Optical study of colloidal quantum dots : toward efficient emission and lasing upon single- and multi-photon excitation

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**Optical study of colloidal quantum dots:
toward efficient emission and lasing upon
single- and multi-photon excitation**

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**Division of Physics and Applied Physics
School of Physical and Mathematical Sciences**

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Frontispiece

Stimulated emission and lasing spanning the whole visible spectral range have been achieved from colloidal quantum dot (CQDs) upon both one- and multi-photon pumping by rational design of CQDs

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Abstract

Colloidal quantum dots (CQDs) have become the research hotspot due to their exceptional merits including the facile emission spectral tunability by size and composition tailoring, the solution processibility, the broad absorption and the narrow emission spectra and so on. In this thesis, main efforts are devoted to explore the fundamental linear and nonlinear optical properties of CQDs and develop applications of CQD-based micro-lasers. The third-order nonlinear optical properties of heavy metal-free InP/ZnS CQDs have been comprehensively studied, which reveals that the InP/ZnS CQDs are potentially excellent fluorescent bio-probes under two-photon excitation. By rationally designing and employing the CdSe/CdS/ZnS core/shell/shell CQDs as the optical gain material, three-photon induced amplified spontaneous emission and lasing have been realized for the first time from CQDs. Record low threshold stimulated emission in blue spectral range have been achieved from the ternary alloy CdZnS/ZnS core/shell CQDs thanks to the intrinsic slow nonradiative Auger recombination. To solve the “green gap” challenge experienced in epitaxial semiconductor lasers, the optical gain properties of the green-emitting quaternary alloy CdZnSeS/ZnS core/shell has been comprehensively investigated for the first time, and ultra-low threshold stimulated emission in green region has been observed. Furthermore, low threshold whispering gallery mode lasers in blue and green regime under quasi-continuous wave pumping have been produced leveraging on CdZnS/ZnS and CdZnSeS/ZnS CQDs, respectively. Our results represent a great progress in the development of CQD-based lasers and hold strong potential in wide range of field in

biology and photonics and their interaction of biophotonics.

Chapter 1

Introduction

1.1 Motivation

Semiconductor-based optoelectronic devices are ubiquitous nowadays, ranging from photon harvesting devices including solar cells and photodetectors to photon generating ones including light emitting diodes (LEDs) and lasers [1-5]. Most of those semiconductors acting as the core material for the above-mentioned devices are produced by vacuum-based processes, such as the pulsed laser deposition and chemical vapor deposition, which are complex and costly[1-3]. The advent of colloidal quantum dots (CQDs), or nanocrystals, synthesized by wet chemistry technique promises a revolution in optoelectronics due to the low cost, solution processibility, facile electronic and optical property tunability by simply manipulating the dot size [6-10]. Until now, CQDs have been widely employed in various optoelectronic devices, such as visible and infrared photodetectors [11, 12], LEDs covering the full visible spectral window [13, 14], solar cells [15] and lasers[6, 9]. However, the performance of the CQD-based devices is far from expectation and there is still plenty of room for improvement [7, 9]. Naturally, the study of optical properties of CQDs becomes essential in view of both fundamental physics interest and practical applications as depicted in Figure 1.1. The focus of this thesis is to investigate the optical properties of CQDs through steady state and time-resolved spectroscopy aiming at shedding light on general design principles for eligible CQDs for various photonic applications, such as fluorescent bioprobes and CQD-based

lasers.

Figure 1.1 Optical spectroscopy links CQDs to fundamental and applied optoelectronics.

1.1 Colloidal quantum dot (CQDs)

1.1.1 Quantum confinement effect

Colloidal quantum dots, or nanocrystals, are crystalline semiconductor nanoparticles, which are fabricated by wet chemistry method [16, 17]. CQDs were first discovered by Louis E. Brus in 1985 [18]. Initially, the photoluminescence quantum yield (PL QY) of CQDs is very low due to the efficient carrier trapping by the abundant surface defects. Later on, by surface passivation with inorganic shells, the emission of CQDs is dramatically enhanced and the deep level emission related to the defect states could be totally eliminated [19, 20]. A canonical example is the CdSe/ZnS CQDs, in which the ZnS with large band gap is epitaxially grown on CdSe core [19]. The typical

structure of core-shell CQDs are schematically portrayed in Figure 1.2a. Normally, the band gap of a certain semiconductor material is fixed. While, when the physical size of the material is reduced to be comparable or less than the free travelling length [21] of the electron hole pair, known as exciton, the exciton will “feel” the rigid boundary of the nanocrystal and react accordingly by tailoring their energy. This phenomenon is called “quantum confinement effect” [22]. As a result, the bandgap of the CQDs can be tailored by size control [23], in particular, the absorption or emission will blue shift with decrease of dot size, as shown in Figure 1.2b. Note that the exciton Bohr radius is material-dependent, for example, it is around 0.6 nm, 3 nm, 6 nm and 15 nm for CuCl [17], CdS [24], CdSe [25] and InP [26], respectively. Therefore, the minimum size for the observation of the quantum confinement effect varies for different semiconductors. Another phenomenon induced by the quantum confinement effect is the collapse of the continuous states in bulk semiconductor towards the discrete atomic-like levels in CQDs [10, 17]. The bandgap changing and energy level splitting in CQDs by quantum confinement are able to be quantitatively understood by “particle-in-a-sphere” model [16]. According to this model, the photoinduced charge carrier is treated as a particle with finite mass confined in the spherical potential well [17]:

$$x < r; V_x = 0$$

$$x > r; V_x = \infty$$

where r denotes the potential well radius. The wavefunction of the charge carrier can be derived by taking the potential well into Schrödinger equation. The equation has

been solved by Flügge in 1971 [27] and the answer is given by:

$$\psi_{nlm}(x, \theta, \phi) = Cx^{-1}J_l(k_{nl}x)Y_l^m(\theta, \phi)$$

where C is constant, $Y_l^m(\theta, \phi)$ is the spherical harmonic, $J_l(k_{nl}x)$ denotes the spherical Bessel function of l -th order and $k_{nl} = \alpha_{nl}/x$, in which α_{nl} is the n -th zero of $J_l(k_{nl}x)$. As a result, the energy of the charge carrier is extracted to be [16]:

$$E_{nl} = \frac{h^2 \alpha_{nl}^2}{8\pi m_0 r^2}$$

where m_0 is the mass of the charge carrier and α_{nl} is constant when (n, l) is fixed, such as $\alpha_{1s} = \pi$, $\alpha_{1p} = 4.493$, $\alpha_{2s} = 2\pi$, etc.

One may argue that this model only apply to the system of a particle in an empty sphere. However, the CQDs are full of atoms rather than empty. While, when Bloch's theorem and effective mass approximation are taken into account, the photoinduced charge carrier in CQD can be simplified to the "particle-in-a-box" model [17]. Specifically, the system could be treated as a particle locating in a sphere. Most importantly, we can get two pieces of information from this simple model: first, the energies of the charge carrier in CQD is similar to kinetic energy of free carrier, the only difference is that the former is quantized, which explains the energy level splitting in CQDs; Second, the energy of the charge carrier in CQD is in reverse proportion to the square of the radius (x) of the CQD, which accounts for nothing but the blue-shift of the emission and absorption of the CQD as the size decreases.

Figure 1.2 (a) Typical schematic structure of core-shell colloidal quantum dots (adopted from Nanotech-Dubna). (b) The relationship between DOS and system dimension (adopted from reference 86). (c) Quantum confinement effect induced band gap variation and emergence of discrete band levels as the dot size decreases. (d) Colorful CdSe CQDs with different sizes (adopted from Evident Technologies, Inc.).

1.1.2 Electronic structure and optical transitions in CQDs

Despite that the simple “particle-in-a-sphere” model can qualitatively explain the increased band gap with the reduction of size and the featured absorption spectra, more advanced model taking into account the complexity of valance band structure, which is common in bulk semiconductors, should be adopted [17]. Taking CdSe CQDs, the most well studied system, as an example, the conduction band is relatively simple because it arises from the 5s atomic orbitals in Cadmium with merely double degeneracy including spin at $k=0$. In contrast, the valence one is constructed by the 4p

orbital in Selenide with 6-fold degeneracy including spin [28]. By virtue of the spin-orbit coupling, the 6-fold degeneracy valence band is transformed to 4-fold band with angular momentum of $J=3/2$ and 2-fold band with $J=1/2$ which is known as the spin-orbit band at $k=0$ [29]. The 4-fold $J=3/2$ band further split into 2-fold heavy-hole and 2-fold light-hole band when $k \neq 0$. In addition, valence band mixing induced by the confinement effect in CQDs should also be considered [30]. Correspondingly, the total angular momentum (T) of the valence bands is the sum of the unit cell contribution (J) and the envelop function contribution (L) owing to the effect of quantum confinement in CQD and the valence bands are referred as $nL_T(h)$ [17]. According the calculation Ekimov *et al.* [31], the energy levels arrange in a rising order is $1S_{3/2}(h)$, $1P_{3/2}(h)$, $2S_{3/2}(h)$, $1P_{1/2}(h)$ and $1S_{1/2}(h)$ (Figure 1.3a). The optical transitions from these bands to the conduction bands have been experimentally observed and agree with the theoretical calculation very well [32]. Figure 1.3b shows the absorption spectrum of high-quality CdSe CQDs, where the first four optical transitions are well-resolved.

Figure 1.3 (a) Optical transitions in CdSe CQDs (adopted from reference 32). (b)

Linear absorption spectra of CdSe CQDs showing the well-resolved optical transitions (adopted from reference 32).

1.1.3 Auger recombination in CQDs

Auger recombination (AR) describes the process that the energy consumed by the annihilation of an exciton is exploited to excite the other electron, hole or exciton rather than emitted as a photon [33]. Therefore, AR usually occurs under high excitation intensities where multi-excitons are generated, and there are three possible channels for the AR, namely, a negative trion, a positive trion and a biexciton as depicted in Figure 1.4 (a) [34]. In bulk semiconductors, the AR is not efficient and exhibits a cubic dependence on the carrier density. Thus, the AR rate can be described by [35, 36]:

$$dn_{eh}/dt = -Cn_{eh}^3$$

where C is the constant coefficient, known as Auger constant [36]. In case of CQDs, the AR differs a lot from that in bulk crystal from several aspects. First, by virtue of the enhanced Coulomb interaction and the reduction of the momentum conservation, the AR becomes dramatically rapid in CQDs [37]. Second, the AR lifetimes become quantized in CQDs instead of being continuous as in bulk semiconductor [36]. The pioneering experimental study of AR in CQDs is done by Klimov *et al.* [36, 38], in which exciton dynamics were investigated by detecting the bleaching of 1S optical transition in standard pump-probe experiments. The scaling of AR lifetime is studied by subtraction method, from which the single-exponential decay dynamics of the 4-, 3- and 2-excitons states are extracted as shown in Figure 1.4b [36]. It is found that the

AR has a cubic dependence on the average number of excitons, similar to that in bulk semiconductor, indicating that the AR is a three-particle process in these CdSe CQDs with strong quantum confinement effect. Another feature is that the AR rate is closely related to the size of CQDs, specifically, the AR rate increases rapidly as the size decreases (Figure 1.4c) [36].

