, the samples were excited with a solid state pulse laser diode of the wavelength of 375 nm and repetition rate of 20 MHz under low excitation power, as shown in Figure 3.9. The decay curve was fitted by single exponential function, and the lifetime constants of fluorescence of the samples with difference ratio of the amount of blue and green CQDs are listed in Table 3.1. The fluorescence lifetime of the donors (blue CQDs, monitored at 456 nm) decreased from 7.43 ns for pure blue CQDs to 5.88 ns when the portion of blue/green equal 1:1. And the lifetime constant of donors increased as the increasing of the donor concentration. Meanwhile, the lifetime of the emission of acceptors increased from 7.66 ns, in the absence of the donors (blue CQDs), to 9.12 ns when the amount ratio between blue and green CQDs was 3:1. And the higher concentration of the donor, the lifetime constant of the acceptor became larger. The experimental results confirm Foster energy transfer (FRET) took place from the donors (blue CQDs) to acceptors (green CQDs), which process can shorten the fluorescence lifetime of the donors but prolong that of the acceptors.

Figure 3.9 (a) Normalized photoluminescence decay of the blue emission from blue emitting CQD layer (black curve), mixture of blue and green emitting CQD with mass ratio of 3:1 (red curve), 2:1 (blue curve), and 1:1 (magenta curve). (b) Normalized photoluminescence decay of the green emission from green emitting CQD layer (black curve), mixture of blue and green emitting CQD with a mass ratio of 1:1 (red curve), 2:1 (blue curve), and 3:1 (magenta curve).

The FRET efficiency can be determined by:

$$\eta_{FRET} = \frac{k_{FRET}}{k_D + k_{FRET}} = \frac{k_{DA} - k_D}{k_{DA}} \quad (3-1)$$

where, k_{FRET} is the rate of FRET process, k_D or k_{DA} denotes the fluorescence decay rate of the blue CQDs in the absence or presence of the green CQDs.[109] Therefore, the FRET efficiency is 0.21 for the mixture with the amount ratio of blue to green CQDs equal 1:1.

Table 3.1 Summary of the single exponential function fitted decay lifetime of the donor (blue CQDs) and acceptor (green CQDs) in the CQD mixture with different blue/green ratio.

Blue : Green	Donor (ns)	Acceptor (ns)
Green CQDs Only	-	7.662

1:1	5.880	8.509
2:1	6.743	9.702
3:1	7.350	9.916
Blue CQDs Only	7.426	-

For one acceptor and one donor system, the changing rate of exciton number can be written as:

$$\frac{dN_B}{dt} = -k_B N_B - k_{FRET} N_B + r_B \quad (3-2)$$

$$\frac{dN_G}{dt} = -k_G N_G + k_{FRET} N_B + r_G \quad (3-3)$$

where, N_B or N_G are numbers of excitons in a blue or green CQD, k_B or k_G is the total recombination rate in the absence of acceptor or donor, k_{FRET} is the energy transfer rate, r_B or r_G is exciton creation rate in the blue or green CQD under optical excitation. For steady state emission,

$$\begin{aligned} \frac{dN_B}{dt} &= 0 \\ \frac{dN_G}{dt} &= 0 \end{aligned}$$

Therefore,
$$N_B = \frac{r_B}{k_B + k_{FRET}} \quad (3-4)$$

$$N_G = \frac{1}{k_G} \left(\frac{k_{FRET}}{k_B + k_{FRET}} r_B + r_G \right) \quad (3-5)$$

Given $r_B = \sigma_B I_{ex}$ and $r_G = \sigma_G I_{ex}$, where σ_B and σ_G are absorption cross section of the blue and green CQDs, I_{ex} is the excitation fluence, the output intensity can be written as:

$$I_B \propto \frac{\sigma_B}{k_B + k_{FRET}} I_{ex} \quad (3-6)$$

$$I_G \propto \frac{1}{k_G} \left(\frac{k_{FRET}}{k_B + k_{FRET}} \sigma_B + \sigma_G \right) I_{ex} \quad (3-7)$$

When the sample of the mixture of blue and green CQDs with the ratio of 1:1 was optically pumped by pulse laser in wavelength of 355 nm, as increasing pumping power, lasing peaks emerged on the low energy side of the spontaneous emission spectrum of green CQDs, as shown in Figure 3.10a, by contrast, the sample with only green CQDs did not lase with the exactly same optical pumping configuration even through under the highest power that the pumping laser can reach (Figure 3.7b). In the sample of the mixture of blue and green CQDs with a ratio of 1:1, the blue CQDs were able to excite the green CQDs indirectly via FRET and reabsorption process at the emission wavelength of the blue CQDs that is around 456 nm. So it is equivalent to that a portion of excitons that accounted for the stimulated emission from the green CQDs did not release much of their energy in the green CQDs but in the blue ones. Therefore, the green CQDs were less hot with the blue CQDs as the indirect pumping sources and thermal buffer. On the other hand, the blue CQDs that play a role of the indirect pumping source only showed spontaneous emission unlike their behaviour in the sample with only blue CQDs. Because a portion of excitons that was formed in blue CQDs transferred to the green CQDs via nonradiative channels, the population inversion in the blue CQDs would be hindered. Moreover, the photons emitted from the blue CQDs were prone to be reabsorbed by the green CQDs, which is not desirable for optical amplification process. Meanwhile, the concentration of the blue CQDs in this mixture was low so that there was not enough gain for their laser action.

When the mixture of blue and green CQDs with a portion of 2:1 in weight, no matter how strong the optical pumping was, both blue and green CQDs only showed spontaneous emission. The acceptors were surrounded by the donors, and more excitons were transferred to the green CQDs, which can be confirmed by the prolonged fluorescence decay of the CQD mixture with blue/green equal 2:1. And more excitons could be relaxed in the blue CQDs

making the green CQDs even less “hot”. However, the green CQDs did not lase even the sample were pumped by the highest energy pulse available. The main reason is the concentration of the green CQDs was not high enough to provide sufficient optical gain.

According to Equation (3-6) and (3-7), the increment rate of the spontaneous emission for both blue and green emission in the CQD mixture is constant. Such linear relation between the excitation and emission can be confirmed in Figure 3.11b, where both blue and green CQDs emitted in the spontaneous emission regime.

If the ratio of the amount blue to green CQDs was increased to 3:1, only blue CQDs started to lase under high optical fluence. In this case, the concentration of the blue CQDs in the mixture was high enough to support optical gain in this medium.

Figure 3.10 (a) to (c) show the emission spectral evolution of the mixture blue and green emitting CQDs in capillary tube with increasing pumping power, when the mass ratio of amount of blue to green emitting CQDs equals 1:1 (a), 2:1 (b), and 3:1 (c).

Figure 3.11 (a) Emission intensity of blue (green) CQDs in the absence of green (blue) CQDs that are excited by pulse laser with a wavelength of 355 nm as the pump energy increased. (b) Emission intensity of the blue and green CQD mixture with a ratio of 2:1 that are excited by pulse laser with a wavelength of 355 nm as the pump energy increased.

The evolution of normalized intensity of blue emission as a function of excitation energy for samples with different blue/green ratio is plotted in Figure 3.12. Since with the portion of the green CQDs in the mixture became larger, an increasing amount of energy from the blue CQDs would be taken to the green ones via energy transfer and reabsorption process. Therefore, the intensity of the blue emission increased slower as the ratio of the amount of blue to green CQDs. If taking a close look at the power transfer function of the blue CQDs with the portion of blue/green equal 1:1 (magenta triangles), the increasing rate of blue emission intensity became smaller (the slope decreased to 52.3% of initial slope under low pump energy) after the pump energy was above the lasing threshold of the green CQDs. Given the intensity evolution of blue emission from the sample with blue/green equal 2:1 (blue triangles), as shown in Figure 3.11b, where the emission intensity of the donors built-up linearly, the spontaneous emission rate and the absorption cross section of the donors would not be changed by increasing the pump energy. So the decelerated built-up of the spontaneous emission cannot be resulted from the Auger process, which indicates a greater contribution

from FRET process. In light of Equation (3-6), the FRET rate should be higher after the acceptor started to lase. This phenomenon can be explained as: after the acceptors began to lase the depletion of the states in the acceptors that accounted for energy transfer process became faster. Therefore, more states that contributed to the FRET process in the acceptors were available, which would increase the rate of FRET from the donors to the acceptors. Given the lifetime measurement below the green lasing threshold (Table 3.1), the FRET rate can be calculated as 0.035 ns^{-1} and 0.19 ns^{-1} for the mixture with the amount ratio of blue/green equal 1:1, when the pump energy was below and above the lasing threshold of the acceptors. We can remark that the lasing process in the acceptors will promote the nonradiative energy transfer from the donors.

Figure 3.12 Normalized integrated intensity of blue emission from blue CQD layer (black square), mixture of blue and green CQDs with a mass ratio of 3:1 (red circle), 2:1 (blue triangle), and 1:1 (magenta triangle). The data points are connected with line to guide the eye.

3.4 Summary

The works that have been done on CQD lasing are reviewed in this chapter. Because the discrete energy levels of CQDs, the CQD laser is more stable and less sensitive to temperature. Along with other merits of CQDs such as the emission colour tunability, high PL quantum yield, solution processability, and etc., CQD is an ideal sort of material for optical gain applications. However, the most significant obstacle for CQD's application as optical gain is the Auger recombination, which is a nonradiative channel that competes with radiative recombination. To alleviate the Auger process, scientists have made many efforts, such as adopting type-II CQDs, nanorods, thick passivation multishells, gradient band alignment and so forth.[63, 91, 95, 96]

ASE observed with stripe excitation configuration, or random lasing of CQDs are two methods to examine their suitability as optical gain medium before they are applied to optical cavity structures.

In light of the tunable emission of cadmium based CQDs and the challenges of III-V compounds in green emission, this sort of CQD is a promising candidate for practical green lasers to bridge the “green gap” in semiconductor lasers. However, if the CdSe based green CQDs are optically pumped with the standard pump wavelength of 355 nm, the threshold of green CQD lasing is extremely high due to the hot carrier relaxation process in the green CQDs. In this chapter, we demonstrated a novel partially indirect pump method of the green CQDs by using blue CQDs as exciton donors. With such indirect pumping scheme, optical gain was observed from the green CQDs under a relevant small pump energy. And the FRET rate of the donors increased after the acceptors started to lase. In conclusion, our indirect pump method enables a considerable reduction of lasing threshold in green CQD lasing with conventional pump laser in quasi-CW pump regime by nonradiative energy transfer processes,

making the green CQD a better candidate for optical gain applications that can fill the “green gap” in semiconductor lasers.

Chapter 4 Flexible One-Dimensional CQD Distributive Feedback laser

4.1 Introduction

Generally, the lasing emission is highly polarized because of its coherent nature, which is partially introduced by the optical resonator. By adopting a suitable optical cavity for the gain medium of spherical CQDs, a laser with high polarized emission can be achieved. In this chapter, recent progress of CQD based one-dimensional (1D) distributed feedback (DFB) lasers are reviewed. In the following section, the analytical description of light diffraction in a medium with periodic variation of the dielectric index is shown to have a better understanding of the scattering condition and out-coupling angle of the Bragg grating. The flexible Bragg substrate is adopted in this work, and its fabrication method and structural characterization is shown in the fourth section. In the next section, highly polarized CQD DFB laser is demonstrated with the flexible Bragg substrate with the periodicity of 380 nm or 400 nm, and the corresponding analyses about the peak energy will be presented as well.

4.2 One Dimensional CQD Distributive Feedback lasers

A DFB laser is a laser device whose amplifying medium is periodically modulated and the output light is characterized by resonant scattering at the wavelength-scaled periodic structures.[110] The simplest type of DFB laser can be achieved by a slab waveguide of gain medium with one-dimensional effective refractive index variation, which can be introduced by the periodic variation of the layer thickness. Many works have been done on CQD lasing with DFB type optical resonators.[111-113] The Bragg grating can be fabricated by interference lithography[111, 114], electron beam lithography[82], polymerization-induced phase separation in polymer-dispersed liquid crystals[112], imprinting Germania sol-gel[113],

imprinting polymer film[83, 115-117], and so forth. By tuning the periodicity of the grating or effective refractive index of the waveguide, the resonance scattering wavelength of the DFB device can be adjusted.[111, 114] Generally speaking, tuning grating's periodicity is a tougher approach which involves tedious fabrication process of the grating itself or the master mould. On the other hand, modification of the effective refractive index is a more feasible way. Two measures can be employed for such effective refractive index adjustment. The first one is that by varying the occupation ratio of the CQDs, so the effective refractive index can be tuned accordingly.[111] Another approach is by adjusting the thickness of the CQD layer on the grating with given groove depth, and consequently, the distribution of electromagnetic wave propagating in the slab waveguide would be changed, which results in the modification of effective refractive index.[114, 116] Generally, as the optical gain layer becomes thicker, the effective refractive index becomes smaller, given that $n_{eff}=n\sin\theta$, where θ is the incident angle for a certain waveguide mode.

As the development of CQD synthesis, the performance of CQD DFB device keeps improving during recent decade, from the device operating at a cryogenic temperature under ultrafast optical pumping to device working at room temperature with long pulse width pumping.[111, 114] C. Dang and his colleagues demonstrated a CQD DFB laser operating with the single optical mode, and good spatial coherence of the emission from the CQD DFB laser was also shown by a well-collimated output beam in the far field.[114] In light of the time constant of Auger recombination, around 120 ps,[26] the pulse width of the pump laser is 270 ps, which 2.25 times longer than the Auger process.[114] Therefore, the CQD DFB laser can be optically pumped by a quasi-CW laser and operate in the regime of the quasi-steady state. Also, C. Dang and his colleagues also showed RGB DFB lasers with CQDs of red, green and blue emission (Figure 4.1).[82] The lasing threshold is very low for the surface-emitting DFB lasers of all three colours due to their high-quality close-packed CQD film, optimized grating structure, and the ideal CQDs that can lase in the single-exciton

regime. In light of the outstanding performance of such laser devices, the CQD RGB DFB lasers with ultra-monochromatic lasing emission and low-threshold are very bright for potential usage in lighting and displays.

Figure 4.1 (a) Spectra of red, green, blue CQD 1D DFB laser. The solid lines represent the single mode CQD second order DFB lasing, and the dotted lines are the ASE and spontaneous emission spectra for the red, green, and blue CQDs. (b) to (d) are laser transfer function of the surface emitting single mode CQD RGB DFB lasers. The inset showed the output beam on a screen below and above lasing threshold when the device was excited with a stripe of 20 μm in width and 200 μm in length. This figure is adopted from [82].

Other than the CQD DFB laser fabricated on a rigid substrate, M.D. Dawson's team at the University of Strathclyde fabricated CQD DFB laser with mechanically flexible Bragg substrate.[83, 115] Their method of imprinting the polymer onto a master Bragg grating finds a cheaper and faster way of fabricating Bragg grating. In addition, this flexible CQD DFB laser can be used for sensing applications by virtue of lasing peak shift with surrounding environment changing.[83] However, polarization characterization and analysis of the output

emission from the flexible CQD DFB laser is still missing, which is essential for our lighting and display applications. In section 4.5, the detailed polarization dependent analysis of the emission beam will be presented.

4.3 Diffraction of Light in Medium of Periodic Refractive Index

Figure 4.2 Sketch of an electromagnetic wave propagating in a medium of periodic dielectric function. The wave vector of the incident wave is k_{inc} , K is the vector represents the periodicity of the medium, θ is the incident angle, φ is the angle the grating vector with respect to the surface normal.

Figure 4.2 illustrates that light enters a medium of the periodic dielectric index, and the incident light is diffracted. If the dielectric distribution of a medium can be written in the form of a sinusoidal function, such as:

$$\varepsilon_r(\vec{r}) = \varepsilon_{r,0} + \Delta\varepsilon \cos(\vec{K} \cdot \vec{r}) \quad (4-1)$$

It is worth to be noted that in the case of the dielectric function in other periodic forms, such dielectric function can be decomposed into Fourier series, which is essentially a linear combination of a series of sinusoidal functions, therefore, in general, the assumption in Equation (4-1) is still valid.