As AR is a nonradiative recombination process, it is regarded as an optical loss channel under high excitation intensities. Due to the much enhanced AR rate, the AR is found to be the main channel that depletes the population inversion, thus hindering the stimulated emission in CQDs [9]. As a result, nowadays, searching ways to suppress AR in CQDs becomes a hot research spot in order to develop CQD-based lasers, LEDs and single photon emitters [39, 40].

Figure 1.4 (a) Schematic description of Auger recombination involving a negative trion (X^-) (left), a positive trion (X^+) (middle) and a biexciton (right), which can be

considered as either a negative trion or a positive trion (adopted from reference 34 and 32). (b) Scale of Auger lifetime with 1-, 2-, 3- and 4-e-h pairs in 2.3 nm-sized CdSe CQDs. (c) Biexcitonic Auger lifetime in different sized CdSe CQDs (adopted from reference 36).

1.1.4 Optical gain in CQDs

The advent of quantum well lasers has greatly improved the performance of semiconductor lasers due to the higher density of state (DOS) of conduction and valence band and larger oscillator strength involved in the emission process compared to those of bulk semiconductors [1, 41]. Naturally, the quantum dot, which possesses even higher DOS for the emission-related state and stronger oscillator strength, will promise further enhanced lasing performance. However, the actual situation is not like what we thought. Owing to the two-fold degeneracy of the lowest state in II-IV CQDs, the excited number of excitons in average per QD, $\langle N \rangle$, is required to be greater than 1 in order to achieve population inversion, a prerequisite for optical gain [42]. As depicted in Figure 1.5, the excitation of single exciton in one CQD, $\langle N \rangle = 1$, will result in optical transparency due to the compensation of the stimulated emission by absorption in the CQD [43]. In order to develop optical gain, where the stimulated emission outplays the optical absorption, more than one exciton has to be excited, as shown in Figure 1.5 [32]. This means that multi-exciton state is involved in the stimulated emission, and that is where the challenge of stimulated emission and lasing from CQDs lies. As depicted above, the development of multiexcitonic state in CQD will activate the nonradiative Auger process which is much faster than that in bulk

counterpart because of the greatly enhanced inter-exciton contacts in CQDs, which hinders the development of stimulated emission. Correspondingly, there are two separate ways to realize stimulated emission from CQDs. One way is to suppress or kill the Auger recombination in CQDs, which can be done by size and shape control, exemplified by the one-dimensional colloidal nanorods and the two-dimensional colloidal quantum wells [44-46], and core-shell heterostructures engineering, such as the “giant” CdSe/CdS CQD [47, 48], the CdSe/CdS dot/rod heterostructures and the thin-shell CdSe/CdS with alloyed core-shell interface [49-51]. Some researchers have reported single-exciton enabled stimulated emission to kill the AR by deliberately designing type-II CdS/ZnSe core-shell CQDs [42] and unconventional pyramid-shaped CdSe/ZnCdS CQDs [6]. The second way is to shorten the buildup time of stimulated emission to make it shorter than the gain depletion time and, then, the development of stimulated emission will dominate over the nonradiative AR since the rate of stimulated emission is much faster than that of AR [9]. The most effective and available method is to increase the concentration or volume fraction of CQDs, which can be easily achieved by solid-state close-packed CQD-films [9].

In this dissertation, we have demonstrated several ways to suppress the AR and achieved stimulated emission and lasing from CQDs in short visible spectral range including blue and green where AR is intense previously. Besides, we demonstrated lasing in liquid state from CQD solution where high concentration or large packing density of CQD is not available.

Figure 1.5 Optical transparency as one exciton is photogenerated (left), Optical gain emerges at least two-exciton is excited in individual CQDs (right).

1.1.5 Basis of lasers

Laser is a device that delivers spectrally, temporally and spatially coherent light source by amplifying the spontaneous emission, known as the stimulated emission [52]. Three components are necessary to build a laser, namely, the gain medium, a source to inject energy into the gain medium and a resonator or cavity to provide the optical feedback as is drawn in Figure 1.6 (a) [53]. The gain media can be classified into three categories in terms of the physical state [54], namely, solid-state gain media including the rare-earth ions and transition metal ions doped crystals and silicate or phosphate glasses and semiconductors (ZnO, GaN, GaAs), liquid gain media including laser dyes dissolved in various solvents and gaseous gain media including mixture of Helium and Cadmium gas. In this dissertation, CQDs are employed as the gain medium due to the potentially low and temperature-insensitive lasing threshold [55, 56], cost effective solution processibility and, most importantly, the facile bandgap tunability by manipulation of the dot size, which renders the achievement of the multi-color lasers by employing single material [6]. As for the energy injection methods, electric and optical pumping are the main channels [54]. Currently, optical

pumping is much more accessible compared to electric counterpart [57], especially, for the solution-processed CQD-lasers, and, thus, is utilized in the works through the thesis. There are mainly three kinds of optical feedbacks contributing to lasing including reflection (Fabry-Perot lasers, Whispering gallery mode (WGM) lasers) [58, 59], diffraction (Distributed feedback lasers, Photonic crystal lasers) [60, 61] and scattering (Random lasers) [62, 63]. The random lasers stand out from the crowd due to the simple fabrication process [64], and WGM lasers are attracting increasing attention thanks to the tiny mode volume and intrinsic large Q-factor [65]. Consequently, these two kinds of optical cavity will be studied and discussed more in detail in the following part.

Random laser: In contrast to traditional lasers, deliberately designed cavity is not necessary for random laser [66]. Consequently, the fabrication of random lasers is simple and cost-effective, which is of great concern toward practical applications. The optical feedback is provided by the scattering in the disordered active system as is schematically depicted in Figure 1.6 (b). Normally, the random laser can be divided into two regimes [63]: weak scattering regime (incoherent random laser), where the average scattering free length is far larger than the optical wavelength, and strong coherent scattering regime (coherent random laser), where the average scattering free length is comparable to or shorter than the optical wavelength. Early random lasers are always made by doping high refractive nanoparticles into the active dye solutions, where the nanoparticles serve as the scattering centers and the dyes behalf as the gain media [67]. In this dissertation, taking advantage of the high refractive index and the

excellent gain properties of the CQDs, they act as both the strong scattering centers and the gain medium, thus achieving the coherent random lasing.

WGM laser: WGM laser is named after the whispering gallery in St Paul's Cathedral where the acoustic wave propagates in a fantastic way around the dome due to the total internal reflection (TIR) [68]. Similarly, when light travels inside a dielectric sphere whose refractive index is larger than that of the environment, TIR around the inside walls will be experienced by the light and standing waves will be formed due to the constructive interference (Figure 1.6 (c)) [69]. In other word, the optical feedback in WGM lasers is provided by the TIR. Consequently, the Q-factor of WGM lasers is extremely high given that the surface of the sphere is optically smooth [70, 71]. Besides the sphere, many derivative structures have been demonstrated to support WGM lasing, such as the micro-fiber [72] whose cross-section naturally serves as the WGM cavity, disk resonator [73], hemisphere resonator [74], ring resonator [75], toroid resonator [76] *et al.*

Figure 1.6 (a) Schematic structure of a typical laser. (b) Working mechanism of random lasers. (c) Working mechanism of whispering gallery mode lasers.

1.2 Objectives and Contributions

CQDs are emerging as the most promising light emitters and gain materials by virtue of the narrow emission linewidth, broadband absorption with large absorption cross-sections, high PL QY, facile emission wavelength tunability by size and cost effective wet chemistry-based fabrication process. The stimulated emission from CQDs has been demonstrated in CdSe-based CQDs in year of 2000 [9], and, subsequently, lasing action has been achieved [32]. However, most of the stimulated emission and lasing demonstration are induced by single-photon absorption, which limit, to a great extent, the potential applications of the CQD-lasers. Whilst, the

nonlinear absorption and emission process in CQDs are of great importance in view of both fundamental interests and practical applications including bio-imaging and bio-sensing [77]. Furthermore, for the CQD-based photonic devices, especially the CQD-lasers, the performance in blue and green spectral range are always inferior to these in red counterparts [34]. As a result, this thesis dedicates to: 1) study the nonlinear optical properties of CQDs and offer clues for designing CQDs for high nonlinear absorption and efficient emission properties; 2) achieve multi-photon induced stimulated emission and lasing from CQDs to extend potential applications of CQD-lasers; 3) unravel the mechanisms for the poor performance of CQD-lasers in blue and green region and find ways to improve the performance of blue and green CQD-lasers to the level of their red counterparts, thus realizing CQD-lasers in the full visible spectral window; 4) develop facile and innovative CQD-based lasers. The major contributions of this dissertation are listed as follows:

1. Although CQDs are potentially ideal probes for bio-imaging and bio-sensing applications, the toxic elements including Cd and Pb in conventional CQDs limit their practical applications in biophotonics. The novel Cd-free InP/ZnS CQDs are found to show broadband tunable emission with high photoluminescence quantum yield (PL QD). Nevertheless, the nonlinear absorption and emission properties, which are of great importance for bio-imaging and bio-sensing, have not yet been explored. We unravel that the two photon absorption cross-section of InP/ZnS CQDs increases with the increasing of dot size and two-photon absorption cross-section as large as $6.2 \times 10^3 \text{ GM}$ is achieved with dot size of 2.8 nm, which

indicates that InP/ZnS CQDs are promising bio-probes.

2. Stimulated emission from CQDs under direct three-photon pumping is achieved for the first time by designing CdSe/CdS/ZnS core/shell/shell CQDs with boosted three-photon absorption cross-section, suppressed Auger process and enhanced photostability. In addition, three-photon induced lasing is observed from clusters of CdSe/CdS/ZnS core/shell/shell CQDs, the lasing mechanism is revealed to be coherent random lasing through excitation intensity-dependent and excitation area dependent PL experiments and power Fourier transform analysis.
3. Realize blue lasers in both liquid and solid states by employing ternary alloy CdZnS/ZnS core/shell CQDs. The thresholds of these blue lasers are extremely low and quasi-continuous wave pumping is accessible. In addition, we unambiguously discovered the underlying mechanisms for the ultra-low thresholds of these blue lasers by steady state and dynamic optical studies. We also offer general rules for designing high-quality CQDs and developing low-threshold CQD-lasers.
4. Epitaxial semiconductor lasers are experiencing “the green death valley of death” because of the technological problems in accessing green wavelength range. CQD-lasers seem to be the ideal problem solver. However, only a few groups have demonstrated the stimulated emission and lasing demonstrations from CQDs in green regime, and the thresholds are unacceptably high due to the greatly boosted Auger recombination rate in the CdSe-based CQDs with strong quantum confinement effect. In contrast, we successfully obtained green emission by

manipulating the constituent of the CQDs rather than leveraging on quantum confinement effect to suppress the Auger recombination, correspondingly, low-threshold stimulated emission and lasing in green regime have been achieved from quaternary alloy CdZnSSe/ZnS CQDs, which can potentially overcome the “green gap” challenging seen in epitaxial semiconductor lasers.

1.3 Outline of the thesis

The main focus of this thesis is to study the optical properties of CQDs in both linear and nonlinear regime including the emission and optical gain properties and to develop CQD-based lasers upon one- and multi-photon excitation.

In Chapter 2, the experimental techniques about the sample fabrication and the optical characterization will be introduced.

In Chapter 3, the third order nonlinear optical properties of heavy metal-free InP/ZnS CQDs including the saturable absorption and two photon absorption and emission are comprehensively studied.

In Chapter 4, the direct three-photon induced stimulated emission and coherent random lasing from solid film of CdSe/CdS/ZnS core/shell/shell CQDs are presented. The underlying mechanisms are studied in detail with the help of comprehensive spectroscopy.

In Chapter 5, we present the record-low threshold stimulated emission in blue spectral range by rationally employing the ternary alloy CdZnS/ZnS core/shell CQDs, and liquid-state lasers with low threshold were produced by infiltrating the solution of CdZnS/ZnS CQDs into silica capillary tubes. Furthermore, by comparatively studying

the optical properties of a series of CdZnS-based CQDs, we attempt to reveal the mechanisms for the superior optical gain properties of CdZnS/ZnS CQDs and shed light on general rules on designing CQDs for low threshold lasers.

In Chapter 6, the optical gain properties of quaternary alloy CdZnSeS/ZnS core/shell CQDs are investigated. The superior optical gain performance from green-emitting CdZnSeS/ZnS CQDs was revealed, which possess potential in overcoming the “green gap” experienced by the epitaxial semiconductor lasers.

Finally, the conclusions and future work will be presented in Chapter 7.

Chapter 2

Experimental techniques

2.1 Material growth

Pyrolysis of metal-organic precursors in hot solvent is the most successful method to grow high-quality CQDs [17] and thus is adopted in this thesis. The typical synthesis setup for CQDs is presented in Figure 2.1 (a). The growth kinetics of CQDs in this method has been studied by La Mer and Dinegar [78]. Generally, the production of CQDs can be divided into three steps: the particle nucleation process and particle growth process and Ostwald ripening (Figure 2.1 (b)). The nucleation process is relatively fast and is triggered by the supersaturation of the monomers obtained by thermal decomposition of the precursors. During nucleation, the monomers are consumed rapidly and nucleation finishes after the monomer concentration decreases to lower than the critical value for nucleation. Next, the growth stage begins, which is well described by diffusion theory. According to this theory, the monomers should first go approaching the particles and then react at the surface, therefore, the particle growth rate is diffusion-limited [79]. Based on the Fick's law of diffusion, the diffusion coefficient, D , in spherical coordinates is mathematically given by:

$$\frac{1}{D} \frac{\partial C}{\partial t} = \frac{2}{x} \frac{\partial C}{\partial x} + \frac{\partial^2 C}{\partial^2 x}$$

where x denotes the separation between the surface of the particle and the area with monomer concentration of C . The solution of this equation is solved based on boundary conditions for colloidal spherical particles with radius R :

$$\frac{\partial R^2}{\partial t} = \frac{2VD}{N_A} (C_t - C_s)$$

where V is the volume of the solution, C_t is the monomer concentration of the bulk solution at time t and C_s is the monomer concentration at the surface of the particle. This equation delivers a piece of important information that the particle size distribution will become narrower as the particles grow. Therefore, the particle growth process is also called “self-focusing” stage [80]. When most of the monomers are consumed, the Ostwald ripening will play a dominate role, in which small particles will shrink and dissolve into the solution, while the big particles will keep growing. Correspondingly, although the average size increases during the Ostwald ripening stage, the size distribution will be deteriorated or “defocus”. Thus, the Ostwald ripening process should be suppressed or size-selective processes involving centrifugation and precipitation should be performed in order to get monodisperse CQDs (size dispersion is less than 5%) [81].

Figure 2.1 (a) Typical setup for the fabrication of CQDs. (b) The nucleation and growth process of CQDs (adopted from reference 17).

2.2 Optical characterization

2.2.1 Linear steady-state absorption

Linear absorption spectroscopy could offer information on the electronic structure and optical transitions of targeted materials. In case of CQDs, the first excitonic absorption peak, thus the band gap, can be obtained from the absorption measurement [32]. We can also estimate the size and the size distribution of the CQDs from the absorption spectra [82]. Furthermore, the absorption cross-sections of the CQDs can be easily derived based on the position of the first exciton absorption feature in absorption spectrum based on the pre-calibrated data in literature without turning to advanced techniques [82]. Figure 2.2 schematically displays the typical setup for absorption measurement. As for the light source, the Xeno lamp which offers broadband continuous emission is usually employed. The photomultiplier (PMT) detector equipped with the standard lock-in technique is used for collecting the transmitted light. In the end, the absorption spectra are obtained by data processing from the transmittance based on Beer-Lambert law [82].

Figure 2.2 The experimental setup for the measurement of absorption.

2.2.2 Single- and multi-photon excited photoluminescence

Photoluminescence describes the light emission process from materials induced by

absorption of photons [83]. Normally, the electrons are first lifted to excited state by a photon with energy exceeds the bandgap of the material, then, the hot electron will relax to the lowest state by releasing energy like phonons, which is known as cooling process [84]. Finally, the electrons at the lowest excited state will go back to the ground state by emitting photons. Photoluminescence measurement could provide a lot of information including the quality of the material, the content and composition of impurities in the material. Furthermore, the exciton binding energy and impurity-exciton binding energy could be derived by performing the temperature dependent PL [85]. Figure 2.3 shows the typical setup for PL measurement. The He-Cd laser providing dual optical wavelength, namely, 325 nm and 441 nm, is exploited as the laser source, and the PL comes into a 750-mm monochromator and detected by PMT combined with standard lock-in technique or a silicon charge coupled device (CCD). By replacing the continuous He-Cd laser by the pulsed laser with high transient power as the laser source, the stimulated emission and lasing properties of the material can be studied [86].

On the other hand, the multi-photon excited PL is highly desired by virtue of the typically long excitation wavelength and the nonlinear increase of the absorption and PL with respect to excitation intensity [87, 88]. The first theoretical study on two-photon absorption is done by Maria Goeppert-Mayer [89]. The two-photon generation rate of electron-hole pairs in an atom or a molecule based on the second-order perturbation theory by absorbing two photons, whose energy and momentum are the same, is given by [90]:

$$W^{(2)} = \frac{2\pi}{\hbar} \sum_{u_1, u_0} |M_{u_1, u_0}| \delta(E_{u_1} - E_{u_0} - 2\hbar\omega),$$

$$M_{u_1, u_0} = \sum_{u_2} \frac{V_{u_1, u_2} V_{u_2, u_0}}{E_{u_2} - E_{u_0} - \hbar\omega - i\hbar\gamma_{u_2}}$$

Here, u_0 , u_1 and u_2 represent the whole set of initial, final and intermediate states with the quantum numbers n , l and m , γ_{u_2} is the reciprocal lifetime and V is the interaction operator described by [16]:

$$V_{f,i} = \left\langle \psi_f \left| \frac{e}{mc} \vec{A} \cdot \vec{P} \right| \psi_i \right\rangle$$

Compared to single-photon absorption, the absorption coefficient is much lower for multi-photon absorption which increases nonlinearly with the increase the excitation intensity [91]. As a result, pulsed lasers, especially femtosecond lasers, which can provide extremely high transient intensities on the order of GWcm^{-2} , are used as the excitation source. In this dissertation, a femtosecond amplified-pulsed laser system providing laser pulses with pulsewidth of 100 fs and repetition rate of 1000 Hz, whose output wavelength could be tuned from 260 nm to 2600 nm, is employed as the excitation source for multi-photon absorption and emission measurements.

Figure 2.2 The experimental setup for the measurements of one- and multi-photon photoluminescence.

2.2.3 Z-scan technique

Z-scan technique represents an advanced and powerful tool for the measurement of the multi-photon absorption, which is invented by Sheik-Bahae *et al.* in 1990 [92]. Due to the simplicity in operation, the Z-scan measurements have been widely adopted in the characterization of nonlinear optical properties of various materials, such as molecules, semiconductors and metals [93-95]. In general, Z-scan technique can be divided into two classes in view of the applications, namely, the open aperture Z-scan, which is applied to detect the multi-photon absorption including two-, three- and even high order-nonlinear absorption, and the closed aperture Z-scan, which is applied to detect the nonlinear refraction properties of materials [92].

In case of open aperture Z-scan, as schematically portrayed in Figure 2.3, the laser beam is focused by an optical lens, thus the intensity in axis of the laser propagating direction is position dependent, where the intensity at the focus plane is the highest. As elaborated above, the nonlinear absorption is sensitively related to the input intensity. Therefore, if we make the targeted sample travel along the laser propagating axis and experience the varied input intensities, we can get a position-dependent transmitted signal, from which the multi-photon absorption coefficients and corresponding cross-section if the concentration is known could be extracted [92, 96]. The detailed mathematical deviation is given as follows. Under the condition that the linear absorption is negligible and that only two-photon absorption is considered, the extinction of light is described by [97, 98]:

$$\frac{dF}{dz} = -\beta F^2 \Rightarrow \int \frac{dF}{F^2} = - \int \beta dz \Rightarrow F_z = \frac{F_0}{1 + \beta F_0 z}$$

where β denotes the two-photon absorption coefficient, and F is the number of photons per unit time and area, which is given by:

$$F_{(r;t)} = F_{0(r=0;t=0)} \frac{w_0^2}{w_z^2} e^{-2r^2/w_z^2} e^{-t^2/\tau^2}$$

The pulse energy before passing through the targeted sample is given by:

$$E = E_{ph} \int_0^\infty F_{0(r=0;t=0)} e^{-2r^2/w_0^2} 2\pi r dr \int_0^\infty e^{-t^2/\tau^2} dt = E_{ph} F_{0(r=0;t=0)} \frac{\pi \sqrt{\pi} w_0^2 \tau}{2}$$

And the pulse energy after penetrating through the sample is derived as followed:

$$\begin{aligned} E_z &= E_{ph} \int_0^\infty 2\pi r dr \frac{F_{z(r;t)}}{1 + \beta F_{z(r;t)}} \int_0^\infty dt \\ &= E_{ph} \int_0^\infty dt \int_0^\infty 2\pi r dr \frac{F_{0(r=0;t=0)} \frac{w_0^2}{w_z^2} e^{-2r^2/w_z^2} e^{-t^2/\tau^2}}{1 + \beta F_{0(r=0;t=0)} \frac{w_0^2}{w_z^2} e^{-2r^2/w_z^2} e^{-t^2/\tau^2}} \\ &= E_{ph} \frac{\pi w_z^2}{2\beta L} \int_0^\infty \ln \left(1 + \frac{q_0 e^{-t^2/\tau^2}}{1 + (z/z_0)^2} \right) \end{aligned}$$

where q_0 is given by:

$$q_0 = \beta L F_{0(r=0;t=0)}$$

At last, the transmittance is defined as the ratio of pulse energy E_z after transmitting the sample and the pulse energy E before passing through the sample:

$$T = \frac{E_z}{E} = \frac{E_{ph} \frac{\pi w_z^2}{2\beta L} \int_0^\infty \ln \left(1 + \frac{q_0 e^{-t^2/\tau^2}}{1 + (z/z_0)^2} \right)}{E_{ph} F_{0(r=0;t=0)} \frac{\pi \sqrt{\pi} w_0^2 \tau}{2}} = \frac{\int_0^\infty \ln \left(1 + \frac{q_0 e^{-t^2/\tau^2}}{1 + (z/z_0)^2} \right)}{\sqrt{\pi} \tau \frac{q_0}{1 + (z/z_0)^2}}$$

Under the condition that $\frac{q_0}{1+(z/z_0)^2} < 1$, the transmittance can be further simplified

based on Taylor series [92]:

$$T = \sum_{m=0}^{\infty} \frac{\left(-\frac{q_0}{1 + \left(\frac{z}{z_0} \right)^2} \right)^m}{(1+m)^{\frac{3}{2}}}$$

Similarly, the three-photon absorption and even more photon-absorption coefficient can be extracted by a parallel approach.