The electromagnetic wave propagating within this medium with periodic dielectric function should take the same periodicity as the grating; thus, the electric field can be written as:

$$\begin{aligned}
 E(\vec{r}) &= A(\vec{r})e^{-j\vec{k}_{inc}\cdot\vec{r}} \\
 E(\vec{r}) &= A(\varepsilon_{r,0} + \Delta\varepsilon \cos(\vec{K} \cdot \vec{r}))e^{-j\vec{k}_{inc}\cdot\vec{r}} \\
 E(\vec{r}) &= A\varepsilon_{r,0}e^{-j\vec{k}_{inc}\cdot\vec{r}} + \frac{A\Delta\varepsilon}{2}e^{-j(\vec{k}_{inc}-\vec{K})\cdot\vec{r}} + \frac{A\Delta\varepsilon}{2}e^{-j(\vec{k}_{inc}+\vec{K})\cdot\vec{r}} \quad (4-2)
 \end{aligned}$$

There are three terms in Equation (4-2), and each term represents an electromagnetic wave propagating through the medium of the periodically modulated optical potential. And, as to these three waves, corresponding to the three terms of Equation (4-2), each of them will also split into other new three electromagnetic waves in the medium of periodic optical potential. Therefore, if the waves keep splitting into new waves, the wave vector of the wave propagating in the medium can be written as:

$$\vec{k}_m = \vec{k}_{inc} - m\vec{K}, \quad m = -\infty, \dots, -2, -1, 0, 1, 2, \dots, \infty \quad (4-3)$$

Equation (4-3) essentially describes all allowed modes for electromagnetic waves propagating in the medium of periodic dielectric function. If we consider the component in x direction,

$$\begin{aligned}
 k_{m,x} &= k_{inc,x} - mK_x \\
 \frac{2\pi}{\lambda_0} n_{eff} \sin \theta_m &= \frac{2\pi}{\lambda_0} n_{inc} \sin \theta_{inc} - m \frac{2\pi}{\Lambda} \sin \varphi
 \end{aligned}$$

$$n_{eff} \sin \theta_m = n_{inc} \sin \theta_{inc} - m \frac{\lambda_0}{\Lambda} \sin \varphi \quad (4-4)$$

where m is an integer, n_{eff} is the effective refractive index of the medium, θ_{inc} and θ_m are the incident angle and diffraction angle of the electromagnetic wave with respect to the surface normal, φ is the orientation of the one dimension grating with respect to the surface normal, λ_0 is the wavelength of the electromagnetic wave in vacuum, Λ is the period of the dielectric modulation of the medium, as illustrated in Figure 4.2. Equation (4-4) is the general form of the Grating Equation, which describes the propagation of electromagnetic wave with a given incident angle in a medium of periodic optical potential.

For a 1D DFB laser device, the electromagnetic wave is confined in the slab waveguide. Therefore, according to Equation (4-4), The m^{th} order of one dimension DFB with respective to a vacuum wavelength λ_0 and grating pitch Λ are related as:

$$2n_{eff}\Lambda = m\lambda_0 \quad (4-5)$$

m is an integer and represents the order of allowed optical mode.

Considering Equation (4-4) and Equation (4-5), the outcoupling direction of the light propagating in the waveguide with periodic optical potential is given by

$$\theta_m = \arcsin \left[n_{eff} \left(1 - \frac{2m'}{m} \right) \right] \quad (4-6)$$

where m and m' are the order of the mode of an electromagnetic wave propagating in the waveguide and the order of the scattering that accounts for out coupling. Therefore, for a second order DFB laser, the direction of the out-coupling beam is along the surface normal of the slab waveguide by virtue of the first order scattering, *i.e.* $m=2$, $m'=1$.

4.4 Fabrication of CQD DFB Laser Devices

The flexible Bragg gratings are provided by Prof. Martin Dawson's group at the Institute of Photonic, University of Strathclyde. The DFB grating was developed on NOA65 epoxy film on top of an acetate sheet by impressing onto a mould with a grating period of 380 nm (or 400 nm) and modulation depth of 50 nm, and the epoxy film was cured under 254 nm UV illumination, as shown in Figure 4.3a. The atomic focus microscopy (AFM) characterization confirms the periodic modulation of the thickness of flexible Bragg substrate (Figure 4.3b and c). The flexible Bragg gratings were spin coated with high concentration toluene solution of red CQDs (100 mg/mL) with a spin rate of 1500 rpm for one minute. The purpose of the employment of CQD solution of such high concentration is to realize a thick CQD layer that is able to provide enough optical gain. Although the CQD layer is comparably thick, the CQD DFB device is still mechanically flexible, as shown in Figure 4.3d.

Figure 4.3 (a) Sketch of the flexible DFB substrate that is used in the experiments. (b) The 3D AFM plot is showing the variation of the thickness of the flexible Bragg substrate. (c) 2D AFM image of the flexible DFB substrate. (d) The flexible DFB substrate with spin coated CQD layer under UV illumination, which can be mechanically bended.

Figure 4.4 shows the SEM images of the flexible Bragg substrate with a periodicity of 380 nm (a) and 400 nm (b). A gold layer of 10 nm in thick was sputtered onto the samples to improve their electrical conductivity and reduce charge accumulation of the sample. For the flexible Bragg substrate in the SEM images, actually they were previously used by spin-coating CQDs and the CQD layer was washed away by hexane after using. The periodic grooves were still well maintained after the cleaning process with an organic solvent, which suggests that even though the flexible Bragg gratings were made of polymer, they still can be recycled and reused.

Figure 4.4 SEM images for of the flexible Bragg substrate with a period of 400 nm (a) and 380 nm (b), after sputtered with 10 nm gold film to make the sample electrically conductive. The images were taken after the CQD coating on flexible Bragg gratings were washed off with hexane, and the periodic structures are still well maintained after cleaning, which indicates the polymer gratings are reusable.

4.5 Stimulated Emission from CQDs on a Flexible Bragg Substrate

When the 380 nm period Bragg substrate spin-coated with CQDs was placed in the laser beam, it yielded a clear x -structure on the screen behind, which suggested the good quality of the

grating, as shown in Figure 4.5.[117, 118] And, the wavelength of the intersection of the structure corresponds to the stop band of the Bragg substrate.

Figure 4.5 Fan shaped beam originated from the first order Bragg scattering.

The setup for the stimulated emission characterization of CQDs on flexible Bragg grating is shown in Figure 4.6. The excitation source was a double frequency Nd: YAG pulsed laser with a pulse width of 520 picoseconds and repetition rate of 100 Hz. A Glan-Thomson Prism was placed after the pump laser to make sure the laser beam was completely linearly polarized. A quarter waveplate was adopted to transform the linearly polarized light into the circularly polarized light so that the transverse electric (TE) and transverse magnetic (TM) modes of the sample could be homogeneously excited. The sample was optically pumped from the bottom of the substrate in order to first excite the CQDs adjacent to the grating. The detection arm was normal to the CQD 1D DFB device to collect the output beam, which coupled out by the first order scattering of the Bragg grating. By tuning the wheel polarizer that was put after the sample, the polarization dependent emission could be analysed, and in the meantime, an

achromatic half-wave plate was rotated accordingly to make sure the light was captured by the detector with the same polarization so that the effect of the polarization-dependent sensitivity of the detector was removed.

Figure 4.6 Schematic illustration of experiment setup for optically pumped polarization dependent lasing measurement. The optical components from left to right are Glan-Thomson prism, quarter waveplate for 532 nm, convex lens, the sample, linear polarizer, and achromatic half-wave plate.

The polarization state of light propagating in the slab waveguide with periodic modulated refractive index is defined as Figure 4.7. The light of TE mode is with electric field along the grooves, and the light of TM mode is with electric field orthogonal to the grooves. The light of TE modes is able to be subject to the optical feedback from the grating structure. Therefore, the output laser beam from the 1D DFB devices should be of TE modes.

Figure 4.7 Schematic illustration of the periodic structure of the flexible Bragg grating.

The electromagnetic wave of TE modes is polarized parallel to the grooves, and the electromagnetic wave of TM modes is polarized perpendicular to the grooves.

The spectral evolution of emission with TE and TM modes from CQDs spin coated flexible Bragg grating (380 nm period) with increasing pump power is shown in Figure 4.8(a) and (b), respectively. A series of lasing modes emerged around 619 nm, 9 nm red-shifted from the spontaneous emission peak when the pumping power was above the threshold for lasing. Moreover, the position of this series of modes was very stable and did not shift as the pump power increasing. As the pump power increased further, another bunch of peaks appeared at 625 nm, 15 nm red shifted away from the spontaneous emission peak, and these peaks developed were, even more, red shifted, if the pumping fluence was further increased. The first bunch of peaks (at 619 nm) was most probably due to optical feedback from the Bragg grating, which reduced the stimulated emission threshold of CQDs and made the position of the lasing peaks stable. The second bunch of lasing peaks, around 625 nm, was ASE of the spin coated CQDs. For semiconductors, the band gap shrinks as the temperature becomes

higher, and when the pump power was increased, the pumped CQDs became hotter. Therefore, the lasing peaks, around 625 nm, developed, even more, red shifted under stronger pumping.

Figure 4.8 Emission spectra of CQDs on flexible Bragg grating with a period of 380 nm. (a) Evolution of the spectra of TE modes with increasing pump power. (b) Evolution of the spectra of TM modes with increasing pump power.

The evolution of intensity of TE ($I_{//}$, parallel to the grooves) and TM ($I_{\perp}$, perpendicular to the grooves) mode emission from the flexible CQD DFB device with 380 nm periodicity as a function of pump power is shown in Figure 4.9. The data points are fitted with “soft threshold” approximation, which is typical for optical microcavity laser.[117] The “soft threshold” is characteristic of the laser action when a substantial portion of spontaneous emission is coupled into laser modes.[83, 119] The lasing threshold for TE and TM mode emission was 0.27 mW and 0.43 mW, respectively. Polarization ratio is defined by Equation (4-7) to characterize the polarization degree of the emission.

$$p = \frac{I_{//} - I_{\perp}}{I_{//} + I_{\perp}} \quad (4-7)$$

As can be seen from the plot of polarization ratio's evolution in Figure 4.9, the difference of polarization between the light of TE and TM modes were small when the pump fluence below the lasing threshold. When the pump power increased, the polarization ratio built up rapidly,

and then this ratio reached a plateau, which is of the value of 0.82, when the device completely operated in stimulated emission regime. The reason for the slight decrease in the polarization ratio under highest pump power is that the portion of ASE, which was not subject to the cavity effect of the grating, was increased under high pump power.

Figure 4.9 The transfer functions of TE (parallel to the grooves, red dot) or TM (perpendicular to the grooves, black square) modes lasing from spin-coated CQDs on flexible Bragg grating with a period of 380 nm. The data points are fitted with soft threshold approximation. The evolution of polarization ratio of this CQD lasing on the flexible Bragg grating as a function of pump power is plotted with magenta triangles.

In comparison with the experiments that were conducted with 380 nm period flexible Bragg grating, CQDs were also spin coated on the grating with the periodicity of 400 nm and the development of the spectra under increasing pump power are shown in Figure 4.10. As can be seen, as pump power increased, lasing peaks developed on the slightly low energy side of the spontaneous emission peak.

Figure 4.10 Emission spectra of CQDs on flexible Bragg grating with a period of 400 nm. (a) Evolution of the spectra of TE modes emission with increasing pump power. (b) Evolution of the spectra of TM modes emission with increasing pump power.

The lasing threshold was 0.17 mW and 0.53 mW for TE and TM mode emission from CQD 1D DFB device. Because of the optical feedback that was enabled by the Bragg grating, the lasing threshold was much lower of TE modes compared to that of TM modes. Similar to the results of the experiment that was carried out with 380 nm grating, the grating had the negligible modulation of spontaneous emission, and the polarization ratio was nearly zero at the beginning and builds up rapidly as increasing the pump fluence. However, the polarization ratio of the emission of the DFB with 400 nm period, which was 0.96, was much higher than the result of the previous experiment with the grating of 380 nm period. This suggests a larger modulation of the CQDs' stimulated emission by the grating of 400 nm periodicity and a better match between the grating periodicity, the thickness of the CQD layer and the wavelength of optical gain.

Figure 4.11 The transfer functions of TE (parallel to the grooves, red dot) or TM (perpendicular to the grooves, black square) mode lasing from spin-coated CQDs on flexible Bragg grating with a period of 400 nm. The data points are fitted with “soft threshold” approximation. The evolution of polarization ratio of this CQD lasing on the flexible Bragg grating as a function of pump power is plotted with magenta triangles.

The emission spectra of TE and TM modes, from CQD 1D DFB structure with 380 nm and 400 nm periodicity, are fitted with Gaussian functions. Although the profiles of these spectra are not in Gaussian form, especially for the lasing peaks and the transitional status from spontaneous emission to stimulated emission, the as fitted Gaussian curves can still provide an overall idea about the collective behaviours of these emission peaks. The variation of the Gaussian fitted peak energy with increasing pumping fluence is plotted in Figure 4.12. The peak energy of TM modes was generally lower than that of TE modes, and this was due to the lower effective refractive index for the TM modes in the waveguide compared to that of TE modes.[83] If we take a look at the data point of the spectra of TM modes, in which direction that the grating structure had no modulation, the spectra of CQDs on 400 nm grating were

red-shifted slightly compared to those of CQDs on 380 nm. A little bit thicker CQD layer on 400 nm grating may account for this red shift, because of a smaller effective refractive index and a larger reabsorption. The assumption of a thicker CQD layer on 400 nm period grating is also consistent with the observation that the CQDs on this 400 nm grating had a stronger emission intensity compared to those on the 380 nm grating under the same pump condition and had a lower lasing threshold. The difference of CQD layer thickness between these two samples may be due to the slow spin rate that was used and high concentration of CQD solution, and as a consequence, the thickness of the spin-coated film may not be well controlled. Another observation from Figure 4.12 is that the shape of line-connected data points is quite different between that of TE and TM modes emission, but the trend of the variation of either TE or TM mode emission peaks are similar for CQD emission on gratings with a period of both 380 nm and 400 nm. The evolution of emission peak energy of TE modes as a function of pump power for both gratings can be divided into three stages, separated by dotted lines in Figure 4.12. The first phase, before the first red (blue) dotted line for TE mode emission peak of CQDs at 380 nm (400 nm) flexible Bragg grating, mainly accounts for the spontaneous emission under low pump fluence. During the initial part of the first stage, far below the lasing threshold, the energy of the emission peaks of both TE and TM modes underwent a slight blue shift as shown in Figure 4.12. As pumping fluence rising, an increasing number of electrons and holes would be excited; therefore, these carriers would have filled the lowest energy band and start to occupy higher energy bands so that the emission would be slightly blue shifted.[120] However, in the late first stage, the peak positions show a significant red shift. This is because as increasing pump power the temperature of CQDs became higher due to the relaxation of a large amount of hot carriers, the band gap of the semiconductor would shrink, and CQDs showed red-shifted emission.[121] The second stage is the transitional stage from spontaneous emission to lasing, between these two dotted lines of the same colour. As the pump power increased, the fraction of spontaneous

emission became smaller and the portion of lasing increased, and eventually the peak position reached a plateau when the lasing peak became dominant. The lasing position was stable with no noticeable red shift during the late second stage by virtue of the cavity effect from the grating structure. If the pump power grew further, it entered the third stage, in which the emission peak energy for both DFB devices of 380 nm and 400 nm grating had a steep drop and then slightly red shift afterwards, after the second dotted line. This phenomenon can be explained as, when pump power was so high, the parts of CQD layer that were not subject to the modulation of the grating are excited and started to give rise stimulated emission, considering the small depth of the grooves of the grating and the thick CQD layer. At this stage, the peak position continued to red shift as the CQDs became hotter.[121] Moreover, the difference between the line connected data points of TE and TM modes is larger for 400 nm grating than those of 380 nm. This result also indicates the 400 nm grating had a bigger modulation of light than that with period of 380 nm, which is consistent with the finding that the emission of 1D DFB of 400 nm period has a bigger polarization compared to that of 380 nm (shown in Figure 4.9 and Figure 4.11) and 400 nm grating matched the emission of CQDs better. In addition, as can be noticed from Figure 4.12, the spin coated CQDs on flexible Bragg grating of 380 nm and 400 nm period lased with the similar peak position. This is because the depth of the grooves is small and the Q-factor of the 1D DFB lasers was low, probably the gain profile of the CQDs played a more considerable part in dictating the lasing peak positions compared to the case with cavity of high quality, where the resonance peaks of the optical microcavity play a more important role, as illustrated in Figure 4.13.

Figure 4.12 Evolution of peak position of the TE and TM modes emission of spin coated CQDs on flexible Bragg grating with a periodicity of 380 nm and 400 nm.

Figure 4.13 Sketch of the resonance peak of flexible Bragg grating (with low Q factor) and the gain profile of CQDs. The blue curves represent the resonance spectra

of the flexible Bragg grating of 380 nm or 400 nm period. The yellow curve stands for the gain profile of the CQDs.

4.6 Summary

In this chapter, highly polarized CQD lasing that is achieved via optical cavity effect is discussed. Firstly, the works of one-dimensional DFB lasers with CQDs as a gain medium are reviewed. Secondly, the behaviour of an electromagnetic wave propagating in a medium with periodic variation of refractive index is described analytically, and the general form of the Grating Equation is derived. Then, one-dimensional DFB lasers with CQD layer as a gain medium on mechanically flexible Bragg grating is demonstrated, which were easily fabricated by simply imprinting and spin coating. Since the Bragg substrate is made of a polymer material, the DFB devices fabricated on this substrate are soft and mechanically flexible. We tested the emission of a spin coated CQD layer on the flexible Bragg substrate with increasing excitation power, and highly polarized lasing emission was obtained with both gratings with 380 nm and 400 nm period. By virtue of polarization dependent analysis, the DFB device with 400 nm period had a higher polarization ratio compared to that of 380 nm period. Along with the plot of the position of emission peaks as a function of pump power, we can come to the conclusion that the grating of 400 nm period had a better match with the emission of the CQD layer that was used. Because the depth of the flexible grating is small, an increasing portion of the thick CQD layer was excited to emit light with little modulation from the grating structure under high pump fluence. Although the quality factor of this sort of DFB laser is not high, which may account for the unchanged lasing wavelength with 380 nm or 400 nm grating, the lasing emission was still highly polarized. Therefore, considering its mechanically flexible nature and lasing emission with high polarization ratio, CQD 1D DFB laser is a promising candidate for future novel display and lighting applications.

Chapter 5 Observation of Anisotropic Gain from

Aligned Nanorods

5.1 Introduction

In light of the discussion in previous chapters, to achieve polarized lasing emission, either polarization selectivity from the optical cavity or an anisotropic gain medium has to been employed. The former approach to achieve polarized lasing has been discussed in Chapter 4, and this chapter will focus on the latter methodology. In order to realize polarized gain medium with CQDs, the “building blocks” of such gain medium have to possess anisotropic optical properties. After the anisotropic CQDs available, the means that can align these anisotropic “building blocks” in large scale should be adopted to show off their anisotropic optical properties macroscopically. In this chapter, the polarized gain medium, aligned CdSe/CdSe dot-in-rods (DRs), in a capillary tube, which serves as a cylindrical optical microcavity with negligible polarization selectivity, will be demonstrated.

In the introduction part, the intrinsic anisotropic properties of semiconduction nanorods, methods to orderly arrange nanorods, and the properties of CdSe/CdS DR will be introduced. The following experimental part will show the verification of the intrinsic anisotropic optical property of CdSe/CdS DRs, the proof of the alignment of CdSe/CdS DRs by SEM images and optical characterization, and Whispering gallery mode (WGM) lasing from the aligned CdSe/CdS DRs in a cylindrical optical microcavity. At last, I will conclude the discussion in the conclusion part of this chapter.

5.1.1 Polarized Emission from Elongated Nanocrystals

When the shape of a CQD changes from spherical to elongated, the symmetry of crystalline structure breaks, and as a consequence, with the aspect ratio of a CdSe nanorod increases, the

emitted light is more polarized.[122] Because a larger dipole moment is present along the c -axis of the nanorod, CdSe nanorod exhibits a higher probability of transition for both absorption and emission that is along its c -axis, as shown in Figure 5.1a.[123, 124] For a CdSe/CdS DR, the CdS rod growth breaks the symmetry of the transitions of its spherical CdSe core. The transition of lowest energy is changed from in the xy plane for CdSe nanodot to along the c -axis of the CdSe/CdS heterostructure (Figure 5.1b).[125] Therefore, the CdSe/CdS DR exhibits a polarization dependent absorption and emission, and it is promising for orientation sensitive applications of CQDs.[125-128]

Figure 5.1 (a) (i) Polarization-dependent excitation of individual CdSe nanorods, i.e., the evolution of emission intensity as a function of excitation polarization angle. The data points are fitted with $\cos^2\theta$ function. (ii) Polarization dependent emission of individuals CdSe nanorod, i.e., the evolution of emission as a function of detection polarization angle. The data points are fitted with $\cos^2\theta$ function. (b) The upper panel shows photoluminescence excitation (PLE) excitation spectrum of CdSe/CdS DR solution. The

lower panel displays the PLE spectrum of CdSe/CdS DR solution. The inset shows exciton energy diagram of CdSe/CdS DR. (a) is adopted from [123]. (b) is adopted from [125].

5.1.2 Techniques for the Alignment of Colloidal Nanorods

In order to take advantage of such polarized optical properties of nanorods in various photonic devices, which are introduced in Section 5.1.1, the nanorods have to be orderly oriented in a collective way. Otherwise, an ensemble of randomly pointed nanorods results in isotropic absorption and emission. Many approaches have been employed to align nanorods in large scale to form a nanorod superlattice, which is capable of showing off anisotropic optical properties, such as:

- Self-Assembly on the Liquid Interface

When nanocrystals are spread on the surface of water, they tend to organize in a way that reduces their interfacial energy.[129] Generally, the arrangement status of elongated nanorods at the interface of air and water is determined by the length and concentration of nanorods.[130, 131] When long nanorods or high concentration nanorod solution are used, the nanorods are liable to self-assembled vertically at the air/water interface; when short nanorods or low concentration nanorod solution are employed, these nanorods tend to align laterally and lay flat on the water surface.[130] A. Rizzo and et al. fabricated a QLED that exhibits polarized electroluminescence (EL).[132] A drop of CdSe/CdS DR in toluene is spread on the surface of water, and this solution evaporates in saturated toluene atmosphere, as shown in Figure 5.2a. By carefully controlling the evaporation rate and the concentration of the CdSe/CdS DR dispersion that is on the water surface, these DRs self-assembled into a thin film floating on the surface of the water in nematic or smectic phase. This thin film with laterally aligned CdSe/CdS DRs is transferred onto an organic film for device fabrication with

a polydimethylsiloxane (PDMS) stamp, as shown in Figure 5.2b to d. The polarization-dependent intensity of emission of this thin film of aligned CdSe/CdS DRs that were excited by circularly polarized laser is shown in Figure 5.2e, which indicates the DRs oriented statistically in a particular direction. Moreover, the QLED that was fabricated with aligned CdSe/CdS DRs shows a significant difference in the EL intensity detected in two orthogonal polarization orientations.

Figure 5.2 The schematics of the methodology of the fabrication of aligned nanorods film

on an organic substrate. (a) CdSe/CdS in toluene is dropped and spread evenly on the surface of the water. (b) After toluene evaporates completely, the as-formed nanorod film on the surface of the water is fished with a PDMS stamp pad. The HRTEM image shows the nanorod self-assembly that is formed on the water surface, which is fished by a TEM copper grid with a carbon coating. (c) The CdSe/CdS film is transferred onto the organic layer with a conformal contact by pressing gently. (d) The last step is to remove the

PDMS stamp, and the nanorod layer is attached to the surface of the organic layer. The inset shows the SEM image of laterally aligned CdSe/CdS nanorods on the surface of the organic layer after transferring. (e) The polar diagram displays the peak intensity of the PL from the thin film of aligned CdSe/CdS nanorod as a function of polarization angle. (f) Normalized EL spectrum from the LED made with an active layer of aligned CdSe/CdS nanorods. The inset shows the EL spectra captured in two orthogonal polarized orientations. This figure is adopted from [132].

- Mechanical Rubbing

Mechanical rubbing is a versatile approach to align nanomaterials.[133] Compared to other techniques to align nanorods, mechanical rubbing is more efficient, economical, suitable for large area fabrication, and has a high yield. As shown in Figure 5.3, just by rubbing a spin-coated CdSe/CdS DR thin film, the DRs will be aligned along the direction of rubbing.[134] Highly polarized spontaneous emission was detected from rubbed spin-coated CdSe/CdS DR film with a polarization ratio of 0.56.[134]

- Electrical Fields Directed Self-Assembly

In light of the intrinsic dipole moment in nanorods, the electric field has been employed to induce nanorods alignment.[135] In the capacitor structure shown in Figure 5.4, nanorod solution is placed between these two electrodes.[136] After the solution is dried, the nanorods orient along the electric field and there forms a close-packed superlattice of vertically aligned nanorods (Figure 5.4c).[136] In addition, the electric field can also be applied laterally, as illustrated in Figure 5.4d.[72] The CdSe/CdS DRs aggregate into some ribbon-like structures that are normal to the parallel electrodes, and from the SEM images, individual DR can be clearly resolved, which shows an alignment of DRs along the electric field.[72] The evolution of PL intensity of the sample, excited by circularly polarized light, as a function of detection

polarization angle is well fitted with $\cos^2\theta$, which also confirms the overall orientation of the aligned CdSe/CdS DRs (Figure 5.4g).[72]

Figure 5.3 (a) The sketch of the alignment of nanorods via a rubbing process. The roll coated with rubbing fabric was pressed on the sample which was spin-coated by nanorods. The rotation of the roll was opposite to the movement of the sample, leading to forming of grooves on the substrate by stacking nanorods. (b) No preferential orientation of nanorods is shown in the SEM image of the as-spin-coated film. (c) The SEM image shows the nanorods that were spin-coated on the substrate were aligned along the rubbing direction, and the inset shows the absorption and emission spectrum of the CdSe/CdS nanorods. This figure is adopted from [134].

Figure 5.4 (a) and (b) Sketch of a capacitor structure for the nanorod alignment. The

copper electrodes are coated by gold with a spacing of 1.2 mm. The parallel electrodes are put in a glass vial which contains saturated toluene vapour. The substrate is a carbon coated TEM copper grid. 50 μL of nanorod solution of toluene is dropped between the two parallel electrodes, and 1 kV voltage is applied. (c) HRTEM image of the electric field assisted perpendicularly aligned CdSe nanorod superlattice with the domain size larger than $0.5 \mu\text{m}^2$. (d) SEM image shows the laterally aligned CdSe/CdS nanorods film formed with applying an electric field. The red arrow marks the direction of the applied electric field. The area in the red square is shown in (e), which is in micrometre size and where individual nanorods can be well resolved. (f) The zoom-in of the ribbon-like structure shown in (e). (g) (i) The schematics of the polarization dependent emission measurement. (ii) The emission spectra of CdSe/CdS nanorods ensemble with the detection polarization angle parallel and perpendicular to the c -axis of nanorods. (iii) The evolution of the emission intensity of aligned CdSe/CdS nanorods as a function of detection polarization angle, which is well fitted with $\cos^2\theta$ function. (a) to (c) are adopted from [136]. (d) to (g) are adopted from [72].

- Flow Fields Directed Self-Assembly

Microfluid of nanorod solution can drive and orient the disordered nanorods into a ordered and densely packed superlattice.[129] Despite the entropy maximization of a microsystem, the driving force applied to a nanoparticle by the fluid is sufficient to overcome the thermal fluctuation.[137] Figure 5.5 shows a coffee ring structure that was fabricated by a microplotter. During the drying process of a drop of CdSe/CdS DR solution on the substrate, the solution at the edge of the drop dries faster, and therefore, a microfluid forms, which conveys the solution from the central part to the edge.[138] CdSe/CdS DRs self-assembled into an order form with an overall orientation.[138] If the evaporation rate is more precisely controlled by atmosphere flow rate and surrounding temperature, a very large area of

CdSe/CdS DR superlattice of high quality can be fabricated.[139] Microfluid can also be driven by capillary force as shown in Figure 5.5g.[140-142] The water solution of gold nanorod climbs above the water surface onto the TEM grid that is inserted into the solution because of capillary action. Along with the drying process that takes place at the front of the raised solution, an influx of gold nanorod solution from the bulk solution generates to compensate the solvent loss due to evaporation, and a number of gold nanorods accumulate on the TEM grid.[140] With the TEM images of the gold nanorod film that formed on the TEM grid, vertically aligned gold nanorod (along the direction of the fluid driven by capillary force) can be revealed.[140]

Figure 5.5 (a) to (d) SEM images of self-assembled coffee ring structure fabricated with Eppendorf femtojet system. (a) The typical coffee ring structure of densely packed CdSe/CdS nanorods. (b) and (c) SEM images of the rectangular areas (b) defined in (a) with higher magnification, in (c), aligned nanorods can be resolved. (d) SEM image of randomly oriented nanorods in the central part of the coffee ring. (e) Schematic illustration of the controlled evaporation experimental setup. (f) TEM image of a superlattice of perpendicularly aligned nanorods (aligned along the *c*-axis of wurtzite nanorod), which is fabricated by controlled evaporation. (g) Sketch of deposition of gold nanorods on a TEM grid. (i) A TEM grid is inserted into a gold nanorod solution by a quarter of its diameter. (ii) Due to capillary action, a layer of solution is raised up. As the water evaporates from the raised thin layer, the nanoparticles and water are transported from the bulk solution to this layer. (iii) The evolution of the thickness of the gold nanorod self-assembly. (a) to (d) are adopted from [138]. (e) and (f) are adopted from [139]. (g) is adopted from [140].

5.1.3 CdSe/CdS DRs as an Optical Gain Medium

CdSe/CdS DR is a sort of newly synthesized nanocrystal of mixed dimensionality, with a CdSe core and seeded CdS rod. The intrinsically polarized absorption and emission properties of CdSe/CdS DR have been shown in 5.1.1, indicating this sort of nanocrystal is a promising candidate for the polarized gain medium application. Furthermore, the facts listed below make CdSe/CdS DR a more desirable material for usages as optical gain medium:

- Suppressed Auger recombination

When the CdSe based CQDs are strongly optically pumped to achieve population inversion that is a prerequisite for optical gain, multiexcitons are generated, and Auger recombination takes place becoming a nonradiative bypass that competes with the process of stimulated

emission.[93, 96, 143] The rate of Auger recombination process is proportional to the square of the carrier density, $r_{\text{Auger}} \propto n^2$, where n is effective carrier concentration.[93] The approaches that use type-II CQDs or nanorods to reduce the effective concentration of carriers were employed to reduce Auger recombination.[91, 144] However, at the same time, the radiative transition rate would be significantly reduced because of the dramatic reduction of the wave functions overlap between electrons and holes. In CdSe/CdS DR, the energy difference of conduction band is considerably small so that the electrons spread throughout the entire seeded CdS rod, but that of the valence band is big enough to confine holes within the CdSe core.[145-147] By tuning the length of the seeded CdS rod, the distribution of electrons and holes can be changed accordingly, as shown in Figure 5.6.[148] As can be seen in Figure 5.6, longer CdS rod leads to a more delocalized electron distribution in the rod, and a longer emission decay lifetime. Resulted from this kind of quasi-type-II band alignment, CdSe/CdS DR is supposed to suppress Auger recombination and meanwhile, maintain a reasonable carrier wave functions overlap.

Figure 5.6 Wave function engineering of CdSe/CdS DR by means of tuning the length of the seeded CdS rod. (a) The calculated wave function for hole and electron in DRs with different length. (b) The decay of PL from DRs with different length. This figure is adopted from [148].

In Figure 5.7a, the optical gain endured for at least 300 ps for all DRs with different length. Meanwhile, the decay kinetics are not pumped fluence dependent, which indicates a nearly complete suppression of Auger process in CdSe/CdS DRs (Figure 5.7b).[149] In light of the remarkable suppression of Auger recombination and the significantly increased gain lifetime that were observed,[149-151] CdSe/CdS DR is an excellent candidate for optical gain applications.