In case of closed aperture Z-scan, the only difference in the setup compared to the open aperture Z-scan is that an additional aperture, which allow only part of the laser beam go into the detector, is placed before the detector, and that is the origin of their names [99]. The working principle is that the nonlinear sample will act as a focus or defocus lens for the laser beam, which changes the size of the laser beam at the aperture position [92]. Therefore, the variation of the laser pulse energy transmitted through the targeted sample will be contributed by nonlinear absorption and the distorted light beam by lens effect. When the nonlinear absorption is negligible or, otherwise, eliminate it from the closed aperture Z-scan signal, the nonlinear refraction coefficient can be extracted.

Figure 2.3 The experimental setup for the measurements of open and close aperture Z-scan.

2.2.4 Time-resolved photoluminescence

Time-resolved photoluminescence (TRPL) represents a spectroscopic method to access the dynamics of the emission [84]. In this thesis, streak camera, which can measure the transition energy or the emission wavelength and the corresponding lifetimes at the same time, from Optronis is employed for the TRPL measurements. The operating principle of the streak camera is schematically portrayed in Figure 2.4. Specifically, optical pulses go through the slit at different time and different position (corresponding to wavelength) and hit onto the photocathode, where electrons whose number is in proportion to the optical pulse intensity are generated. Then, the electrons will pass through a pair of sweep electrodes and the high voltage of the sweep electrode is synchronized to the incident optical pulse with the help of the trigger signal. As a result, the electrons entering the sweep electrode at different time will experience a different degree of deflection, thus hitting at the detector, the micro-channel plate, at different position in vertical direction. Eventually, the wavelength and timeline of the optical pulses manifest themselves at different positions in horizontal and vertical direction on the phosphor screen, respectively.

Figure 2.4 Working principle of streak camera (adopted from Hamamatsu).

2.2.5 Transient absorption: pump-probe technique

Transient absorption is investigated by the femtosecond pump-probe measurement

which is an advanced technique to explore the ultrafast information including the dynamics of carrier recombination, excited state absorption, saturable absorption and stimulated emission or optical gain upon photo-excitation [100, 101]. In the pump-probe measurement, a femtosecond optical pulse hits the targeted sample and generates some excited carriers in the sample, which is known as the pump pulse. Then, a subsequent optical pulse whose time delay is adjustable by a movable stage will pass through the sample and experience the induced changes in the sample, which is known as the probe pulse. By monitoring the change of probe pulse versus the time delay, the information on the decay of optical processes activated by the pump pulses, such as the carrier recombination, excited state absorption, saturable absorption and stimulated emission can be obtained. When the transmission of the probe pulse is detected, the differential transmittance and its relationship with transient absorption are given by [34]:

$$\frac{\Delta T}{T_0} = \frac{T_t - T_0}{T_0} = 10^{-\Delta A} - 1$$

where T_0 is the linear transmittance without pump and T_t is the transient transmittance at time delay of t with respect to the pump pulse. Figure 2.5 displays the schematic setup used in this thesis for pump-probe measurements. In our system, the pump pulse at optical wavelength of 400 nm is generated by second-harmonic generation of the fundamental pulse (800 nm, 100 fs, 1 KHz) from the titanium-sapphire regenerative amplifier system, and the probe pulse is provided by an optical parameter amplifier seeded by the remaining part of the fundamental pulse (800 nm, 100 fs, 1 KHz) from the titanium-sapphire regenerative amplifier system.

For the signal collection, a Silicon-based photodiode is employed equipped with the standard lock-in technique.

Figure 2.5 Schematic setup used for the pump-probe measurements

Chapter 3

One- and two-photon absorption and photoluminescence from InP/ZnS Quantum dots

3.1 Introduction

As a result of the tunable emission with high photoluminescence quantum yield (PL QY), high photostability, narrow emission linewidth and the broadband absorption spectra enabling the multi-color emission by single wavelength excitation, CQDs are intrinsically better fluorescent probes than commonly used dyes which have relatively narrow absorption band, broad emission linewidth and poor photostability [102, 103]. In field of biophotonics, such as bioimaging and bisensing, it is well-known that the two-photon excitation is strongly desired thanks to the deep penetration depth, low damage to the tissue and cells, high signal-to-noise ratio, better spatial resolution and isolation of excitation wavelength away from the emission wavelength [104, 105]. The most commonly used CQDs probes in two-photon bioimaging and biosensing are CdSe, CdS and CdTe [95, 102, 106], which contain toxic heavy-metal Cadmium, posing threats to their practical applications in biology. In contrast, Indium Phosphide (InP) CQDs are able to show similar optical properties to those of CdSe CQDs [107, 108], such as the continuously tunable emission wavelength across the full visible range, but possessing no hazard to tissues or cells due to the sturdiness of the bonding existing in III-V group semiconductors instead of the weak bond in the II-VI counterparts [109, 110], thus no toxic ions will leak out. However, to date, the optical

studies of InP CQDs are limited within the linear part, and reports on the nonlinear optical properties of InP CQDs are void [108, 110]. The reason lies in the lacking of high-quality InP CQDs because of the challenges in the synthesis arising from the much stronger coordinating strength of indium ligands than that of cadmium ligands [108]. In fact, the previously fabricated InP CQDs always suffers from the broad size distribution, broad emission linewidth and low emission QY. Very recently, Xuyong Yang *et al.* successfully produced high-quality InP/ZnS core/shell CQDs with a narrow size distribution and high emission QY comparable to CdSe CQDs using one-pot solvo-thermal method by employing noncoordinating solvent and capping InP with ZnS shell of optimized thickness [108], which provide a platform for the comprehensive optical study, especially the unexplored nonlinear optical properties, of environmental-friendly InP/ZnS CQDs. The InP/ZnS CQDs are found to show strong emission based on two-photon absorption even at relatively low excitation intensities. The two-photon absorption cross-section is measured to be as large as 6.2×10^3 GM at 800 nm for InP/ZnS CQDs, which is comparable or even higher than those of conventional Cd-contained CQDs with similar sizes. In addition, strong saturable absorption is observed under femtosecond excitation, which is ascribed to high exciton Bohr radius of InP [111]. The results suggest that the heavy-metal free InP/ZnS CQDs are not only very promising fluorescent probes for biological research and applications, but also hold great potential in saturable absorption related fields, such as the passive mode-locking.

3.2 Sample fabrication

The samples were provided by our collaborators. For the typical synthesis procedure of the high-quality InP/ZnS core/shell CQDs adopted in the thesis, indium myristate ($\text{In}(\text{MA})_3$) (0.3 mmol), tris(trimethylsilyl) phosphine ($\text{P}(\text{TMS})_3$) (0.3 mmol) and 1-octadecene (ODE) (3 mL) were mingled under nitrogen condition. Subsequently, the solution will transform from colorless to yellow by naked eye, which indicates the nucleation of InP nanocrystals. Then, the solution of the fabricated InP nuclei nanocrystals was introduced into a flask (50 mL) with three-neck. After that, zinc stearate (Zn-St_2) (0.3 mmol) and ODE (21 mL) were injected into the reaction mixture. Then, the temperature was increased to 260–300 °C rapidly by heating under Argon atmosphere, during which strong agitation was carried on. Finally, the temperature of the solution stays fixed for certain period of time (10–30 min), which allows the growth of InP cores. After this stage, the temperature of the solution of InP-core was decreased to 60 °C and 1-dodecanethiol (DDT) (0.3 mmol) or sulfur (S) powder was put into the cooled solution, after which the temperature of the solution was increased again to 300 °C and fixed for 10 min. Subsequently, the solution was cooled and zinc diethyldithiocarbamate ($\text{Zn}(\text{DDTC})_2$) (54 mg) and ODE (3mL) was injected into the solution for the growth of the ZnS shell. Then, the temperature of the reaction solution was increased to 220–230 °C and kept for 20 min. Finally, the InP/ZnS CQDs are obtained. Purification process was also performed to remove the remained chemicals. To do so, a mixture (3 mL) of chloroform /ethanol (volume ratio of 2:1) and an excess volume of acetone were introduced, then, the whole solution was centrifugated. This process was repeated for three times to fully clean the sample. Finally, the precipitated

InP/ZnS CQDs were dissolved in toluene for later use.

3.3 Linear absorption and emission

Figure 3.1 shows the one-photon induced photoluminescence (PL) excited at 441 nm of two different-sized InP/ZnS QDs at room temperature, where a continuous He-Cd laser was exploited as the light source. From now on, we denote the two different-sized InP/ZnS CQDs as CQD606 and CQD548, respectively, according to their emission peaks for simplicity. The corresponding UV-visible absorption spectra are also presented in Figure 3.1 as indicated by the arrows, from which the diameters of QD606 and QD548 are determined to be 2.8 nm and 2.2 nm, respectively, based on the positions of their first exciton absorption peaks [110, 112]. It is found that the emission linewidths are quite narrow and the first excitonic absorption peaks are clear, which indicate that the InP/ZnS CQDs adopted here are quite uniform or have a narrow size distribution [108]. The insets in figure 3.1 show the corresponding transmission electron microscopy (TEM) images, which validate the high quality of the nanocrystals. The PL QY were measured to be 58% and 39% for QD548 and QD606, respectively, compared to Rhodamine 6G in ethanol with assured QY of 95% using the formula [113]:

$$QY_{sample} = QY_{ref} \left(\frac{F_{sample}}{F_{ref}} \right) \left(\frac{A_{ref}}{A_{sample}} \right) \left(\frac{n_{sample}^2}{n_{ref}^2} \right)$$

where F_{sample} , F_{ref} , A_{sample} , A_{ref} , n_{sample} and n_{ref} are the integrated intensity of the measured fluorescence, the absorbance at the excitation wavelength, and the refractive index and reference dye (Rhodamine 6G in our case), respectively.