Figure 5.7 (a) Kinetics of the transient absorption ($-\Delta\alpha/\alpha$) at the peak of optical gain for three CdSe/CdS DR samples with different lengths. (b) The time evolution of $-\Delta T/T$ for DRs of 25 nm in length with increasing pump fluence (from $13 \mu\text{J}/\text{cm}^2$ to $1560 \mu\text{J}/\text{cm}^2$, generated one to ten electron-hole pairs in individual CdSe/CdS DR). This figure is adopted from [149].

- Temperature insensitive stimulated emission threshold

The lasing emission with CQDs as gain medium shows a more temperature insensitive lasing peak position and threshold, due to their atomic-like band structure.[111] CdSe/CdS DR preserves this merit and exhibits an almost temperature-independent stimulated emission threshold.[152]

- Large absorption cross section

The dramatically increased absorption cross section at a shorter wavelength from CdS seeded rod, which acts as an antenna, facilitates harvesting a larger number of excitation photons. Moreover, the exciton that forms in the CdS rod transports to the CdSe core so that it promotes the population inversion in the core.[153]

- Tunable stimulated emission colour

The stimulated emission from CdSe/CdS in blue, green, and red colour has been demonstrated by tuning the core size, rod diameter, and rod length.[152, 154] Generally speaking, the red to green colour stimulated emission can be achieved by shrinking the size of CdSe core, which leads to a blue shift of the emission; on the other hand, the emission in blue range was only obtained from the exciton's recombination in the CdS rod.[152, 154] With careful selection of the dimension of core and rod, the stimulated emission from both core and seeded rod can be observed simultaneously.[152] Moreover, the stimulated emission wavelength can also be fine-tuned by band engineering.[155] Therefore, CdSe/CdS DR is a suitable sort of CQD for RGB lasing for displays and lighting.

5.2 Characterization of the Intrinsic Anisotropic Optical Properties of CdSe/CdS DRs

The intrinsic anisotropic optical property of CdSe/CdS DRs was verified by the fluorescence anisotropy measurement for a diluted CdSe/CdS DR solution in a 1 cm cuvette, where reabsorption was negligible. A frequency-doubled Nd: YAG continuous wave laser at 532 nm was employed for excitation in the experiment setup, and a Glan–Thompson prism was placed before the sample to make sure the excitation laser beam was purely vertically polarized, as shown in Figure 5.8a. Given the polarization-dependent sensitivity of the detector, an achromatic half-wave plate was mounted before the detection to keep the polarization of the detected signal unchanged. The fluorescence spectra of the diluted CdSe/CdS DR solution, which were captured with the detection polarization parallel ($//$) and perpendicular ($\perp$) with respect to the excitation, are presented in Figure 5.8b. As can be observed, the collective

emission from the diluted DR solution tends to have the same polarization with that of the excitation laser beam. The integrals of the fluorescence spectrum from the diluted CdSe/CdS DR solution as a function of detection polarization angle (θ) with respect to the excitation polarization are plotted in Figure 5.8c, and the emission intensity is well fitted with a cosine square function ($\cos^2\theta$). As a comparison with the experiment of CdSe/CdS DR solution, fluorescence anisotropy was measured for a diluted spherical CdSeS/ZnS nanodot solution, shown in Figure 5.9a, and negligible emission difference was observed. In order to rule out the effects of the crystalline structure, similar measurement was also carried out with a diluted zinc blende spherical CdSe/CdS/ZnS nanodot solution, which showed no anisotropic fluorescence (Figure 5.9b). (The CdSeS/ZnS nanodots of wurtzite crystalline structure were synthesized with one-pot method according to [56], and The CdSe/CdS/ZnS nanodots of zinc blende crystalline structure were synthesized with successive ion layer adsorption and reaction (SILAR) method according to [156].)

Figure 5.8 Fluorescence anisotropy measurement for a diluted CdSe/CdS DR solution.

(a) Schematic illustration for fluorescence anisotropy measurement. The sample was excited by vertically polarized laser beam and the polarizer before the detection was used to select the polarization of the fluorescence. The achromatic half-wave plate was employed to maintain the emission polarized in the same direction (horizontally) before captured by the detector. (b) Spectra of PL emission from the diluted CdSe/CdS DR solution, which were collected in parallel ($//$) and perpendicular ($\perp$) polarization to that of the excitation laser. The high-resolution TEM image of the CdSe/CdS DR used in the experiment is shown in the inset (scale bar is 10 nm). (c) The intensity of emission from the diluted CdSe/CdS DR solution as a function of the detection polarization angles with respect to the excitation polarization, and the data points were well fitted with cosine-square function. (d) The plot of Equation (5-3), which is the evolution of fluorescence anisotropy with the increasing ratio between dipole moments along and normal to the c -axis for a nanocrystal with cylindrical symmetry.

To characterized the degree of the emission anisotropy, fluorescence anisotropy is introduced as:[106]

$$r = \frac{I_{//} - I_{\perp}}{I_{//} + 2I_{\perp}}, \quad (5-1)$$

where $I_{//}$ and $I_{\perp}$ are the intensities of emission that are measured along and orthogonal to the polarization of the excitation laser beam, respectively. Thus, the fluorescence anisotropy that was calculated based the fitting curve in Figure 5.8c is 0.12.

For molecules, whose absorption and emission dipole is collinear, the maximum anisotropy is 0.4.[106] If there is a displacement, β , between the transition dipole of absorption and emission, the anisotropy can be written as:

$$r_0 = 0.4 \left(\frac{3 \cos^2 \beta - 1}{2} \right) \quad (5-2)$$

Figure 5.9 Spectra of PL emission from diluted (a) wurtzite CdSeS/ZnS spherical nanodot solution (b) zinc blende CdSe/CdS/ZnS spherical nanodot solution, which was detected with polarization parallel (//) and perpendicular ($\perp$) to the polarization of excitation, respectively. High-resolution TEM images for a single (a) wurtzite CdSeS/ZnS spherical nanodot and (b) zinc blende CdSe/CdS/ZnS spherical nanocrystal are shown in the inset (scale bar, 5 nm).

The fluorescence anisotropy measurement from the CdSe/CdS DR solution suggested that the different transition rate of the dipole that oriented along and normal to the c -axis of the nanorod. The difference between the dipole moments between these two orientations, along (μ_c) and normal (μ_a, μ_b) to the c -axis, mainly accounts for the difference in transition rate. As a result, in the case of DRs, there are three dipoles in three dimensions that contribute to the overall transition, as illustrated in Figure 5.10. Therefore, I corrected the intrinsic anisotropy accordingly as:

$$r = 0.4 \frac{1}{1+2x^2} \cdot \frac{3\cos^2\left(\arctan(\sqrt{2}x)\right)-1}{2} + 2 \cdot 0.4 \cdot \frac{x^2}{1+2x^2} \cdot \frac{3\cos^2\left(\arctan\left(\frac{\sqrt{1+x^2}}{x}\right)\right)-1}{2} \quad (5-3)$$

where $x = \frac{\mu_a}{\mu_c}$, $\beta = \arctan(\sqrt{2}x)$.

Moreover, this equation is plotted in Figure 5.8d. For spherical nanodots, the dipole moments are identical in the all three orthogonal directions ($\mu_a = \mu_b = \mu_c$), which gives no effect of fluorescence anisotropy. While, for ideal nanorod, whose dipole normal to the c -axis is extremely small compared to that along the c -axis ($\mu_a = \mu_b \ll \mu_c$), the fluorescence anisotropy value is 0.4; and for ideal nanodisk, whose dipole normal to the c -axis is remarkably larger compared to that along the c -axis ($\mu_a = \mu_b \gg \mu_c$), the fluorescence anisotropy value is 0.1, as shown in Figure 5.8d. Here, according to the fluorescence anisotropy measurement for diluted CdSe/CdS DR solution, which gave the value of fluorescence anisotropy $r = 0.12$, the corresponding relation between dipole moments in three orthogonal directions is $\mu_a = \mu_b = 0.46\mu_c$. Such anisotropy in the dipole moments as shown in the experiment and calculation gives rise to the anisotropic optical properties of CdSe/CdS DRs, and these properties will be further utilized and discussed in following sections.

Figure 5.10 The schematic diagram of the dipole moments distribution in three orthogonal directions of a CdSe/CdS DR.

5.3 Preparation of CdSe/CdS DR Layer Attached to the Inner wall of Capillary Tube

The reason that capillary tube is adopted is that capillary tube is not only an excellent container for various materials as the gain medium. Moreover, it can also play a role of cylindrical optical microcavity that provides optical feedback and holds WGM lasing.[80, 81, 86] In the case that the capillary tube is filled with a solution of optical gain materials, the refractive index difference between the solution and the glass capillary tube is small, which results in a reduced overlap of propagating electromagnetic wave with the gain medium and greater optical loss at the interface. In addition, if nanorods are dissolved in solution, they will be randomly oriented, and therefore, their intrinsic polarized optical properties cannot be utilized.[86] Considering the problems of gain medium solution (weak optical modes confinement in gain medium, low gain medium concentration, and random orientation of DRs), we address these problems by deposition of closely packed aligned CdSe/CdS DR onto the inner wall of the capillary tube.

CdSe/CdS DRs in hexane solution were filled into a capillary tube of 300 μm in diameter by capillary action. The hexane solution of CdSe/CdS DRs was dried at room temperature under reduced temperature or in the air. Due to capillary force and microfluid that is generated during the drying process, the CdSe/CdS DRs would be liable to orient along the axis of the capillary tube,[157] and a densely packed film can be formed.

5.4 Electron Microscopy Characterization for the Dried DR Ensemble in Capillary

To examine the arrangement of CdSe/CdS DRs in the capillary tube, SEM was adopted. However, it proved to be not an easy task. The challenges are mainly from the poor electric conductivity of our samples because the glass capillary where the nanorod film attaches is

electrically insulated and the shape of the capillary fragment is curled up, which makes the contact between the sample and the conductive carbon tape underneath even worse. Therefore, we needed to deposit a relatively thicker gold layer to improve the electric conductivity. However, the trade-off is that thin gold layer may hide the structures of interest. I repeated such imaging studies and some proofs were found to verify the alignment of DRs in a capillary tube. I cracked the capillary tube with aligned DRs, which was affixed on conductive carbon tape (as shown in Figure 5.11a). To improve the electrical conductivity of the sample for SEM imaging, a thin (~5-10 nm) gold film was sputtered onto the surface of the SEM samples.

While cracking the capillary tube, some small peel-off region formed at the edge of the glass capillary fragments, as shown in the red frame of Figure 5.11a, where the surface is rough enough to reveal the features that survived from the gold coating. Figure 5.11b and Figure 5.11c are SEM images taken from the area within the peel-off region (in the red frame) shown in Figure 5.11a. Single nanorod can be resolved clearly from both SEM images, and we are able to observe that nanorods are commonly oriented along the capillary tube, as indicated by the blue arrows in figures. The typical surface of our samples is really smooth, as illustrated in the yellow frame of Figure 5.11a, and given the relatively large grain size of the gold coating layer and charging effect of SEM technique on non-conducting materials, we were not able to resolve these nanorods as presented in Figure 5.11d.

On the other hand, the TEM characterization requires depositing the sample onto a copper grid; meanwhile, peeling off the thin film (hundreds of nm thick) from the tube and handling it is very difficult. Therefore, we did not succeed with TEM despite our numerous trials.

Figure 5.11 SEM images of CdSe/CdS DR layer attached to the inner wall of a capillary tube. (a) The capillary tube coated with dried CdSe/CdS DRs on its inner surface was cracked and affixed to the SEM sample holder with conductive carbon tape. The sample was covered by 5-10 nm gold to improve electrical conductivity. (b), (c) A small peel-off region shown in the red frame of (a) illustrates that DRs are statistically oriented along the capillary tube. The blue arrows indicate the orientation of the capillary tube. (d) The area in the yellow frame of (a) where DR film is flat and smooth. The finite grain size of the gold coating layer together with smoothness and non-conducting nature of the glass capillary limited us to take high-quality SEM images. The black region in (b) and (c) is caused by the charging effect in our sample which is not very conductive.

5.5 Optical Characterization for Dried DR Ensemble in Capillary

In light of CdSe/CdS DR's anisotropic optical properties shown in the previous section, if they demonstrated an overall orientation in a dried film, such ensemble of DRs should also show anisotropic optical behavior. Therefore, observation of anisotropic optical behaviors of the DR ensemble can reveal the arrangement status of the DRs in it. Here, two approaches were adopted to confirm the alignment of DRs dried in a capillary tube (Figure 5.12). Firstly, as sketched in Figure 5.12b, the sample is excited by a linearly polarized laser beam. The angle between the polarization of the excitation laser and the axis of the capillary tube is tuned by a half waveplate for 532 nm light, in the meantime, the PL spectra of the DR film on the capillary tube inner wall is recorded. As to the second approach, the sample is excited by a circularly polarized laser beam that is generated with a quarter waveplate for 532 nm light, and we analyzed the polarization behaviors of PL spectra of the sample by tuning the angle between the polarizer before the detector and the axis of the capillary tube, as shown in Figure 5.12c. As we can see, by the varying the polarization angle of the excitation laser or detection respect to the axis of the capillary, essentially the anisotropic absorption or emission of the sample is measured. In case that the nanorods are oriented in the capillary without any order, which means the dipole moment in the DRs are evenly distributed over all solid angles, the variation of the PL spectra of the dried DR layer in capillary tube will not be observed when tuning the polarization angle of excitation or emission detection.

The experimental results of these two approaches, i.e. the evolutions of the PL intensity of the nanorod ensemble as a function of the excitation or emission detection polarization angles with respect to the axis of the axis of the capillary tube, are presented in Figure 5.12d. The experimental results indicate a more dominant polarization orientation, for both absorption and emission of the sample, was along the axis capillary tube. Figure 5.12e shows the results of the exactly same measurements that were conducted for dried spherical nanodots layer in a

capillary tube, and the variation of the PL intensity spherical nanodot ensemble, while changing the excitation or emission detection polarization angles, was insignificant.

Figure 5.12 Anisotropic absorption and emission measurement for the verification of the alignment of CdSe/CdS DRs in a capillary tube. (a) Top view of the optical measurement configuration. (b) Measurement of anisotropic absorption with linearly polarized laser: tuning the polarization angle of the excitation laser (θ) and capturing the PL of the sample. (c) Measurement of anisotropic absorption with circularly polarized laser: tuning the polarization angle of the emission detection (ϕ) by a polarizer before the detection and monitoring the PL of the sample. (d, e) Evolution of normalized PL intensity of the CdSe/CdS DRs (d) and CdSeS/ZnS spherical nanodots (e) loaded and dried in a capillary tube at different polarization angle with respect to the axis of the capillary tube.

To rule out the polarization effect from the capillary tube, the anisotropic optical properties were measured by cracking the capillary tube that contained dried DR layer, as shown in Figure 5.13a. Given results of anisotropic optical property measurement, Figure 5.13b, the

contribution from the cylindrical optical microcavity to the overall polarization behaviour of the sample is negligible, consistent with reports concerning optical microcavities relatively large in size.[158]

$I_{//}$ and $I_{\perp}$, standing for the PL intensity of the polarized excitation (or emission) oriented parallel (0°) and perpendicular (90°) to the axis of the capillary, were used to calculate the polarization difference ratio p , which was introduced to characterize the anisotropy degree of the polarized optical property:[106]

$$p = \frac{I_{//} - I_{\perp}}{I_{//} + I_{\perp}} \quad (5-4)$$

Cosine-squared function ($\cos^2\theta$) was employed to fit the data points: polarization angle of the excitation laser or the emission detection versus the PL intensity. According to the fitting curve of the data points in Figure 5.12d, the polarization difference ratios p were determined as 0.296 and 0.252 for absorption and emission, respectively. Therefore, the CdSe/CdS ensemble had a higher probability of the transition for both excitation and emission along the capillary tube's axis. On the other hand, the transition of highest rate for single CdSe/CdS DR is collinear with the c -axis of the nanorod. Therefore, it comes to the conclusion that the DRs in the dried ensemble statistically oriented along the axis of the capillary tube. And, this finding is consistent with the SEM image of the cracked sample as shown in Figure 5.11b and c.

Figure 5.13 (a) Fragments of cracked capillary tube coated with dried CdSe/CdS DRs attached to its inner wall and the capillary tube was crushed into pieces on double-sided carbon tape to retain the orientation of capillary tube. (b) Evolution of normalized PL intensity of cracked capillary tubes with CdSe/CdS DRs with the excitation polarization angle of a linearly polarized laser beam with respect to the capillary tube axis.

5.6 Observation of Whispering-gallery Mode Lasing with a Large Polarization

As the capillary tube can serve as a cylindrical optical microcavity, combined with the aligned CdSe/CdS DRs as the gain medium, lasing action from such laser device under optical pump was investigated. To deposit a CdSe/CdS DR film onto the inner wall of the capillary tube, which should be thick enough for optical gain, a CdSe/CdS solution of a higher concentration (10 mg/mL) was loaded into the capillary tube by capillary action and dried. The device was optically pumped by a frequency-doubled Nd: YAG pulsed laser at 532 nm (the repetition rate is 60 Hz, and pulse duration is 1 ns), and a quarter waveplate for 532 nm was placed before the sample to make the pumping beam circularly polarized. The emission was analysed by tuning the polarizer before the detector, as illustrated in Figure 5.12c. An achromatic half-wave plate was used to correct the polarization of the signal horizontally to remove the effect of the polarization-dependent sensitivity of the detector.

Initially, when the pump energy was low, spontaneous emission was observed from the device of interest with a relatively big FWHM of 34 nm, comparable to the spectra captured in above tests. As the excitation energy was increased above the threshold, the width of emission spectrum narrowed down, and in the meantime, a series of spiky peaks grew on the red side of the spontaneous emission peak, as shown in Figure 5.14a. The lasing spectral range (from 615 nm to 625 nm) was zoomed in, shown in Figure 5.14b, and the plot of the lasing peak position versus peak number can be well fitted with a straight line (Figure 5.14c), which indicated lasing peaks were equally spaced with a free spectral range of $\delta\lambda=0.21$ nm. These distinct lasing peaks also suggest the layer of aligned DRs is optically smooth with little optical scattering, which can be confirmed with the SEM image that shows the smooth CdSe/CdS layer attached to the inner wall of capillary tubes (Figure 5.11d). A control experiment was done with a capillary tube with a reduced diameter of 100 μm in the same lasing configuration. The emission spectra of the sample of DR ensemble in capillary tube of 100 μm in diameter with increasing pumping energy from below to above the lasing threshold are shown in Figure 5.15a, and the plot of wavelength of each lasing mode versus mode number can be linearly well fitted, where the free spectral range $\delta\lambda=0.59$ nm can be obtained. The FSR of lasing action in 100 μm capillary tube is about three times of that in 300 μm capillary tube, and therefore, this result proves the WGMs lasing took place in the capillary tube that acts as cylindrical optical microcavity. And, the FSR for WGMs is written as:

$$\delta\lambda = \frac{\lambda^2}{2\pi n R}, \quad (5-5)$$

where the lasing central wavelength λ is 620 nm and the radius of the cylindrical optical microcavity R is 150 μm , and hence, the effective refractive index n is around 1.92. As seen from this calculation, such a high effective refractive index discloses that the lasing action mainly took place at the dense CdSe/CdS DR film but not in the wall of the capillary tube, whose refractive index is only about 1.46. The high overlap between the optical modes and

the gain medium, which is a desirable lasing configuration, is guaranteed by the significant refractive index contrast between the closely packed CdSe/CdS DR layer and the glass. Compared to the lasing configuration presented here, the lasing modes will have a much smaller overlap with the gain medium in dissolved in organic solvent, which leads to a higher lasing threshold.

According to Figure 5.14b, negligible wavelength difference between the TE modes, where the electric field is normal to the axis of the cylindrical cavity, *i.e.* 90 ° or -90 °, and TM modes, where the electric field is along the axis of the cylindrical cavity, *i.e.* 0 °, was observed. However, the emission intensity of TM and TE modes are quite different. As can be noticed in the Figure 5.14b, the intensity of lasing of TM modes was considerably greater compared to that of TE modes. The plot of the evolution of lasing intensity, integrated from 615 nm to 625 nm, as a function of detection polarization angle with reference to the axis of the capillary tube, when pumping energy was 7 μ J, is shown in Figure 5.14d, which can be well fitted by $\cos^2\theta$ function.

In comparison with such lasing configuration with aligned DRs as gain medium, similar experiment was conducted except for that spherical CdSeS/ZnS nanodots layer served as gain medium, and the spectra shows the intensity of lasing emission that polarized perpendicular to the tube axis (TE modes) is slightly higher than that polarized parallel to the tube axis (TM modes), as shown in Figure 5.16a. To have a more straightforward comparison, the variation of lasing intensity from the sample with DRs (red dots) and spherical nanodots (black squares) as a function of detection polarization angle is plotted in Figure 5.16b. This experimental data in contrast to the results from our DR film really shows off the effect of the DR alignment.

Figure 5.14 Observation of lasing action from CdSe/CdS DRs in a capillary tube with a diameter of 300 μm . (a) Emission spectra of CdSe/CdS DRs that were optically pumped below and above the lasing threshold in a capillary tube. (b) Zoom-in of lasing peaks from the sample that was pumped optically by a circularly polarized laser from CdSe/CdS DRs in a capillary with the detection polarization angle is 0° (along the tube, TM modes) and -90° and 90° (perpendicular to the tube axis, TE modes). (c) The plot of the wavelength of laser peaks as a function of the peak number and the data points were linearly fitted. (d) Evolution of lasing intensity as varying the detection angle with reference to the axis of the capillary tube, and the corresponding cosine-square function fitting.

Figure 5.15 Observation of lasing action from CdSeS/ZnS DRs in a capillary tube with a diameter of 100 μm . (a) Emission spectra of DRs in the capillary tube when increasing the pumping energy from below to above the lasing threshold. (b) The plot of the wavelength of laser peaks as a function of the peak number and the data points were linearly fitted.

Figure 5.16 Lasing measurement for a capillary tube with CdSeS/ZnS spherical nanodots layer on its inner wall. (a) Lasing spectra from CdSeS/ZnS spherical nanodots in the capillary, which was pumped by a circularly polarized laser and the detection polarization angle was 0° parallel (TM modes) and then 90° perpendicular (TE modes), respectively. (b) Lasing intensity from CdSeS/ZnS spherical nanodots (black squares) and DRs (red dots) in capillary tubes as a function of the detection polarization angle with reference to

the axis of the capillary tube.

The reason for this slightly stronger intensity of the normal polarization is because we were measuring the scattered light (Figure 5.17a), but not the light propagating in the gain medium, which is reflected by the inner wall of the capillary tube (due to the total internal reflection). According to Fresnel equations,

$$\frac{T_{//}}{T_{\perp}} = \frac{1 - \left| \frac{n_1 \cos \theta_i - n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2}}{n_1 \cos \theta_i + n_2 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2}} \right|^2}{1 - \left| \frac{n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2} - n_2 \cos \theta_i}{n_1 \sqrt{1 - \left(\frac{n_1}{n_2} \sin \theta_i\right)^2} + n_2 \cos \theta_i} \right|^2} \quad (5-6)$$

the light polarized orthogonal to the axis of the capillary tube is more liable to transmit out when it reaches the wall of the capillary tube. On the other hand, please note that Fig. 4a in Ref. [86] shows almost identical emission when it was measured parallel and normal to the capillary tube, which is due to the small refractive index contrast between the nanorod solution and the glass used by Uri Banin et al. As the plot shown in Figure 5.17b below, the larger the refractive index contrast between the medium inside the capillary tube, the more of the light polarized normal to the tube would be transmitted out. Therefore, in our case, the higher refractive contrast between semiconductor nanocrystal layer and glass makes the measured intensity difference between TE and TM more appreciable in Figure 5.16.

Figure 5.17 (a) Out-scattering of the light from the capillary tube. n_1 and n_2 denote the refractive index of the medium inside the capillary tube and glass, respectively. (b) Evolution of the ratio of transmittance of light polarized along and normal to the capillary tube with a variation of the refractive index contrast between the medium in the capillary tube and the glass, when the incident angle is $\pi/6$.

The evolution of lasing intensity for TE and TM modes of our lasing configuration with increasing pump energy are presented in Figure 5.18a. This power transfer function was well fitted with “soft threshold” approximation, which is typical for microcavity laser structure.[117] From the fitting, the lasing threshold of both TE and TM mode was around 5.2 μJ . As can be observed clearly, the TM modes lasing intensity was slightly higher than that of TE modes lasing when pump energy was below the lasing threshold. However, the intensity difference between TE and TM modes built up rapidly as increasing the pump energy. The polarization difference ratio, p , with rising pumping energy is plotted in Figure 5.18b. At the initial stage, where pumping energy was low, the polarization difference ratio of spontaneous emission for the sample was about 0.05; and when the sample was pumped above the lasing threshold, the polarization difference ratio grew rapidly and saturated at 0.72. Here, what is needed to be noticed is that the spontaneous emission polarization difference ratio of the thicker DR layer in capillary tube reduced compared to the results shown in Figure 5.12d. In the thicker DR film for lasing, the increased reabsorption could account for such reduction of

polarization difference ratio of spontaneous emission. Nevertheless, the CdSe/CdS DRs preferably oriented along the axis of the cylindrical optical microcavity, so that the polarized gain medium was created with a high gain coefficient for amplifying light whose electric vector paralleled to the cavity axis. As a consequence, along with the nonlinear nature of stimulated emission[159], light, which was amplified in the polarized gain medium with a relatively small anisotropy, can turn out a very high polarization difference ratio of 0.72.

Figure 5.18 Power transfer function measured for CdSe/CdS DRs ensemble in a capillary tube. (a) The evolution of the intensity of all lasing peaks, for both TE and TM WGMs lasing from 615 nm to 625 nm, as a function of pumping energy. (b) The plot of polarization difference ratio versus pumping energy.

5.7 Summary

In conclusion, the employment of the intrinsic optical anisotropic optical properties of CdSe/CdS DRs in a macroscopical scale for optical gain application was demonstrated for the first time. A thin film of aligned CdSe/CdS DRs on the inner wall of a capillary tube was fabricated by evaporating a CdSe/CdS DR solution loaded in the tube under the condition of reduced pressure or in the air. Two methods were adopted to examine the degree of the alignment of DRs dried in a capillary tube, i.e. polarization dependent absorption and emission measurement, and the resulted the polarization difference ratios are 0.296 and 0.252 for absorption and emission, respectively. Moreover, when the excitation power increased, the

device was operating above lasing threshold with WGMs reaching the maximum polarization difference ratio is 0.72.

Capillary tubes can serve as a moisture and water-proof container for nanocrystals after sealing in inert gas atmosphere. Thus, the stability and lifetime of the laser devices can be much improved. Recently, a new sort of TVs was developed with CQDs loaded in capillary tubes as colour converters.[160] In light of the fact that the colour of stimulated emission from CdSe/CdS DRs can be varied from blue to green to red by wave function engineering,[152, 154] the aligned CdSe/CdS DRs in capillary tube, which emit highly polarized WGM lasing, are very promising for novel displays and laser lighting applications.

Chapter 6 Conclusion and Outlook

6.1 Conclusion

Solid state lighting has been revolutionizing the artificial illumination for significant energy saving and efficiency. However, the “efficiency droop” of current LED devices is still a fundamental problem that hinders the realization of high power LED with a high input power density no matter numerous efforts have been made.[13] On the other hand, intrinsically, stimulated emission of a laser is more efficient compared to spontaneous emission at high power density, and hence, laser can serve as an economical source of photons under high power density.[3] To achieve a laser white illumination, the combination of red, green, and blue lasers should be employed. Nonetheless, for current semiconductor laser technology, it is difficult to realize an efficient semiconductor laser at any wavelength in the full visible spectrum.[161]

For the current widely used LCD technology, in an LCD unit, the polarizer causes at least 50% loss of the energy of the nonpolarized white backlighting. In addition, broad band pass filters for RGB colours only allow an LCD screen to display a small portion of colours of the NTSC standard.[11] To address these problems of energy loss and small colour gamut, polarized white backlighting with saturated primary colours should be adopted.

In this thesis, CQD lasing is studied to address the problems of modern lighting and display technologies. After the advent of CQDs, by carefully designing the size, structure, morphology, and chemical composition of CQDs, the emission of CQDs can be tuned precisely to emit almost any desirable wavelength in the visible range with a high quantum yield. In recent years, the laser with CQDs as a gain medium has been fabricated with red, green, and blue emission.[26, 82] The demonstration of RGB lasing, especially the green laser,

reveals the CQDs' potential applications for white laser light source and bridging the "green gap" in semiconductor lasers.[26] If the CQDs are coupled to a particular optical cavity structure, due to the optical feedback, the lasing emission can be highly polarized, which makes such a laser device suitable for obtaining a polarized light source. As discussed here, laser light source is very unique, which is highly polarized and with ultra-narrow RGB component, notwithstanding, it can generate a comparable visual perception for human compared to conventional light sources.[5]

In Chapter 2, the basic properties, synthesis methods and characterization approaches of CQDs were introduced. There are many "degree-of-freedom", such as size, shape, structure, dopant, and chemical composition, which can be used to adjust the band structure, and hence the optical properties.[46] I am trained to synthesize various sorts of CQDs, and the corresponding optical and electron microscopic characterizations are shown and analysed. The comprehensive training on synthesis and characterization facilitate my further subsequent investigation of on CQD lasing.

In Chapter 3, the development of CQD lasing was reviewed, and optical gain from red, green, and blue CQDs was demonstrated experimentally. The atomic-like discrete energy structure of a CQD, which results from the quantum confinement effect, enables the temperature insensitivity of the laser action from CQDs. Although CQDs show optical gain under optical pumping, the Auger recombination can be a very undesirable nonradiative channel that competes with the stimulated emission under high pumping fluence.[93] Possible means for the suppression of Auger effect are briefly presented in this chapter as well. We used Nd:YAG pulse laser, which is the most common and standard laser source for optical pumping, to pump the CQDs. However, because the energy of excitation photon is much higher than the band edge and other nonradiative channels are hence promoted, the optical gain from green CQDs was not observed with the pumping wavelength of 355 nm. We developed an indirect

method that is assisted by FRET process to pump the green CQDs by mixing in the blue CQDs. With the blue CQDs as donors, the lasing threshold of the green CQDs is reduced dramatically.

As the RGB lasing had been shown in Chapter 3, to achieve another target of my Ph.D. project was to observe the polarized lasing emission with CQDs as the gain medium. In Chapter 4, the cavity effect was discussed. The mechanically flexible Bragg grating was employed, and the CQDs were incorporated into the Bragg substrate via spin coating. The constructive scattering from the cavity structure provides the polarization-selective optical feedback, and the second order DFB lasing from CQDs on Bragg substrate was observed. The highly polarized emission was mainly originated from TE modes.

Recently, CQDs have been loaded into capillary tubes for replacement of conventional phosphors of LCDs.[11] Capillary tube is not only a very oxygen- and moisture-proof container for CQDs but also can support WGM lasing as a cylindrical optical cavity.[107] However, unlike the Bragg substrate shown in Chapter 4, for a cylindrical cavity with a large diameter (hundreds of micrometres), the polarization selectivity is extremely small for TE and TM modes. Thus, to achieve a 1D polarized lasing emission from a relative wide cylindrical cavity, the polarized gain medium should be used. A layer of CdSe/CdS DR was deposited onto the inner wall of a capillary tube via drying under reduced pressure or air. It turns out that the DRs aligned statistically along the axis of the capillary tube. Moreover, the alignment was confirmed via SEM and optical characterizations. When the sample was optically pumped, the highly polarized WGM lasing with a polarization ratio of 0.72 was observed, where TM modes of WGMs were dominant.

I have shown the RGB lasing from CQDs and polarized lasing emission that is obtained by cavity effect and polarized gain medium. As a conclusion, in light of the unique properties

and flexible processability of CQDs, my Ph.D. work shows the feasibility of the potential applications of CQDs lasing for future novel lighting and displays.