Figure 3.1 Linear absorption and emission spectra of QD606 and QD548. The corresponding TEM images are presented as the insets.

3.4 Two-photon absorption and emission

To investigate the two-photon absorption and emission properties of our high-quality InP/ZnS core/shell CQDs, the wavelength of 800 nm, a widely used wavelength for the bioimaging and biosensing applications [102, 109], is chosen as the excitation wavelength. Figure 3.2 (a) shows the PL spectra of QD548 and QD606 and the PL images are also presented as the insets. To confirm the two-photon absorption and emission process under excitation wavelength of 800 nm, power dependent PL measurements at 800 nm was carried out [114]. Figure 3.2 (b) displays the PL intensity of QD548 and QD606 versus the excitation intensity at 800 nm in log-log scale, which can be well-fitted by linear function with slope of 1.93 and 2.03, respectively. The nearly quadratic relationship between the PL intensity and the

excitation intensity unambiguously indicates the two photon absorption process under excitation wavelength of 800 nm [94, 115]. Notably, the two-photon induced PL spectra of QD548 and QD606 are found to be almost the same as the corresponding PL spectra under one-photon excitation. This phenomenon suggests that the hot carriers induced by both single- and two-photon absorption cool down to the same lowest state, where the radiative recombination or emission take places [115]. This whole process from excitation to cooling and finally radiative recombination is schematically portrayed in Figure 3.2 (c).

Figure 3.2 (a) Two-photon excited PL spectra from QD548 and QD606 under excitation wavelength of 800 nm, the insets display the corresponding PL images under excitation wavelength of 800 nm. (b) Power dependent PL intensity, confirming the two-photon absorption and emission process. (c) The schematic diagram showing the emission processes based on one and two photon absorption in these QDs.

In view of two-photon related applications, such as the two-photon bioimaging, the two-photon absorption cross-section is a key parameter to characterize the CQDs as fluorescent probes [102, 116]. High two-photon absorption cross-section is always

desired in order to decrease the incident laser intensity as much as possible. However, the two-photon absorption cross-section of InP/ZnS CQDs has not yet been explored, which is the motivation for this work. To this goal, single beam Z-scan method is exploited to measure the two-photon absorption cross-sections of the high-quality InP/ZnS CQDs [92]. Before the measurements, the authority of the Z-scan system is checked by calibration measurements on liquid carbon disulfide (CS_2) whose third-order nonlinearity is well-known [117]. As the laser source, an amplified-pulsed laser (pulse-width: 100 fs, repetition rate: 1 KHz) was employed so that the thermal effects can be neglected. From our measurements, the nonlinear refractive coefficient is determined to be $3.5 \times 10^{-6} \text{ cm}^2/\text{GW}$, which is consistent with the results in literature measured under similar conditions, thus confirming the authority of the Z-scan system [93, 117]. Figure 3.3 displays the open aperture Z-scan results of QD548 and QD606, and the curves are shifted in y-axis for clarity. To ensure that the nonlinear absorption signals totally arise from InP/ZnS CQDs, the excitation intensity is kept as low as $45 \text{ GW}/\text{cm}^2$. The response curve of pure solvent shows a nearly horizontal line, which indicates the nonlinear absorption of the solvent at this intensity is negligible, thus confirming the signals are completely attributed to the InP/ZnS CQDs [118]. The normalized transmittance of QD606 and QD548 can be well-fitted according to Z-scan theory by theoretical formula [92]:

$$T_{OA}(z) = \pi^{-1/2} q_0 \int_{-\infty}^{\infty} \ln(1 + q_0 \exp(-x^2)) dx$$

where $q_0 = \beta I_0 L_{eff}$, β denotes the two-photon absorption index and $L_{eff} = (1 - \exp(-\alpha_0 L))/\alpha_0$, α_0 is the linear absorption index and $L = 1 \text{ mm}$ is the length of the

cuvette used in the measurements, and $I_0 = I/(1 + z^2/z_0^2)$, where I is the peak power intensity along the laser propagation axis and $z_0 = \pi\omega^2/\lambda$ is referred as the Rayleigh range. The best-fit of the curves extracts the two-photon absorption coefficients of QD606 and QD548 to be 0.012 cm/GW and 0.009 cm/GW, respectively. Based on the known two photon absorption coefficients, together with the concentration of the CQDs, the two photon absorption cross-sections (σ_2) of QD606 and QD548 can be derived by [95, 96]:

$$\sigma_2 = \beta \hbar \gamma / N$$

where $\hbar \gamma$ represent the energy of the photon and N is the concentration of the CQD solution, Here, N is determined to be $4.8 \times 10^{19}/\text{L}$ and $6.6 \times 10^{19}/\text{L}$ for QD606 and QD548, respectively, based on the reported empirical relationship between the first excitonic absorption peak values molar extinction coefficients and the corresponding sizes. As a result, the σ_2 of QD606 and QD548 are calculated to be $6.2 \times 10^{-47} \text{ cm}^4 \text{ s photon}^{-1}$, corresponding to $6.2 \times 10^3 \text{ GM}$, and $3.5 \times 10^{-47} \text{ cm}^4 \text{ s photon}^{-1}$, corresponding to $3.5 \times 10^3 \text{ GM}$, respectively. These values are comparable or even higher than those of the similar-sized CdSe ($5.1 \times 10^3 \text{ GM}$) [106, 114], CdTe ($2.1 \times 10^2 \text{ GM}$) [119] and CdS ($4.4 \times 10^3 \text{ GM}$) [95] CQDs, thus suggesting that the high-quality InP/ZnS core/shell CQDs are extremely promising fluorescent probes in two-photon related applications. It is noteworthy that the relationship between the two-photon absorption cross-section and the dot size is complex. For example, the two-photon absorption cross-sections of CdSe and CdS CQDs were found to increase with the increasing of dot size [95, 116], while those for ZnS and ZnSe

CQDs have opposite dependence on size [96]. The complexity of the relationship between the two-photon absorption cross-section and the dot size comes from the interplay between the increased density of state and the reduced quantum confinement effect as the sizes of the CQDs increase [112, 120]. As for the InP/ZnS CQDs, the two-photon absorption cross-section of QD606 with larger size is measured to be higher than the small-sized QD548, which suggests that the increased density of state dominates over the decreased quantum confinement effect in InP/ZnS core/shell CQDs. In addition, the intrinsic two-photon absorption coefficients (β^{QD}) of QD548 and QD606 are extracted to be 516.9 cm/GW and 487.3 cm/GW, respectively, by considering the local field effect and the volume fraction based on the formula [111, 116]:

$$\beta^{QD} = \beta / (f^4 V_f)$$

where $f = 3\varepsilon_s / (\varepsilon_{QD} + 2\varepsilon_s)$ denotes the local-field factor, ε_{QD} is the dielectric constant of InP/ZnS QDs and ε_s denotes the dielectric constant of solvent, in which ε_{QD} are calculated to be 9.72 and 9.92 for QD548 and QD606 [111], respectively, V_f denotes the volume fraction of CQDs relative to solvent. The much increased intrinsic two-photon absorption coefficients of InP/ZnS CQDs with respect to the that of bulk InP crystal is ascribed to the boosted oscillator strength by quantum confinement effect [121], which is further confirmed by the increased intrinsic two-photon absorption coefficient of smaller-sized QD548 compared to that of bigger-sized QD606.

Figure 3.3 Open-aperture Z-scan responses of QD606, QD548 and the pure solvent under input wavelength of 800 nm. The solid curves are the best-fitting traces according to the Z-scan theory.

To comprehensively study the third-order nonlinearity of InP/ZnS CQDs, the near resonant third-order nonlinearity of InP/ZnS CQDs, where the input optical wavelengths locate within the absorption band, are explored at optical wavelength of 527 nm. Figure 3.4 (a) shows the typical open aperture Z-scan response of QD548 and QD606 under excitation intensity of 5.5 GW/cm². We can see that the transmittances reach the maximum at focus plane, which means that less light is absorbed when the input intensity increases, indicating the occurrence of saturable absorption [122]. The emergence of saturable absorption in InP/ZnS CQDs is mainly attributed to two reasons: 1) when the input intensity is very high, the ground state carriers will be depleted, thus reducing the transition probability. 2) as most of the

ground state carriers are pumped onto the excited states, the excited state will become almost occupied [10]. Consequently, the Pauli exclusion principle will come into play, which also reduces the possibility of optical transitions. According to the Z-scan theory [92], the nonlinear absorption coefficient (α_2) can be extracted. From the best-fit of the normalized transmittances, α_2 is derived to be -1.93 cm/GW, corresponding to $\text{Im } \chi_{(3)} = -28.01 \times 10^{-13}$ esu, and -0.59 cm/GW, corresponding to $\text{Im } \chi_{(3)} = -9.17 \times 10^{-13}$ esu for QD606 and QD548, respectively. Noticeably, the figure of merit (FOM) of $|\text{Im } \chi^{(3)} / \alpha_0|$ was introduced by Schrof *et al.* in order to better characterize the saturable absorption property [118]. In our case, the FOM of QD606 and QD548 are determined to be 11.3×10^{-14} esu cm and 8.0×10^{-14} esu cm, respectively, which are even high than the gold nanoparticles (3×10^{-14} esu cm) determined at the surface plasmon resonance [118]. The saturation intensities (I_s), an important parameter for saturable absorbers, of QD606 and QD548 are also measured in order to check the possibility of InP/ZnS CQDs as a saturable absorber [122]. To do so, the input intensity dependent Z-scan measurements were performed. In particular, we tuned the excitation intensity from 3.3 GW/cm^2 to 37.5 GW/cm^2 . Figure 3.4 (b) illustrates the normalized transmittance change ($\Delta T/T_0$) with respect to the input intensity, where T_0 denotes the linear transmittance. It is found that $\Delta T/T_0$ saturates when the input intensities keep increasing. This is a typical phenomenon for a saturable absorber, for example, semiconducting single-walled carbon nanotubes is found to undergo similar phenomena by Ostojic *et al* [122]. In addition, the natural logarithm of transmittance T with respect to excitation intensity I_0 is presented in

Figure 3.4 (c). The saturation intensities of QD606 and QD548 can be obtained by fitting the data using formula [123]:

$$LnT = -\alpha_0 L / (1 + I / I_s)$$

where $\alpha_0 / (1 + I / I_s)$ represents the absorption coefficient at varying excitation intensities. From the best-fitting of the data, the saturation intensities of QD606 and QD548 are derived to be 10.9 GW/cm² and 19.8 GW/cm², respectively, which are only a little higher than that of semiconducting single-walled carbon nanotubes (~7 GW/cm²) [122], an excellent saturable absorber, thus suggesting that the InP/ZnS CQDs hold great potential as saturable absorber. The good saturable absorption properties of InP/ZnS CQDs could be attributed to the large exciton Bohr radius (α_{ex}) (15 nm) of InP [120]. Based on the reported theoretical analysis, the absorption change $\Delta\alpha$ of CQDs in near resonant region is only in proportion to the cubic of the exciton Bohr radius under the condition that the size of the CQDs and input intensity are constant [120]:

$$\Delta\alpha = 24\pi 10^{13} \alpha_{ex}^3 I / (c^2 R^3 \text{Im } \tilde{\chi}_3)$$

where R is the CQD radius and $\tilde{\chi}_3$ is a material-independent constant, representing the normalized third-order susceptibility. As is known that InP/ZnS CQDs possess a large exciton Bohr radius of ~15 nm, which is much higher than those of CdSe (~5 nm) and CdTe (~7 nm) CQDs [26], indicating strong third-order nonlinearity in InP/ZnS CQDs, which accounts for the superior saturable absorption properties of InP/ZnS CQDs.