6.2 Outlook

Recently, a new type of semiconductor nanocrystals, nanoplatelets (NPL), has been synthesized.[162] Because the very precisely controlled thickness of NPLs, their emission is very narrow, and the emission wavelength can be tuned discretely by the number of the monolayers of CdSe.[162] The NPLs are characterized by the transitions with giant oscillator strength.[163] And, due to the large oscillator strength, the fluorescence lifetime is much shorter than that of conventional CQDs.[164] NPLs also exhibited an optical gain in some reports.[87, 88, 165] Especially, the lasing threshold was very small in NPLs; even optical gain was reported under CW laser pumping, which makes the CQD lasing one more step towards practical usage.[88, 165] Moreover, NPLs tend to stack together, and the polarized emission was observed from such needle-like self-assembly.[166] Therefore, it is very interesting to look into lasing from NPLs for lighting and display applications.

Author's Publications

Journal Papers

Gao, Y., X. Zhao, Y. Wang, R. Chen, E. Mutlugun, K. E. Fong, S. T. Tan, C. Dang, X. W. Sun H. Sun and H. V. Demir (2015). "Observation of polarized gain from aligned colloidal nanorods." Nanoscale **7**(15): 6481-6486.

Gao, Y. et al., " Colloidal Quantum Lasing in Green Enabled by Partial Nonradiative Resonant Energy Transfer from Blue Quantum Dots", in preparation

Co-author

Guilhabert, B., C. Foucher, A.-M. Haughey, E. Mutlugun, Y. Gao, J. Herrnsdorf, H. Sun, H. V. Demir, M. Dawson and N. Laurand (2014). "Nanosecond colloidal quantum dot lasers for sensing." Optics Express **22**(6): 7308-7319.

He, T., R. Chen, Z. B. Lim, D. Rajwar, L. Ma, Y. Wang, Y. Gao, A. C. Grimsdale and H. Sun (2014). "Efficient Energy Transfer under Two-Photon Excitation in a 3D, Supramolecular, Zn (II)-Coordinated, Self-Assembled Organic Network." Advanced Optical Materials **2**(1): 40-47.

He, T., Y. Gao, Y. Gao, X. Lin, R. Chen, W. Hu, X. Zhao, Y. Wang, H. V. Demir, Q. Fan, A. C. Grimsdale and H. Sun (2016). "Unusual Fluorescent Properties of Stilbene Units and CdZnS/ZnS Quantum Dots Nanocomposites: White-Light Emission in Solution versus Light-Harvesting in Films." Macromolecular Chemistry and Physics **217**(1): 24-31.

Leck, K. S., Y. Divayana, D. Zhao, X. Yang, A. P. Abiyasa, E. Mutlugun, Y. Gao, S. Liu, S. T. Tan, X. W. Sun and H. V. Demir (2013). "Quantum dot light-emitting diode with quantum dots inside the hole transporting layers." ACS Applied Materials & Interfaces **5**(14): 6535-6540.

Mutlugun, E., B. Guzelturk, A. P. Abiyasa, Y. Gao, X. W. Sun and H. V. Demir (2014). "Colloidal Quantum Dot Light-Emitting Diodes Employing Phosphorescent Small Organic Molecules as Efficient Exciton Harvesters." The Journal of Physical Chemistry Letters **5**(16): 2802-2807.

Peng, B., Z. Li, E. Mutlugun, P. L. H. Mart ínez, D. Li, Q. Zhang, Y. Gao, H. V. Demir and Q. Xiong (2014). "Quantum dots on vertically aligned gold nanorod monolayer: plasmon enhanced fluorescence." Nanoscale **6**(11): 5592-5598.

Ta, V. D., S. Yang, Y. Wang, Y. Gao, T. He, R. Chen, H. V. Demir and H. Sun (2015). "Multicolor lasing prints." Applied Physics Letters **107**(22): 221103.

Wang, Y., K. E. Fong, S. Yang, Van D. Ta, Y. Gao, Z. Wang, V. Nalla, H. V. Demir and H. Sun (2015). "Unraveling the ultralow threshold stimulated emission from CdZnS/ZnS quantum dot and enabling high-Q microlasers." Laser & Photonics Reviews **9**(5): 507-516.

Wang, Y., K. S. Leck, V. D. Ta, R. Chen, V. Nalla, Y. Gao, T. He, H. V. Demir and H. Sun (2015). "Blue Liquid Lasers from Solution of CdZnS/ZnS Ternary Alloy Quantum Dots with Quasi-Continuous Pumping." Advanced Materials **27**(1): 169-175.

Wang, Y., V. D. Ta, Y. Gao, T. C. He, R. Chen, E. Mutlugun, H. V. Demir and H. D. Sun (2014). "Stimulated Emission and Lasing from CdSe/CdS/ZnS Core-Multi-Shell Quantum Dots by Simultaneous Three-Photon Absorption." Advanced Materials **26**(18): 2954-2961.

Wang, Y., X. Yang, T. He, Y. Gao, H. V. Demir, X. Sun and H. Sun (2013). "Near resonant and nonresonant third-order optical nonlinearities of colloidal InP/ZnS quantum dots." Applied Physics Letters **102**(2): 021917.

Yang, X., E. Mutlugun, C. Dang, K. Dev, Y. Gao, S. T. Tan, X. W. Sun and H. V. Demir (2014). "Highly flexible, electrically driven, top-emitting, quantum dot light-emitting stickers." ACS Nano **8**(8): 8224-8231.

Yang, X., E. Mutlugun, Y. Zhao, Y. Gao, K. S. Leck, Y. Ma, L. Ke, S. T. Tan, H. V. Demir and X. W. Sun (2014). "Solution Processed Tungsten Oxide Interfacial Layer for Efficient Hole-Injection in Quantum Dot Light-Emitting Diodes." small **10**(2): 247-252.

Zhao, X., Y. Gao, Y. Wang, H. V. Demir, S. Wang and H. Sun (2015). "Manipulating Optical Properties of ZnO/Ga: ZnO Core-Shell Nanorods Via Spatially Tailoring Electronic Bandgap." Advanced Optical Materials.

Zhao, Y., R. Chen, Y. Gao, K. S. Leck, X. Yang, S. Liu, A. P. Abiyasa, Y. Divayana, E. Mutlugun, S. T. Tan and H. V. Demir (2013). "AC-driven, color-and brightness-tunable organic light-emitting diodes constructed from an electron only device." Organic Electronics **14**(12): 3195-3200.

Zhao, Y., J. Zhang, S. Liu, Y. Gao, X. Yang, K. S. Leck, A. P. Abiyasa, Y. Divayana, E. Mutlugun, S. T. Tan and H. V. Demir (2014). "Transition metal oxides on organic semiconductors." Organic Electronics **15**(4): 871-877.

Conference Paper

Y. Gao, V. D. Ta, X. Zhao, Y. Wang, R. Chen, Y. Zhao, C. Dang, X. W. Sun, H. D. Sun, and H. V. Demir, "Anisotropic stimulated emission from aligned CdSe/CdS dot-in-rods," in *Photonics Conference (IPC), 2014 IEEE*, 2014, pp. 530-531.

References

- [1] Y. Narukawa, M. Ichikawa, D. Sanga, M. Sano, and T. Mukai, "White light emitting diodes with super-high luminous efficacy," *Journal of Physics D: Applied Physics*, vol. 43, p. 354002, 2010.
- [2] Y. C. Shen, G. O. Mueller, S. Watanabe, N. F. Gardner, A. Munkholm, and M. R. Krames, "Auger recombination in InGaN measured by photoluminescence," *Applied physics letters*, vol. 91, p. 141101, 2007.
- [3] J. J. Wierer, J. Y. Tsao, and D. S. Sizov, "Comparison between blue lasers and light-emitting diodes for future solid-state lighting," *Laser & Photonics Reviews*, vol. 7, pp. 963-993, 2013.
- [4] J. J. Wierer, J. Y. Tsao, and D. S. Sizov, "The potential of III-nitride laser diodes for solid-state lighting," *physica status solidi (c)*, vol. 11, pp. 674-677, 2014.
- [5] A. Neumann, J. J. Wierer, W. Davis, Y. Ohno, S. R. Brueck, and J. Y. Tsao, "Four-color laser white illuminant demonstrating high color-rendering quality," *Optics express*, vol. 19, pp. A982-A990, 2011.
- [6] S. Pimputkar, J. S. Speck, S. P. DenBaars, and S. Nakamura, "Prospects for LED lighting," *Nat Photon*, vol. 3, pp. 180-182, 2009.
- [7] J. M. Phillips, M. E. Coltrin, M. H. Crawford, A. J. Fischer, M. R. Krames, R. Mueller - Mach, *et al.*, "Research challenges to ultra - efficient inorganic solid - state lighting," *Laser & Photonics Reviews*, vol. 1, pp. 307-333, 2007.
- [8] E. F. Schubert, T. Gessmann, and J. K. Kim, *Light emitting diodes*: Wiley Online Library, 2005.
- [9] W. Rushton, "Review lecture. Pigments and signals in colour vision," *The Journal of physiology*, vol. 220, pp. 1-31, 1972.
- [10] S. Coe-Sullivan, W. Liu, P. Allen, and J. S. Steckel, "Quantum dots for LED downconversion in display applications," *ECS Journal of Solid State Science and Technology*, vol. 2, pp. R3026-R3030, 2013.
- [11] G. J. Supran, Y. Shirasaki, K. W. Song, J.-M. Caruge, P. T. Kazlas, S. Coe-Sullivan, *et al.*, "QLEDs for displays and solid-state lighting," *MRS Bulletin*, vol. 38, pp. 703-711, 2013.
- [12] Available:
http://www.sony.net/SonyInfo/csr_report/environment/chemical/products/index1-1.html
- [13] S. Nakamura, "Current Status of GaN-Based Solid-State Lighting," *MRS Bulletin*, vol. 34, pp. 101-107, 2009.
- [14] S. Singh, *Polarization and laser*. New Delhi: Discovery Pub. House, 2009.
- [15] T. Borogovac and T. D. Little, "Laser visible light communications," in *Proceedings of IEEE Photonics Society Summer Topical Meeting Series,(IEEE, 2012)*, 2012, pp. 117-118.
- [16] N. S. Holliman, N. Dodgson, G. E. Favalora, and L. Pockett, "Three-dimensional displays: a review and applications analysis," *Broadcasting, IEEE Transactions on*, vol. 57, pp. 362-371, 2011.
- [17] A. Ekimov, A. L. Efros, and A. Onushchenko, "Quantum size effect in semiconductor microcrystals," *Solid State Communications*, vol. 56, pp. 921-924, 1985.
- [18] A. L. Efros and A. L. Efros, "Interband absorption of light in a semiconductor sphere," *Soviet Physics Semiconductors-Ussr*, vol. 16, pp. 772-775, 1982.
- [19] A. Rogach, "Quantum Dots Still Shining Strong 30 Years On," *ACS Nano*, vol. 8, pp. 6511-6512, 2014/07/22 2014.

References

- [20] S. Deka, A. Quarta, M. G. Lupo, A. Falqui, S. Boninelli, C. Giannini, *et al.*, "CdSe/CdS/ZnS double shell nanorods with high photoluminescence efficiency and their exploitation as biolabeling probes," *Journal of the American Chemical Society*, vol. 131, pp. 2948-2958, 2009.
- [21] S. Coe, W.-K. Woo, M. Bawendi, and V. Bulović, "Electroluminescence from single monolayers of nanocrystals in molecular organic devices," *Nature*, vol. 420, pp. 800-803, 2002.
- [22] Q. Sun, Y. A. Wang, L. S. Li, D. Wang, T. Zhu, J. Xu, *et al.*, "Bright, multicoloured light-emitting diodes based on quantum dots," *Nature Photonics*, vol. 1, pp. 717-722, 2007.
- [23] I. Gur, N. A. Fromer, M. L. Geier, and A. P. Alivisatos, "Air-stable all-inorganic nanocrystal solar cells processed from solution," *Science*, vol. 310, pp. 462-465, 2005.
- [24] O. E. Semonin, J. M. Luther, S. Choi, H.-Y. Chen, J. Gao, A. J. Nozik, *et al.*, "Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell," *Science*, vol. 334, pp. 1530-1533, December 16, 2011 2011.
- [25] Z. Han, F. Qiu, R. Eisenberg, P. L. Holland, and T. D. Krauss, "Robust photogeneration of H₂ in water using semiconductor nanocrystals and a nickel catalyst," *Science*, vol. 338, pp. 1321-1324, 2012.
- [26] C. Dang, J. Lee, C. Breen, J. S. Steckel, S. Coe-Sullivan, and A. Nurmikko, "Red, green and blue lasing enabled by single-exciton gain in colloidal quantum dot films," *Nat Nano*, vol. 7, pp. 335-339, 05//print 2012.
- [27] V. Klimov, A. Mikhailovsky, S. Xu, A. Malko, J. Hollingsworth, C. Leatherdale, *et al.*, "Optical gain and stimulated emission in nanocrystal quantum dots," *Science*, vol. 290, pp. 314-317, 2000.
- [28] J. Bao and M. G. Bawendi, "A colloidal quantum dot spectrometer," *Nature*, vol. 523, pp. 67-70, 07/02/print 2015.
- [29] D. S. Dolzhenkov, H. Zhang, J. Jang, J. S. Son, M. G. Panthani, T. Shibata, *et al.*, "Composition-matched molecular "solders" for semiconductors," *Science*, vol. 347, pp. 425-428, 2015.
- [30] A. M. Fox, *Optical properties of solids*. Oxford: Oxford University Press, 2001.
- [31] M. G. Bawendi, M. L. Steigerwald, and L. E. Brus, "The quantum mechanics of larger semiconductor clusters (" quantum dots")," *Annual Review of Physical Chemistry*, vol. 41, pp. 477-496, 1990.
- [32] Y. Wang and N. Herron, "Nanometer-sized semiconductor clusters: materials synthesis, quantum size effects, and photophysical properties," *The Journal of Physical Chemistry*, vol. 95, pp. 525-532, 1991/01/01 1991.
- [33] V. I. Klimov, "Spectral and dynamical properties of multiexcitons in semiconductor nanocrystals," *Annu. Rev. Phys. Chem.*, vol. 58, pp. 635-673, 2007.
- [34] V. I. Klimov, *Nanocrystal Quantum Dots, Second Edition*: CRC Press, 2010.
- [35] X. Zhong, Y. Feng, W. Knoll, and M. Han, "Alloyed Zn x Cd1-x S Nanocrystals with Highly Narrow Luminescence Spectral Width," *Journal of the American Chemical Society*, vol. 125, pp. 13559-13563, 2003.
- [36] C. de Mello Donega, "Synthesis and properties of colloidal heteronanocrystals," *Chemical Society Reviews*, vol. 40, pp. 1512-1546, 2011.
- [37] P. Reiss, M. Protiere, and L. Li, "Core/shell semiconductor nanocrystals," *small*, vol. 5, pp. 154-168, 2009.
- [38] T. Erdem and H. V. Demir, "Semiconductor nanocrystals as rare-earth alternatives," *Nature Photonics*, vol. 5, pp. 126-126, 2011.
- [39] L. Qian, Y. Zheng, J. Xue, and P. H. Holloway, "Stable and efficient quantum-dot light-emitting diodes based on solution-processed multilayer structures," *Nature photonics*, vol. 5, pp. 543-548, 2011.