Figure 3.4 (a) Saturable absorption of QD548 and QD606 under excitation wavelength of 527 nm. The solid curves are the best-fitting traces based on the Z-scan theory. (b) Normalized transmittance with respect to excitation intensity for QD548 and QD606. (c) Transmittance at the focus plane versus the excitation intensity.

Finally, the nonlinear refraction of InP/ZnS CQDs was measured using the closed aperture Z-scan technique. However, the determination of nonlinear refraction is complicated by the strong two-photon absorption in InP/ZnS CQDs. To avoid the influence of nonlinear absorption on the nonlinear refraction, the open aperture Z-scan measurements were also conducted. Through dividing the closed aperture result (CA)

by the open aperture result (OA) measured at the same input intensity, the nearly centrosymmetric curves are obtained, indicating the elimination of two-photon absorption effect [92]. Figure 3.5 shows the CA/OA curves of QD606, QD548 and the solvent (toluene). It is found that the divergence of the peak from the valley is decreased for InP/ZnS CQDs solution compared to that of the pure solvent, which indicates the opposite signs of the nonlinear refraction between the solvent and the InP/ZnS CQDs. The valley-followed-by-a-peak shape of the pure solvent indicates the positive nonlinear refraction of toluene or negative nonlinear refraction for InP/ZnS CQDs [92, 121]. Furthermore, the value of the nonlinear refraction index can be derived based on Z-scan theory using formula [92]:

$$T = 1 - \frac{4\Delta\Phi_0 \frac{z}{z_0}}{\left(\left(\frac{z}{z_0}\right)^2 + 9\right)\left(\left(\frac{z}{z_0}\right)^2 + 1\right)}$$

where $\Delta\Phi = kn_2I_0L_{eff}$ represents the nonlinear phase change. From the best-fitting results of the experimental data, the nonlinear refractive coefficients are extracted to be $1.3 \times 10^{-6} \text{ cm}^2/\text{GW}$, $-0.71 \times 10^{-6} \text{ cm}^2/\text{GW}$ and $-0.57 \times 10^{-6} \text{ cm}^2/\text{GW}$ for toluene, QD606 and QD548, respectively. If the local field effect and the volume fraction are considered, the intrinsic nonlinear refraction (n_2^{QD}) of InP/ZnS CQDs can be calculated by [119]:

$$n_2^{QD} = \left(n_2 - (1 - V_f)n_2^{sol} \right) / (f^4 V_f)$$

As a result, the intrinsic nonlinear refractions of QD606 and QD548 are derived to be $-2.9 \times 10^{-2} \text{ cm}^2/\text{GW}$ and $-3.1 \times 10^{-2} \text{ cm}^2/\text{GW}$, respectively. Both of these values are much higher than that of bulk InP counterpart [124], which stems from the enhanced

two-photon absorption in InP/ZnS CQDs since the third-order nonlinear refraction far from the resonant region are mainly contributed by the two-photon absorption term [92].

Figure 3.5 Closed-aperture responses divided by the open aperture responses of QD548, QD606 and the pure solvent. The dash lines are the fitting curves based on Z-scan theory.

3.5 Summary

We have comprehensively investigated the nonlinear optical properties of high-quality InP/ZnS CQDs. The large two-photon absorption cross-sections and high PL QY suggest the heavy-metal-free InP/ZnS CQDs are promising fluorescent probes for various applications including bioimaging and bisensing. In addition, we revealed that the InP/ZnS CQDs exhibit superior saturable absorption properties, thus holding great potential as excellent saturable absorbers. These results show that the InP/ZnS CQDs

could be ideal alternatives to the conventional but toxic CdSe-based CQDs.

Chapter 4

Three-photon excited stimulated emission and lasing from solid film of CdSe/CdS/ZnS core/shell/shell quantum dots

4.1 Introduction

In last chapter, we have comprehensively studied the multi-photon absorption and emission properties of the heavy metal-free InP/ZnS CQDs. However, the fabrication of high-quality InP/ZnS CQDs are still challenging. For example, the emission quantum yield (QY) of InP/ZnS CQDs stays still relatively low compared to that of the canonical CdSe-based CQDs, despite that much progress in synthesis of high-quality InP/ZnS CQDs has been made. In addition, the photo- and chemical-stability of InP/ZnS CQDs are not as good as that for CdSe-based CQDs due to the easy oxidation. Consequently, it is extremely tough to achieve stimulated emission from InP/ZnS CQDs, especially, via multi-photon pumping [107]. As a result, in order to achieve stimulated emission and lasing, we turn our attention to the much more mature CdSe-based CQDs, which are the most studied CQDs and high-quality CdSe-based CQDs with emission QY as high as ~100% can be easily fabricated based on reported recipes in literature. Unsurprisingly, the first demonstration of stimulated emission from CQDs was from the very CdSe CQDs by Klimov *et al.* in year of 2000 [9]. From then on, the research on the optical gain and lasing properties of CQDs has long been a hot research spot [6, 34, 107].

However, most of the stimulated emission and lasing demonstrations from CQDs

are based on one-photon absorption [6, 9, 42], which limits their applications to a great extent due to the low spatial resolution and relatively short penetration depth [105, 125, 126]. For example, it is known that the surface of a various of gain materials tends to be contaminated, which will influence their lasing performance under one-photon excitation [105]. Moreover, sometimes, only selected part or interested area is anticipated to be excited, which is difficult to be achieved by one-photon excitation [49]. On the other hand, multi-photon pumping has attracted increasing attention by virtue of fundamental interests and their unique advantages [77, 127]. Particularly, the typically long excitation wavelengths in near-infrared or infrared range for multi-photon pumping render much deeper penetration depth, and the high order dependence of the absorption and emission on the input intensity enables much better spational resolution by only effectively exciting the samples in the middle of the focus point. Indeed, the employment of two-photon pumping has demonstrated a boosted penetration depth and higher spatial resolution compared to one-photon counterpart [105, 128, 129]. Naturally, the performance based on the even higher nonlinear pumping with even longer excitation wavelengths using three-photon absorption (3PA) is expected to be further improved [77, 91]. Besides, refering to the field of biology and biophotonics including bioimaging and biosensing, deep penetration depth, large isolation of the excitation wavelength from the emission wavelength and minimized damage to the tissues are strongly desired, which can be simutaneously satisfied by using long pump wavelengths and high-order nonliear absorption. For instance, the exploitation of two-photon absorption has successfully prolonged the penetration depth

into the tissues as deep as a few hundreds of micrometers [77, 126]. However, as the rapidly increased requirements in biophotonics, even larger penetration depths of up to several millimeters are required, which can be realized by means of three-photon excitation [126, 130].

Stimulated emission via 3PA was first observed from organic dyes in solution [131]. Nevertheless, the poor photostability of organic dyes hinders the long-term operation and makes it extremely challenging to develop 3PA induced stimulated emission in solid state, which greatly limits their practical applications. However, although stimulated emission and lasing have been demonstrated from a variety of CQDs based on one-photon pumping, the multi-photon induced stimulated emission or lasing from CQDs is still difficult due to the greatly reduced multi-photon absorption cross-section with respect to one-photon counterpart and the insufficient robustness of CQDs to bear the typically high pumping intensity [125, 132]. Up till now, only a few reports have developed two-photon induced stimulated emission and lasing from CQDs [49, 129, 132, 133]. However, three-photon excited stimulated emission or lasing action from CQDs have not yet been achieved, despite that the demonstration of stimulated emission and lasing from CQDs could certainly offer new possibilities in a wide range of fields, such as biology and photonics. Here, we rationally engineered the CdSe/CdS/ZnS core/shell/shell (CSS) CQDs aiming at suppressing the nonradiative Auger recombination and enhancing the 3PA and photostability, and finally, for the first time, developed stimulated emission and coherent random lasing by simultaneous 3PA from these CQDs.

4.2 Sample fabrication

The samples were provided by our collaborators. For the fabrication of CdSe/CdS/ZnS CSS CQDs, the facile one-pot method is adopted [134, 135]. As a contrast test, CdSe/CdS core/shell (CS) CQDs are also fabricated. Specifically, cadmium oxide (CdO, 99.99 %) (1 mmol) and zinc acetate ($\text{Zn}(\text{acet})_2$, 99.9 %) (2 mmol) was mingled with oleic acid (OA) (18.85 mmol) in a flask (100 mL), which was evacuated and heated to 150 °C. Then, 1-octadecene (1-ODE) (25 mL) was injected into the flask. Subsequently, the temperature of the mixed solution was increased to 300 °C by heating under nitrogen gas condition and transparent solution of $\text{Zn}(\text{OA})_2$ and $\text{Cd}(\text{OA})_2$ is obtained. Then, selenium powder (Se) (0.2 mmol) was dissolved into trioctylphosphine (TOP, 0.2 mmol), serving as the Se precursor, and the solution was rapidly added into the flask at high temperature of 300 °C to react with $\text{Cd}(\text{OA})_2$. Around three minutes later, dodecanethiol (DT) (0.3 mL) was slowly added into the reaction mixture, and the reaction was kept for 20 minutes so as to get the CdSe/CdS CS CQDs. After that, sulfur powder (2 mmol) was dissolved into TOP (1 mmol), and the S-solution was quickly injected into the CdSe/CdS CS CQDs solution to consume the excess Cd ions and react with Zn-precursors to form the ZnS shell, thus further passivating the CdSe/CdS CS CQDs. Finally, the CdSe/CdS/ZnS CSS CQDs were obtained. The CdSe/CdS CS CQDs and CdSe/CdS/ZnS CSS CQDs were washed by methanol for several times and finally dispersed in toluene for later use.

4.3 Linear absorption and emission

Figure 4.1 shows the linear steady state absorption and emission spectra of CdSe/CdS

CS CQDs and CdSe/CdS/ZnS CSS CQDs at room temperature. From the fabrication process, the CdS-layer in CdSe/CdS/ZnS CSS CQDs is anticipated to be thicker than that in CdSe/CdS CS CQDs due to the second growth of CdS during the formation of ZnS shell, which is further validated by the absorption measurements. In the absorption spectra, there is obvious extra absorption of CdSe/CdS/ZnS CSS CQDs compared to that of CdSe/CdS CS CQDs at short spectral range from ~500 nm, and this extra absorption just stems from the thicker CdS-layer [40, 49]. The three lowest exciton transitions of the samples, corresponding to $1S_{\text{e}}-1S_{3/2\text{h}}$, $1S_{\text{e}}-2S_{3/2\text{h}}$ and $1P_{\text{e}}-1P_{3/2\text{h}}$, respectively, are finely identified [17, 32], which suggests the high quality of the samples. In addition, the PL linewidth of the samples are both ~30 nm, indicating the good uniformity in size distribution. It is worth mentioning that there are mainly two criterions for the choice of shells to passivate CdSe-core: small lattice mismatch between the shell material and CdSe-core and large conduction band offset and valence band offset compared to those of CdSe-core [136, 137]. CdS-shell is known to own similar lattice parameters to CdSe-core (lattice mismatch of ~3.9%) [136, 138], satisfying the first criterion. However, the small band offsets, especially for the conduction band, cannot provide favorable electronic passivation. To solve this problem, additional ZnS-shell with much higher conduction band and valence band offsets are introduced to fully passivate and protect the CdSe-core in this work. The PL QY measurements reveal a nearly one-fold increase of the PL QY of CdSe/CdS/ZnS CSS CQDs (70%) with respect to that of CdSe/CdS CS CQDs (40%) based on the same method used for InP/ZnS CQDs in Chapter 3, confirming the better

surface passivation by CdS/ZnS-multi-shell than that by CdS-shell. The TEM images are displayed as the insets in Figure 4.1, which show good monodispersity of the samples and the sizes of the CdSe/CdS CS QDs and CdSe/CdS/ZnS CSS QDs are determined to be ~4.96 nm and ~6.57 nm, respectively.

Figure 4.1 The linear absorption and emission spectra of CdSe/CdS CS QDs and CdSe/CdS/ZnS CSS QDs at room temperature. The corresponding TEM images are presented as the insets.

4.4 Three-photon absorption characterization

The three-photon absorption properties of CdSe/CdS CS QDs and CdSe/CdS/ZnS

CSS CQDs were studied by performing open-aperture Z-scan measurements [92]. Before the investigation on the samples, the Z-scan system was carefully calibrated, as was done in InP/ZnS CQDs measurements. A femosecond amplified-pulsed laser delivering optical pulse with wavelength of 1300 nm, pulsewidth of 100 fs and repetition rate of 1000Hz was employed as the laser source. Different from the two-photon absorption measurement at 800 nm for InP/ZnS CQDs, the Si-biased detector was replaced by the near-infrared Ge-biased detector, and the standard lock-in technique was utilized (See Figure 4.2). In doing Z-scan measurements of the samples, CdSe/CdS CS CQDs and CdSe/CdS/ZnS CSS CQDs with concentrations of 2.6×10^{20} CQDs/L and 2.3×10^{20} CQDs/L, respectively, were stored in 1-mm-thick cuvettes, which would move back and forth around the focus plane controlled by the step motor. The Z-scan response curves of the sample are shown in Figure 4.3. To confirm the singals are totally from the sample, the response of pure solvent, toluene, was also recorded at the same input intensity. The nearly flat open aperture Z-scan curve of the solvent verifies that the nonlinear absorption singals completely come from the CdSe/CdS CS CQDs and CdSe/CdS/ZnS CSS CQDs. The three-photon absorption coefficients of the samples can be obtained by fitting the data based on Z-scan theory using the formula [139]:

$$T = \pi^{-1/2} p_0^{-1} \exp(-\alpha_0 L) \int_{-\infty}^{\infty} \ln \left\{ 1 + p_0^2 \exp(-2x^2) \right\}^{1/2} + p_0 \exp(-x^2) dx$$

where $p_0 = (2\gamma I_0^2 L_{eff})^{1/2}$, I_0 denotes the input intensity on the line of the laser propagation direction, $L_{eff} = (2\alpha_0)^{-1} [1 - \exp(-2\alpha_0 L)]$, and here $L = 1$ mm denotes the thickness of the sample, and γ denotes the 3PA coefficient. From the best-fit of the

data, the 3PA cross-sections (3PAC) of the CdSe/CdS CS CQDs and CdSe/CdS/ZnS CSS CQDs are derived to be 4.3×10^{-78} and $2.8 \times 10^{-77} \text{ cm}^6 \text{ s}^2 \text{ photon}^{-2}$, respectively. The 3PAC of commonly used CQDs and dyes from the literature as well as our results are listed in Table 1 for comparison.

Figure 4.2 The experimental setup for the measurements of Z-scan.

Table 1. Summary of results in this work and data available in the literature about 3PAC of commonly used CQDs and dyes

Samples	Diameters (nm)	Parameters of excitation pulse	3PAC ($\text{cm}^6 \text{ s}^2$ photon^{-2})
CdSe/CdS CQDs	4.95	100 fs, 1300 nm	4.3×10^{-78}
CdSe/CdS/ZnS CQDs	6.57	100 fs, 1300 nm	2.8×10^{-77}

CdSe CQDs [114]	3.9	160 fs, 1300 nm	$\sim 10^{-78}$
CdS CQDs [140]	NA	100 fs, 1000 nm	$\sim 10^{-79}$
ZnS CQDs [141]	2.5	120 fs, 620-780 nm	$\sim 10^{-78}$
Rhodamine 6G [138]	NA	150 fs, 1300 nm	6×10^{-81}
a: Experimental uncertainty: $\pm 15\%$			

We can see that the 3PAC of the CdSe/CdS/ZnS CSS CQDs are much higher than those of the common CQDs and nearly four order of magnitude higher than that of the mostly used dye of Rhodamine 6G [138]. Several factors may contribute to the extraordinarily high 3PAC of the CdSe/CdS/ZnS CSS CQDs including the antenna-like effect of the thick CdS-shell [142], which effectively absorbs laser light and the photoexcited carriers will rapidly transfer into the CdSe-core for emission, the local field effect [143] and the photoinduced screening of the internal field effect [144]. The antenna-like effect is expected to play the dominate role and explains the nearly seven-fold enhancement of the 3PAC of CdSe/CdS/ZnS CSS CQDs compared to those of CdSe/CdS CS CQDs. In addition, to further confirm the 3PA and emission process, the excitation power dependent PL measurements were carried out [130]. The PL intensity of CdSe/CdS/ZnS CSS CQDs excited at 1300 nm with respect to the input power are plotted in Figure 4.3 in double-log scale. Apparently, the PL intensity exhibits a cubic dependence on the input power, which unambiguously corroborates the three-photon absorption and emission process [130].

Figure 4.3 (a) The open aperture Z-scan responses of CdSe/CdS CS CQDs, CdSe/CdS/ZnS CSS CQDs and the pure solvent. (b) The power dependent spectrally integrated PL intensity under excitation wavelength of 1300 nm.

4.5 Three-photon induced stimulated emission

To investigate the stimulated emission properties by direct three-photon absorption, the thin film of close-packed CdSe/CdS/ZnS CSS CQDs was pumped using the stripe configuration, in which the laser beam was focused onto the sample along the vertical direction by a cylindrical lens (focus length:75 mm) and the emission was detected from the edge of the sample, as was schematically portrayed in Figure 4.4 (c). The surface of the CQD film was investigated by optical microscope (Figure 4.3 (a)). We can see that the optically smooth surfaces are formed due to the hydrophobic ligands [6]. The film thickness is measured to be about 5 μm from the cross section image of the film (Figure 4.3 (b)). It is noted that the film sometimes will crack due to the in-plane stress after the solvent evaporation [6]. Nevertheless, we can easily find

enough smooth area without cracks from the film (Figure 4.3 (a)) for the stimulated emission measurements. In addition, the surface was also studied by atomic force microscopy (AFM) measurement (Figure 4.4 (b)), from which the peak-to-peak and root-mean-square surface roughness are extracted to be 20.2 nm and 1.8 nm, respectively, further confirming that the optically smooth CQD film was formed.

Figure 4.3 (a) The surface of the close-packed film of CdSe/CdS/ZnS CSS CQDs. (b) Cracking can be observed in these close-packed films. (c) The cross section of the close-packed film of CdSe/CdS/ZnS CSS CQDs.

Figure 4.4 (a) shows the three-photon induced PL spectra from the film of CdSe/CdS/ZnS CSS CQDs as a function of excitation intensity under excitation wavelength of 1300 nm. It is found that, under low excitation intensity, the PL spectra are dominated by the relatively broad spontaneous emission

(full-width-at-half-maximum (FWHM): ~ 30 nm). With the increase of the pump intensity, a sharp peak (FWHM of ~ 8 nm) appeared, indicating the achievement of stimulated emission. The plot of the PL intensity as a function of the excitation intensity (inset in Figure 4.4 (a)) exhibits a threshold behavior, further confirming the occurrence of stimulated emission [9], and the threshold is derived to be 14.5 mJ/cm^2 . The typical optical photographs of the sample below and above the stimulated emission threshold are presented as the insets of (1) and (2), respectively, in Figure 4.4 (a). The obvious bright spot under high pumping intensity is a signature of the development of stimulated emission [6]. Importantly, the stimulated emission peak stays on the blue side of the spontaneous emission, which stands in stark contrast to the type-I CQDs with typically red-shifted stimulated emission peak [42, 107, 145]. This blueshift of the stimulated emission peak manifests the repulsive exciton-exciton interaction in CdSe/CdS/ZnS CSS CQDs with quasi-type-II alignment [42, 49], where the electrons are delocalized over the CdSe-core and the CdS-shell, in contrast, the holes are localized merely in the CdSe-core, as is depicted in Figure 4.4 (d) [40]. As a result, the attractive electron-hole interaction dramatically decreases, while the repulsive electron-electron and hole-hole interaction are strongly enhanced, which results in the transformation from the attractive inter-exciton communication in type-I CQDs into the repulsive counterpart in these quasi-type-II CdSe/CdS/ZnS CQDs [49, 142]. Notably, the quasi-type-II band alignment is very beneficial for suppressing the nonradiative Auger recombination, which is known as the main obstacle towards the achievement of stimulated emission and lasing from CQDs [40]. Particularly, it has