- [40] H. Ron, "A Toxicologic Review of Quantum Dots: Toxicity Depends on Physicochemical and Environmental Factors," *Environmental Health Perspectives*, vol. 114, pp. 165-172, 2006.
- [41] T. W.-M. Fan, S. J. Teh, D. E. Hinton, and R. M. Higashi, "Selenium biotransformations into proteinaceous forms by foodweb organisms of selenium-laden drainage waters in California," *Aquatic Toxicology*, vol. 57, pp. 65-84, 2002.
- [42] M. C. Henson and P. J. Chedrese, "Endocrine disruption by cadmium, a common environmental toxicant with paradoxical effects on reproduction," *Experimental Biology and Medicine*, vol. 229, pp. 383-392, 2004.
- [43] S. J. Rosenthal, J. McBride, S. J. Pennycook, and L. C. Feldman, "Synthesis, surface studies, composition and structural characterization of CdSe, core/shell and biologically active nanocrystals," *Surface Science Reports*, vol. 62, pp. 111-157, 2007.
- [44] C. Murray, D. J. Norris, and M. G. Bawendi, "Synthesis and characterization of nearly monodisperse CdE (E= sulfur, selenium, tellurium) semiconductor nanocrystallites," *Journal of the American Chemical Society*, vol. 115, pp. 8706-8715, 1993.
- [45] Z. A. Peng and X. Peng, "Formation of high-quality CdTe, CdSe, and CdS nanocrystals using CdO as precursor," *Journal of the American Chemical Society*, vol. 123, pp. 183-184, 2001.
- [46] D. V. Talapin, J.-S. Lee, M. V. Kovalenko, and E. V. Shevchenko, "Prospects of colloidal nanocrystals for electronic and optoelectronic applications," *Chemical reviews*, vol. 110, pp. 389-458, 2009.
- [47] X. Peng, M. C. Schlamp, A. V. Kadavanich, and A. Alivisatos, "Epitaxial growth of highly luminescent CdSe/CdS core/shell nanocrystals with photostability and electronic accessibility," *Journal of the American Chemical Society*, vol. 119, pp. 7019-7029, 1997.
- [48] C. B. Murray, C. Kagan, and M. Bawendi, "Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies," *Annual Review of Materials Science*, vol. 30, pp. 545-610, 2000.
- [49] G. Schmid, *Nanoparticles: From Theory to Application*: Wiley, 2011.
- [50] I. Mekis, D. V. Talapin, A. Kornowski, M. Haase, and H. Weller, "One-pot synthesis of highly luminescent CdSe/CdS core-shell nanocrystals via organometallic and "greener" chemical approaches," *The Journal of Physical Chemistry B*, vol. 107, pp. 7454-7462, 2003.
- [51] S. Xu, J. Ziegler, and T. Nann, "Rapid synthesis of highly luminescent InP and InP/ZnS nanocrystals," *Journal of Materials Chemistry*, vol. 18, pp. 2653-2656, 2008.
- [52] J. J. Li, Y. A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson, *et al.*, "Large-scale synthesis of nearly monodisperse CdSe/CdS core/shell nanocrystals using air-stable reagents via successive ion layer adsorption and reaction," *Journal of the American Chemical Society*, vol. 125, pp. 12567-12575, 2003.
- [53] A. B. Greytak, P. M. Allen, W. Liu, J. Zhao, E. R. Young, Z. Popović, *et al.*, "Alternating layer addition approach to CdSe/CdS core/shell quantum dots with near-unity quantum yield and high on-time fractions," *Chemical Science*, vol. 3, pp. 2028-2034, 2012.
- [54] O. Chen, J. Zhao, V. P. Chauhan, J. Cui, C. Wong, D. K. Harris, *et al.*, "Compact high-quality CdSe-CdS core-shell nanocrystals with narrow emission linewidths and suppressed blinking," *Nat Mater*, vol. 12, pp. 445-451, 2013.
- [55] W. K. Bae, K. Char, H. Hur, and S. Lee, "Single-step synthesis of quantum dots with chemical composition gradients," *Chemistry of Materials*, vol. 20, pp. 531-539, 2008.
- [56] W. K. Bae, J. Kwak, J. Lim, D. Lee, M. K. Nam, K. Char, *et al.*, "Multicolored Light-Emitting Diodes Based on All-Quantum-Dot Multilayer Films Using Layer-by-Layer Assembly Method," *Nano letters*, vol. 10, pp. 2368-2373, 2010/07/14 2010.

- [57] V. Kloper, R. Osovsky, D. Cheskis, A. Sashchiuk, and E. Lifshitz, "Suppressed blinking in CdTe/CdSe core /shell quantum dots," *physica status solidi (c)*, vol. 6, pp. 2719-2721, 2009.
- [58] D. Dorfs, T. Franzl, R. Osovsky, M. Brumer, E. Lifshitz, T. A. Klar, *et al.*, "Type-I and Type-II Nanoscale Heterostructures Based on CdTe Nanocrystals: A Comparative Study," *small*, vol. 4, pp. 1148-1152, 2008.
- [59] V. Kloper, R. Osovsky, J. Kolny-Olesiak, A. Sashchiuk, and E. Lifshitz, "The growth of colloidal cadmium telluride nanocrystal quantum dots in the presence of CdO nanoparticles," *The Journal of Physical Chemistry C*, vol. 111, pp. 10336-10341, 2007.
- [60] O. Micic, H. Cheong, H. Fu, A. Zunger, J. Sprague, A. Mascarenhas, *et al.*, "Size-dependent spectroscopy of InP quantum dots," *The Journal of Physical Chemistry B*, vol. 101, pp. 4904-4912, 1997.
- [61] O. I. Micic, C. J. Curtis, K. M. Jones, J. R. Sprague, and A. J. Nozik, "Synthesis and characterization of InP quantum dots," *The Journal of Physical Chemistry*, vol. 98, pp. 4966-4969, 1994.
- [62] L. Li and P. Reiss, "One-pot synthesis of highly luminescent InP/ZnS nanocrystals without precursor injection," *Journal of the American Chemical Society*, vol. 130, pp. 11588-11589, 2008.
- [63] G. E. Cragg and A. L. Efros, "Suppression of Auger processes in confined structures," *Nano letters*, vol. 10, pp. 313-317, 2009.
- [64] K. Kim, H. Lee, J. Ahn, and S. Jeong, "Highly luminescing multi-shell semiconductor nanocrystals InP/ZnSe/ZnS," *Applied physics letters*, vol. 101, p. 073107, 2012.
- [65] T. Greco, C. Ippen, and A. Wedel, "InP/ZnSe/ZnS core-multishell quantum dots for improved luminescence efficiency," in *SPIE Photonics Europe*, 2012, pp. 842439-842439-9.
- [66] J. Lim, W. K. Bae, D. Lee, M. K. Nam, J. Jung, C. Lee, *et al.*, "InP@ ZnSeS, core@ composition gradient shell quantum dots with enhanced stability," *Chemistry of Materials*, vol. 23, pp. 4459-4463, 2011.
- [67] P. M. Allen, B. J. Walker, and M. G. Bawendi, "Mechanistic insights into the formation of InP quantum dots," *Angewandte Chemie International Edition*, vol. 49, pp. 760-762, 2010.
- [68] S. Kim, T. Kim, M. Kang, S. K. Kwak, T. W. Yoo, L. S. Park, *et al.*, "Highly luminescent InP/GaP/ZnS nanocrystals and their application to white light-emitting diodes," *Journal of the American Chemical Society*, vol. 134, pp. 3804-3809, 2012.
- [69] M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmüller, and U. Resch-Genger, "Determination of the fluorescence quantum yield of quantum dots: suitable procedures and achievable uncertainties," *Analytical Chemistry*, vol. 81, pp. 6285-6294, 2009.
- [70] K. Suzuki, A. Kobayashi, S. Kaneko, K. Takehira, T. Yoshihara, H. Ishida, *et al.*, "Reevaluation of absolute luminescence quantum yields of standard solutions using a spectrometer with an integrating sphere and a back-thinned CCD detector," *Physical Chemistry Chemical Physics*, vol. 11, pp. 9850-9860, 2009.
- [71] Z. L. Wang, "Transmission Electron Microscopy of Shape-Controlled Nanocrystals and Their Assemblies," *The Journal of Physical Chemistry B*, vol. 104, pp. 1153-1175, 2000/02/01 2000.
- [72] L. Carbone, C. Nobile, M. De Giorgi, F. D. Sala, G. Morello, P. Pompa, *et al.*, "Synthesis and micrometer-scale assembly of colloidal CdSe/CdS nanorods prepared by a seeded growth approach," *Nano letters*, vol. 7, pp. 2942-2950, 2007.
- [73] Z. L. Wang, Y. Liu, and Z. Zhang, *Handbook of nanophase and nanostructured materials*. New York: Kluwer Academic/Plenum, 2003.

-
- [74] K. Nozawa, H. Gailhanou, L. Raison, P. Panizza, H. Ushiki, E. Sellier, *et al.*, "Smart control of monodisperse Stöber silica particles: effect of reactant addition rate on growth process," *Langmuir*, vol. 21, pp. 1516-1523, 2005.
 - [75] J. J. Coleman, A. C. Bryce, and C. Jagadish, *Advances in semiconductor lasers* vol. 86: Academic Press, 2012.
 - [76] M. Asada, Y. Miyamoto, and Y. Suematsu, "Gain and the threshold of three-dimensional quantum-box lasers," *Quantum Electronics, IEEE Journal of*, vol. 22, pp. 1915-1921, 1986.
 - [77] Y. V. Vandyshchev, V. Dneprovskii, and V. Klimov, "Manifestation of dimensional quantization levels in the nonlinear transmission spectra of semiconductor microcrystals," *JETP Letters*, vol. 53, p. 314, 1991.
 - [78] V. I. Klimov and M. G. Bawendi, "Ultrafast carrier dynamics, optical amplification, and lasing in nanocrystal quantum dots," *MRS Bulletin*, vol. 26, pp. 998-1004, 2001.
 - [79] J. Schafer, J. P. Mondia, R. Sharma, Z. Lu, A. Susa, A. Rogach, *et al.*, "Quantum dot microdrop laser," *Nano letters*, vol. 8, pp. 1709-1712, 2008.
 - [80] Y. Wang, K. S. Leck, V. D. Ta, R. Chen, V. Nalla, Y. Gao, *et al.*, "Blue Liquid Lasers from Solution of CdZnS/ZnS Ternary Alloy Quantum Dots with Quasi - Continuous Pumping," *Advanced Materials*, vol. 27, pp. 169-175, 2014.
 - [81] A. V. Malko, A. A. Mikhailovsky, M. A. Petruska, J. A. Hollingsworth, H. Htoon, M. G. Bawendi, *et al.*, "From amplified spontaneous emission to microring lasing using nanocrystal quantum dot solids," *Applied Physics Letters*, vol. 81, pp. 1303-1305, 2002.
 - [82] K. Roh, C. Dang, J. Lee, S. Chen, J. S. Steckel, S. Coe-Sullivan, *et al.*, "Surface-emitting red, green, and blue colloidal quantum dot distributed feedback lasers," *Optics Express*, vol. 22, pp. 18800-18806, 2014/07/28 2014.
 - [83] B. Guilhabert, C. Foucher, A. M. Haughey, E. Mutlugun, Y. Gao, J. Herrnsdorf, *et al.*, "Nanosecond colloidal quantum dot lasers for sensing," *Optics Express*, vol. 22, pp. 7308-7319, 2014/03/24 2014.
 - [84] Y. Wang, V. D. Ta, Y. Gao, T. C. He, R. Chen, E. Mutlugun, *et al.*, "Stimulated Emission and Lasing from CdSe/CdS/ZnS Core - Multi - Shell Quantum Dots by Simultaneous Three - Photon Absorption," *Advanced Materials*, vol. 26, pp. 2954-2961, 2014.
 - [85] Y. Chen, J. Herrnsdorf, B. Guilhabert, Y. Zhang, I. M. Watson, E. Gu, *et al.*, "Colloidal quantum dot random laser," *Optics Express*, vol. 19, pp. 2996-3003, 2011.
 - [86] M. Kazes, D. Y. Lewis, Y. Ebenstein, T. Mokari, and U. Banin, "Lasing from semiconductor quantum rods in a cylindrical microcavity," *Advanced Materials*, vol. 14, pp. 317-321, 2002.
 - [87] B. Guzelturk, Y. Kelestemur, M. Olutas, S. Delikanli, and H. V. Demir, "Amplified spontaneous emission and lasing in colloidal nanoplatelets," *ACS nano*, vol. 8, pp. 6599-6605, 2014.
 - [88] J. Q. Grim, S. Christodoulou, F. Di Stasio, R. Krahne, R. Cingolani, L. Manna, *et al.*, "Continuous-wave biexciton lasing at room temperature using solution-processed quantum wells," *Nature nanotechnology*, vol. 9, pp. 891-895, 2014.
 - [89] V. Menon, M. Luberto, N. Valappil, and S. Chatterjee, "Lasing from InGaP quantum dots in a spin-coated flexible microcavity," *Optics express*, vol. 16, pp. 19535-19540, 2008.
 - [90] S. Gao, C. Zhang, Y. Liu, H. Su, L. Wei, T. Huang, *et al.*, "Lasing from colloidal InP/ZnS quantum dots," *Optics express*, vol. 19, pp. 5528-5535, 2011.
 - [91] V. I. Klimov, S. A. Ivanov, J. Nanda, M. Achermann, I. Bezel, J. A. McGuire, *et al.*, "Single-exciton optical gain in semiconductor nanocrystals," *Nature*, vol. 447, pp. 441-446, 2007.

- [92] X. Wang, X. Ren, K. Kahen, M. A. Hahn, M. Rajeswaran, S. Maccagnano-Zacher, *et al.*, "Non-blinking semiconductor nanocrystals," *Nature*, vol. 459, pp. 686-689, 2009.
- [93] V. Klimov, A. Mikhailovsky, D. McBranch, C. Leatherdale, and M. Bawendi, "Quantization of multiparticle Auger rates in semiconductor quantum dots," *Science*, vol. 287, pp. 1011-1013, 2000.
- [94] D. Katz, T. Wizansky, O. Millo, E. Rothenberg, T. Mokari, and U. Banin, "Size-Dependent Tunneling and Optical Spectroscopy of CdSe Quantum Rods," *Physical Review Letters*, vol. 89, p. 086801, 07/31/ 2002.
- [95] H. Htoon, J. Hollingsworth, R. Dickerson, and V. Klimov, "Effect of zero-to one-dimensional transformation on multiparticle auger recombination in semiconductor quantum rods," *Physical review letters*, vol. 91, p. 227401, 2003.
- [96] F. Garc ía-Santamar ía, Y. Chen, J. Vela, R. D. Schaller, J. A. Hollingsworth, and V. I. Klimov, "Suppressed auger recombination in "giant" nanocrystals boosts optical gain performance," *Nano letters*, vol. 9, pp. 3482-3488, 2009.
- [97] M. Ferhat, J. Furthmüller, and F. Bechstedt, "Gap bowing and Stokes shift in In_xGa_{1-x}N alloys: First-principles studies," *Applied Physics Letters*, vol. 80, pp. 1394-1396, 2002.
- [98] J. Kundu, Y. Ghosh, A. M. Dennis, H. Htoon, and J. A. Hollingsworth, "Giant nanocrystal quantum dots: stable down-conversion phosphors that exploit a large stokes shift and efficient shell-to-core energy relaxation," *Nano letters*, vol. 12, pp. 3031-3037, 2012.
- [99] P. Kambhampati, "Hot exciton relaxation dynamics in semiconductor quantum dots: radiationless transitions on the nanoscale," *The Journal of Physical Chemistry C*, vol. 115, pp. 22089-22109, 2011.
- [100] B. Redding, M. A. Choma, and H. Cao, "Speckle-free laser imaging using random laser illumination," *Nature photonics*, vol. 6, pp. 355-359, 2012.
- [101] D. Hofstetter and R. L. Thornton, "Loss measurements on semiconductor lasers by Fourier analysis of the emission spectra," *Applied physics letters*, vol. 72, pp. 404-406, 1998.
- [102] D. Hofstetter and R. L. Thornton, "Measurement of optical cavity properties in semiconductor lasers by Fourier analysis of the emission spectrum," *Quantum Electronics, IEEE Journal of*, vol. 34, pp. 1914-1923, 1998.
- [103] K.-H. Lee, J.-H. Lee, H.-D. Kang, B. Park, Y. Kwon, H. Ko, *et al.*, "Over 40 cd/A efficient green quantum dot electroluminescent device comprising uniquely large-sized quantum dots," *ACS nano*, vol. 8, pp. 4893-4901, 2014.
- [104] K.-H. Lee, J.-H. Lee, W.-S. Song, H. Ko, C. Lee, J.-H. Lee, *et al.*, "Highly efficient, color-pure, color-stable blue quantum dot light-emitting devices," *ACS nano*, vol. 7, pp. 7295-7302, 2013.
- [105] H. Shen, X. Bai, A. Wang, H. Wang, L. Qian, Y. Yang, *et al.*, "High - Efficient Deep - Blue Light - Emitting Diodes by Using High Quality Zn_xCd_{1-x}S/ZnS Core/Shell Quantum Dots," *Advanced Functional Materials*, vol. 24, pp. 2367-2373, 2014.
- [106] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*: Springer, 2007.
- [107] Y. Gao, X. Zhao, Y. Wang, R. Chen, E. Mutlugun, K. E. Fong, *et al.*, "Observation of polarized gain from aligned colloidal nanorods," *Nanoscale*, vol. 7, pp. 6481-6486, 2015.
- [108] E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, and C. B. Murray, "Structural diversity in binary nanoparticle superlattices," *Nature*, vol. 439, pp. 55-59, 2006.
- [109] N. Hildebrandt, "How to Apply FRET: From Experimental Design to Data Analysis," in *FRET – Förster Resonance Energy Transfer*, ed: Wiley-VCH Verlag GmbH & Co. KGaA, 2013, pp. 105-163.

- [110] J. H. L. Herrnsdorf, "Organic Lasers and Nanostructured Organic Films for Hybrid Integration," Doctor of Philosophy, University of Strathclyde, 2012.
- [111] H.-J. Eisler, V. C. Sundar, M. G. Bawendi, M. Walsh, H. I. Smith, and V. Klimov, "Color-selective semiconductor nanocrystal laser," *Applied Physics Letters*, vol. 80, pp. 4614-4616, 2002.
- [112] S. Gao, C. Zhang, Y. Liu, H. Su, L. Wei, T. Huang, *et al.*, "Lasing from colloidal InP/ZnS quantum dots," *Optics Express*, vol. 19, pp. 5528-5535, 2011/03/14 2011.
- [113] F. Todescato, I. Fortunati, S. Gardin, E. Garbin, E. Collini, R. Bozio, *et al.*, "Soft-Lithographed Up-Converted Distributed Feedback Visible Lasers Based on CdSe–CdZnS–ZnS Quantum Dots," *Advanced Functional Materials*, vol. 22, pp. 337-344, 2012.
- [114] C. Dang, J. Lee, K. Roh, H. Kim, S. Ahn, H. Jeon, *et al.*, "Highly efficient, spatially coherent distributed feedback lasers from dense colloidal quantum dot films," *Applied Physics Letters*, vol. 103, p. 171104, 2013.
- [115] Y. Chen, B. Guilhabert, J. Herrnsdorf, Y. Zhang, A. R. Mackintosh, R. A. Pethrick, *et al.*, "Flexible distributed-feedback colloidal quantum dot laser," *Applied Physics Letters*, vol. 99, p. 241103, 2011.
- [116] C. Foucher, B. Guilhabert, J. Herrnsdorf, N. Laurand, and M. D. Dawson, "Diode-pumped, mechanically-flexible polymer DFB laser encapsulated by glass membranes," *Optics Express*, vol. 22, pp. 24160-24168, 2014/10/06 2014.
- [117] J. Herrnsdorf, B. Guilhabert, Y. Chen, A. Kanibolotsky, A. Mackintosh, R. Pethrick, *et al.*, "Flexible blue-emitting encapsulated organic semiconductor DFB laser," *Optics express*, vol. 18, pp. 25535-25545, 2010.
- [118] I. D. W. Samuel, E. B. Namdas, and G. A. Turnbull, "How to recognize lasing," *Nat Photon*, vol. 3, pp. 546-549, 2009.
- [119] Y. Boucher and P. Feron, "Generalized transfer function: A simple model applied to active single-mode microring resonators," *Optics Communications*, vol. 282, pp. 3940-3947, 2009.
- [120] X. Liu, Q. Zhang, J. N. Yip, Q. Xiong, and T. C. Sum, "Wavelength Tunable Single Nanowire Lasers Based on Surface Plasmon Polariton Enhanced Burstein–Moss Effect," *Nano Letters*, vol. 13, pp. 5336-5343, 2013/11/13 2013.
- [121] P. Jing, J. Zheng, M. Ikezawa, X. Liu, S. Lv, X. Kong, *et al.*, "Temperature-Dependent Photoluminescence of CdSe-Core CdS/CdZnS/ZnS-Multishell Quantum Dots," *The Journal of Physical Chemistry C*, vol. 113, pp. 13545-13550, 2009/08/06 2009.
- [122] J. Hu, L.-s. Li, W. Yang, L. Manna, L.-w. Wang, and A. P. Alivisatos, "Linearly polarized emission from colloidal semiconductor quantum rods," *Science*, vol. 292, pp. 2060-2063, 2001.
- [123] X. Chen, A. Nazzal, D. Goorskey, M. Xiao, Z. A. Peng, and X. Peng, "Polarization spectroscopy of single CdSe quantum rods," *Physical Review B*, vol. 64, p. 245304, 2001.
- [124] S. A. Blanton, R. L. Leheny, M. A. Hines, and P. Guyot-Sionnest, "Dielectric Dispersion Measurements of CdSe Nanocrystal Colloids: Observation of a Permanent Dipole Moment," *Physical Review Letters*, vol. 79, pp. 865-868, 08/04/ 1997.
- [125] I. Hadar, G. B. Hitin, A. Sitt, A. Faust, and U. Banin, "Polarization properties of semiconductor nanorod heterostructures: from single particles to the ensemble," *The Journal of Physical Chemistry Letters*, vol. 4, pp. 502-507, 2013.
- [126] B. T. Diroll, A. Koschitzky, and C. B. Murray, "Tunable optical anisotropy of seeded CdSe/CdS nanorods," *The Journal of Physical Chemistry Letters*, vol. 5, pp. 85-91, 2013.
- [127] J. S. Kamal, R. Gomes, Z. Hens, M. Karvar, K. Neyts, S. Compennolle, *et al.*, "Direct determination of absorption anisotropy in colloidal quantum rods," *Physical Review B*, vol. 85, p. 035126, 2012.

- [128] D. B. Tice, D. J. Weinberg, N. Mathew, R. P. Chang, and E. A. Weiss, "Measurement of Wavelength-Dependent Polarization Character in the Absorption Anisotropies of Ensembles of CdSe Nanorods," *The Journal of Physical Chemistry C*, vol. 117, pp. 13289-13296, 2013.
- [129] M. Grzelczak, J. Vermant, E. M. Furst, and L. M. Liz-Marzán, "Directed self-assembly of nanoparticles," *ACS nano*, vol. 4, pp. 3591-3605, 2010.
- [130] F. Pietra, F. T. Rabouw, W. H. Evers, D. V. Byelov, A. V. Petukhov, C. de Mello Donegá, *et al.*, "Semiconductor nanorod self-assembly at the liquid/air interface studied by in situ GISAXS and ex situ TEM," *Nano letters*, vol. 12, pp. 5515-5523, 2012.
- [131] A. V. Titov and P. Král, "Modeling the self-assembly of colloidal nanorod superlattices," *Nano letters*, vol. 8, pp. 3605-3612, 2008.
- [132] A. Rizzo, C. Nobile, M. Mazzeo, M. D. Giorgi, A. Fiore, L. Carbone, *et al.*, "Polarized light emitting diode by long-range nanorod self-assembling on a water surface," *ACS nano*, vol. 3, pp. 1506-1512, 2009.
- [133] W. A. deHeer, W. S. Bacsá, A. Châtelain, T. Gerfin, R. Humphrey-Baker, L. Forro, *et al.*, "Aligned Carbon Nanotube Films: Production and Optical and Electronic Properties," *Science*, vol. 268, pp. 845-847, May 12, 1995 1995.
- [134] Y. Amit, A. Faust, I. Lieberman, L. Yedidya, and U. Banin, "Semiconductor nanorod layers aligned through mechanical rubbing," *physica status solidi (a)*, vol. 209, pp. 235-242, 2012.
- [135] M. Mohammadimasoudi, L. Penninck, T. Aubert, R. Gomes, Z. Hens, F. Strubbe, *et al.*, "Fast and versatile deposition of aligned semiconductor nanorods by dip-coating on a substrate with interdigitated electrodes," *Optical Materials Express*, vol. 3, pp. 2045-2054, 2013/12/01 2013.
- [136] K. M. Ryan, A. Mastroianni, K. A. Stancil, H. Liu, and A. Alivisatos, "Electric-field-assisted assembly of perpendicularly oriented nanorod superlattices," *Nano letters*, vol. 6, pp. 1479-1482, 2006.
- [137] Y. Cui, M. T. Björk, J. A. Liddle, C. Sönnichsen, B. Boussert, and A. P. Alivisatos, "Integration of Colloidal Nanocrystals into Lithographically Patterned Devices," *Nano Letters*, vol. 4, pp. 1093-1098, 2004/06/01 2004.
- [138] B. Guzelturk, P. L. H. Martinez, Q. Zhang, Q. Xiong, H. Sun, X. W. Sun, *et al.*, "Excitonics of semiconductor quantum dots and wires for lighting and displays," *Laser & Photonics Reviews*, vol. 8, pp. 73-93, 2014.
- [139] J. L. Baker, A. Widmer-Cooper, M. F. Toney, P. L. Geissler, and A. P. Alivisatos, "Device-scale perpendicular alignment of colloidal nanorods," *Nano letters*, vol. 10, pp. 195-201, 2009.
- [140] B. Nikoobakht, Z. Wang, and M. El-Sayed, "Self-assembly of gold nanorods," *The Journal of Physical Chemistry B*, vol. 104, pp. 8635-8640, 2000.
- [141] S.-Y. Zhang, M. D. Regulacio, and M.-Y. Han, "Self-assembly of colloidal one-dimensional nanocrystals," *Chemical Society Reviews*, vol. 43, pp. 2301-2323, 2014.
- [142] L. Malaquin, T. Kraus, H. Schmid, E. Delamarche, and H. Wolf, "Controlled particle placement through convective and capillary assembly," *Langmuir*, vol. 23, pp. 11513-11521, 2007.
- [143] L.-W. Wang, M. Califano, A. Zunger, and A. Franceschetti, "Pseudopotential theory of Auger processes in CdSe quantum dots," *Physical review letters*, vol. 91, p. 056404, 2003.
- [144] A. Shabaev and A. L. Efros, "1D Exciton Spectroscopy of Semiconductor Nanorods," *Nano Letters*, vol. 4, pp. 1821-1825, 2004/10/01 2004.
- [145] C. Grivas, C. Li, P. Andreakou, P. Wang, M. Ding, G. Brambilla, *et al.*, "Single-mode tunable laser emission in the single-exciton regime from colloidal nanocrystals," *Nature communications*, vol. 4, 2013.

- [146] G. Rainò, T. Stöferle, I. Moreels, R. Gomes, J. S. Kamal, Z. Hens, *et al.*, "Probing the Wave Function Delocalization in CdSe/CdS Dot-in-Rod Nanocrystals by Time- and Temperature-Resolved Spectroscopy," *ACS Nano*, vol. 5, pp. 4031-4036, 2011/05/24 2011.
- [147] D. Steiner, D. Dorfs, U. Banin, F. Della Sala, L. Manna, and O. Millo, "Determination of band offsets in heterostructured colloidal nanorods using scanning tunneling spectroscopy," *Nano letters*, vol. 8, pp. 2954-2958, 2008.
- [148] J. Müller, J. Lupton, P. Lagoudakis, F. Schindler, R. Koepppe, A. Rogach, *et al.*, "Wave function engineering in elongated semiconductor nanocrystals with heterogeneous carrier confinement," *Nano letters*, vol. 5, pp. 2044-2049, 2005.
- [149] M. Zavelani-Rossi, M. G. Lupo, R. Krahne, L. Manna, and G. Lanzani, "Lasing in self-assembled microcavities of CdSe/CdS core/shell colloidal quantum rods," *Nanoscale*, vol. 2, pp. 931-935, 2010.
- [150] M. Zavelani-Rossi, M. G. Lupo, F. Tassone, L. Manna, and G. Lanzani, "Suppression of biexciton auger recombination in cdse/cds dot/rods: Role of the electronic structure in the carrier dynamics," *Nano letters*, vol. 10, pp. 3142-3150, 2010.
- [151] F. Pisanello, G. Lemégnier, L. Martiradonna, L. Carbone, S. Vezzoli, P. Desfonds, *et al.*, "Non-Blinking Single-Photon Generation with Anisotropic Colloidal Nanocrystals: Towards Room-Temperature, Efficient, Colloidal Quantum Sources," *Advanced Materials*, vol. 25, pp. 1974-1980, 2013.
- [152] I. Moreels, G. Rainò, R. Gomes, Z. Hens, T. Stöferle, and R. F. Mahrt, "Nearly Temperature - Independent Threshold for Amplified Spontaneous Emission in Colloidal CdSe/CdS Quantum Dot - in - Rods," *Advanced Optical Materials*, vol. 24, pp. OP231-OP235, 2012.
- [153] G. Xing, Y. Liao, X. Wu, S. Chakraborty, X. Liu, E. K. Yeow, *et al.*, "Ultralow-threshold two-photon pumped amplified spontaneous emission and lasing from seeded CdSe/CdS nanorod heterostructures," *ACS nano*, vol. 6, pp. 10835-10844, 2012.
- [154] R. Krahne, M. Zavelani-Rossi, M. G. Lupo, L. Manna, and G. Lanzani, "Amplified spontaneous emission from core and shell transitions in CdSe/CdS nanorods fabricated by seeded growth," *Applied Physics Letters*, vol. 98, p. 063105, 2011.
- [155] Y. Kelestemur, A. F. Cihan, B. Guzelturk, and H. V. Demir, "Type-tunable amplified spontaneous emission from core-seeded CdSe/CdS nanorods controlled by exciton-exciton interaction," *Nanoscale*, vol. 6, pp. 8509-8514, 2014.
- [156] O. Chen, J. Zhao, V. P. Chauhan, J. Cui, C. Wong, D. K. Harris, *et al.*, "Compact high-quality CdSe-CdS core-shell nanocrystals with narrow emission linewidths and suppressed blinking," *Nature materials*, vol. 12, pp. 445-451, 2013.
- [157] T. Papathanasiou and D. C. Guell, *Flow-induced alignment in composite materials*: Elsevier, 1997.
- [158] N. Frateschi, A. Kanjamala, A. Levi, and T. Tanbun - Ek, "Polarization of lasing emission in microdisk laser diodes," *Applied physics letters*, vol. 66, pp. 1859-1861, 1995.
- [159] B. E. A. Saleh and M. C. Teich, *Fundamentals of Photonics*: Wiley, 2013.
- [160] R. J. Nick, C. A. BREEN, C. M. Denton, S. Sadasivan, and J. R. Linton, "Method of making components including quantum dots, methods, and products," ed: Google Patents, 2014.
- [161] S. Nakamura and G. Fasol, *The Blue Laser Diode: GaN Based Light Emitters and Lasers*: Springer Berlin Heidelberg, 2013.
- [162] S. Ithurria and B. Dubertret, "Quasi 2D colloidal CdSe platelets with thicknesses controlled at the atomic level," *Journal of the American Chemical Society*, vol. 130, pp. 16504-16505, 2008.

References

- [163] S. Ithurria, M. Tessier, B. Mahler, R. Lobo, B. Dubertret, and A. L. Efros, "Colloidal nanoplatelets with two-dimensional electronic structure," *Nature materials*, vol. 10, pp. 936-941, 2011.
- [164] M. D. Tessier, C. Javaux, I. Maksimovic, V. Lorient, and B. Dubertret, "Spectroscopy of single CdSe nanoplatelets," *ACS nano*, vol. 6, pp. 6751-6758, 2012.
- [165] C. She, I. Fedin, D. S. Dolzhenkov, A. Demortière, R. D. Schaller, M. Pelton, *et al.*, "Low-Threshold Stimulated Emission Using Colloidal Quantum Wells," *Nano Letters*, vol. 14, pp. 2772-2777, 2014/05/14 2014.
- [166] B. Abécassis, M. D. Tessier, P. Davidson, and B. Dubertret, "Self-Assembly of CdSe Nanoplatelets into Giant Micrometer-Scale Needles Emitting Polarized Light," *Nano letters*, vol. 14, pp. 710-715, 2014.