been theoretically and experimentally demonstrated that the Auger process in CQDs closely relates to the spatial overlay between the electron and hole which involve in the Auger recombination, the core-shell interfacial profile and the strength of the exciton-exciton interactions in CQDs [39, 42]. Apparently, the electrons and holes in CdSe/CdS/ZnS CQDs have released overlap due to the spatial isolation compared to that in type-I CQDs, thus suppressing the Auger recombination [142]. In order to confirm the above analysis, time-resolved PL experiments were comparatively carried out on CdSe/CdS CS CQDs and CdSe/CdS/ZnS CSS CQDs under excitation wavelength of 1300 nm. Note that the lifetime of CQDs varies with the excited number of excitons in average per CQD, $\langle N \rangle$. Consequently, the same number of excitons of CdSe/CdS CS CQDs and CdSe/CdS/ZnS CSS CQDs following excitation rather the excitation intensity is set for comparison [142]. Figure 4.4 (e) displays the PL decay traces of CdSe/CdS CS CQDs and CdSe/CdS/ZnS CSS CQDs at $\langle N \rangle = 1.05$, corresponding to the multiexciton states but below the stimulated emission threshold. Here, $\langle N \rangle$ is calculated by [139]:

$$\langle N \rangle = \pi^{1/2} \sigma_3 I^3 \tau / (3^{3/2} \hbar \omega_3)$$

where I is the excitation intensity (W/cm^2), τ denotes the laser pulse-width (seconds) and $\hbar \omega_3$ is the photon energy at wavelength of 1300 nm. It is found that the PL decays are constituted by two decay pathways, namely, the fast decay pathway, corresponding to the Auger recombination [146], and the slow decay pathway, corresponding to the single exciton recombination [40]. By fitting the decay curve of CdSe/CdS/ZnS CQDs based on a two-exponential-decay function:

$$I_t = A_1 \exp^{-t/\tau_1} + A_2 \exp^{-t/\tau_2}$$

where τ_1 and A_1 denotes the Auger lifetime and the corresponding amplitude, and τ_2 and A_2 denotes the single exciton lifetime and the corresponding amplitude. The best-fit of the data extracts the Auger lifetime to be ~310 ps and the single exciton lifetime of 15.1 ns, which agrees well with that (16.5 ns, Figure 4.5 (a)) measured under low excitation intensity: $\langle N \rangle = 0.06$, thus further confirming the single exciton recombination in origin of the slow decay pathway. In a similar way, the Auger lifetime of CdSe/CdS CQDs under $\langle N \rangle = 1.05$ is resolved to be only ~130 ps, which corroborates the suppressed Auger recombination in CdSe/CdS/ZnS CQDs as a result of the reduced overlap for the electron and hole with the help of the leakage of electron into to thick-CdS-shell.

Figure 4.4 (a) The excitation dependent PL spectra under excitation wavelength of 1300 nm. The PL images under and above stimulated emission threshold are presented as the insets of (1) and (2), respectively. (b) Tapping mode AFM image of CdSe/CdS/ZnS CQDs film. (c) The schematic configuration for the measurement of power dependent PL via stripe pumping configuration. (d) The conduction and valence band alignments of CdSe/CdS/ZnS CSS CQDs. (e) PL dynamic of CdSe/CdS CS CQDs and CdSe/CdS/ZnS CSS CQDs with photoexcited average number of excitons of 1.05.

Although the nonradiative Auger recombination is fast compared to the single exciton radiative recombination, the development of stimulated emission with timescale of less than 50 ps can outcompete the Auger recombination when the excitation intensity exceed the threshold [147]. Figure 4.5 (b), (c) and (d) show the

evolution of PL decay dynamics under different excitation intensity regimes, namely, the single exciton regime, the multi-exciton regime and the development of stimulated emission, respectively. We can see that slow single exciton recombination dominates under low excitation intensity (Figure 4.5 (b)); As the excitation increases, the CQDs enters the multi-exciton regime, where the fast Auger recombination appears (Figure 4.5 (c)); Under high excitation intensity above the threshold, the development of stimulated emission manifests a much faster decay rate and a narrow spectral linewidth (Figure 4.5 (d)).

Figure 4.5 (a) PL decay under low excitation intensity, corresponding to single exciton regime. The best-fitting of the data (the red line) gives the single exciton lifetime of 16.5 ns. (b) The PL spectrogram showing the exciton decay dynamics under low excitation intensity. (c) The PL spectrogram showing the exciton decay

dynamics under relatively higher excitaiton intensity, corresponding to multi-exciton regime. (d) The PL spectrogram showing the exciton decay dynamics under excitation intensity of above the stimulated emission threshold.

To comprehensively study the three-photon induced stimulated emission, the stimulated emissions induced by one- and two-photon absorption are also investigated. Figure 4.6 presents the stimulated emission spectra of CdSe/CdS/ZnS CSS QDs under pumping wavelength of 480 nm (excitation intensity of 0.8 mJ/cm^2), 800 nm (excitation intensity of 8.5 mJ/cm^2) and 1300 nm (excitation intensity of 15.4 mJ/cm^2), corresponding to the absorption of 1-photon, 2-photon and 3-photon, respectively. Table 2 lists the summary of the parameters of the stimulated emission via 1-, 2- and 3PA. It is revealed that the stimulated emission peaks induced by 2- and 3-photon absorption gradually shift to longer wavelength compared to that by 1-photon, which is ascribed to size-selective effect [125]. Because the multi-photon absorption cross-sections of QDs increase nonlinearly with size, the subset of larger dots in the QD ensemble will contribute more to the PL intensity, thus resulting in a red-shifted stimulated emission upon multi-photon excitation [138, 148]. Importantly, the unfavorable reabsorption effect can be reduced thanks to the increased Stokes shift or redshift of the stimulated emission peaks, which should be accounted for the decreased stimulated emission threshold in view of average number of excitons per QD, $\langle N \rangle$, under 1- ($\langle N \rangle = 1.9$), 2- ($\langle N \rangle = 1.5$) and 3-photon ($\langle N \rangle = 1.2$) excitation as listed in Table 2.

Figure 4.6 The comparison of stimulated emission from the solid film of CdSe/CdS/ZnS CSS CQDs via 1-, 2- and 3PA. The corresponding absorption spectrum of the solid film of CdSe/CdS/ZnS CQDs is also presented.

Table 2. Stimulated emission (SE) parameters via 1-, 2- and 3PA.

	Excitation wavelength [nm]	SE peak wavelength [nm]	Δ_{xx} [meV]	Threshold [mJ/cm ²]	Average excitons per QD at SE threshold
1-photon	480	625	23	0.6	1.9
2-photon	800	628	23	8.2	1.5
3-photon	1300	635	22	14.5	1.2

One of the most important advantages of CQDs compared to the commonly used dyes is the enhanced photostability due to the semiconductor in nature [138]. To check the stability of the three-photon excited stimulated emission from the CdSe/CdS/ZnS CQDs, the PL intensity of the stimulated emission peak was monitored with respect to the number of excitation pulses (wavelength: 1300 nm, pulse-width: 100fs, repetition

rate: 1000 Hz). The excitation intensity of 16 mJ/cm^2 is set to make the stimulated emission dominate the PL emission, depicted in the inset of Figure 4.7. As shown in Figure 4.7, the stimulated emission peak is able to keep 90% of its initial value over more than 1×10^6 shots, indicating the viability of CdSe/CdS/ZnS CQDs as the three-photon absorption enabled gain media [132, 145].

Figure 4.7 The plot of the stimulated emission peak intensity from close-packed film of CdSe/CdS/ZnS CQDs under excitation wavelength of 1300 nm. The inset displays the initial stimulated emission spectrum from the solid film of CdSe/CdS/ZnS CQDs and the spontaneous emission spectrum from the solid film of CdSe/CdS/ZnS CQDs under low excitation intensity.

4.6 Three-photon excited coherent random lasing

Different from conventional lasers, where deliberately designed resonators are necessary, random lasers provide lasing oscillation by random scattering, no need of

additional cavities [64, 149, 150]. As a result, the random lasers can be cost-effectively fabricated. In addition, random laser possess its own features, such as the intense light emission with broad spatial distribution and the sensitivity of the lasing spectra on the scatterers [63], which make random lasers hold great potential in a wide range of applications [66, 151]. Typically, random lasers are consisted of two components [149, 150]: 1) gain materials, such as laser dyes and conjugated polymers; 2) scattering media including TiO_2 or ZnO nanoparticles with relatively high refractive index. In this work, we revealed that the self-assembled CdSe/CdS/ZnS CQDs clusters can simultaneously serve as the optical gain and the strong scattering centers, therefore, random lasing can be achieved without doping with additional nanoparticles. To prepare the self-assembled CdSe/CdS/ZnS CQDs clusters, the CQDs suspensions were dropcasted onto a hydrophobic glass slide and let it dry at elevated temperature of 50~60 °C in an oven. Due to the much faster evaporation rate of the solvent than that at room temperature, abundant CQD clusers or aggregations are formed, which can be clearly observed from the optical microscopy image in Figure 4.8 (d). In addition, the AFM measurement shows that the peak-to-peak surface roughness is ~189.2 nm, suggesting a very rough surface of the CdSe/CdS/ZnS CQDs film. To investigate the lasing action from these CdSe/CdS/ZnS CQDs clusters, we adopted the stripe pumping configuartion as was similarly used in the stimulated emission measurements. The PL spectra with varied excitation intensities under excitation wavelength of 1300 nm are presented in Figure 4.8 (a). It is found that the broad spontaneous emission (FWHM: ~30 nm) dominates the PL

spectra under low pumping intensities of less than $\sim 17.1 \text{ mJ/cm}^2$. As the pumping intensity increases, sharp peaks with a narrow linewidth ($\sim 0.4 \text{ nm}$) appears, indicating the achievement of the random lasing, and the number of these sharp spikes rises with excitation intensity [152, 153]. The plot of the integrated PL intensity from optical wavelength of 632 to 642 nm as a function of the excitation intensity are shown in the inset of Figure 4.8 (a). Clearly, the integrated PL intensity increases abruptly from certain excitation intensity, which further confirms the development of random lasing with a threshold of 17.1 mJ/cm^2 [154, 155]. As introduced in Chapter 2, there are two types of random lasing classified based on the distinct feedback mechanisms [63]. When the scattering in the disordered system is weak that the light cannot be guided back to its initial point so as to form a closed loop, the feedback depends on intensity. Consequently, the the lasing is wavelength insensitive and the lasing spectra are very similar to those for stimulated emission. This kind of random lasing is known as the incoherent random lasing. In contrast, when the scattering in the disordered system is so strong that the light can be scattered back to its initial point to form a closed loop (Figure 4.8 (c)), which actually behalves as the resonator for conventional lasers, the feedback is field or amplitude in nature due to the constructive interference of the multiple scattering in the closed loop. As a result, the lasing spectra are very sensitive to the wavelength and only specific wavelengths will be enhanced so that the discrete spikes with typically narrow linewidth of less than 1 nm are observed [156, 157]. This kind of random lasing is referring as the coherent random lasing [149].

Figure 4.8 (a) Power dependent PL spectra from self-assembled CdSe/CdS/ZnS CQDs films with rich aggregations. The spectrally integrated PL intensity with respect to excitation intensity is presented in the inset. (b) The schematic discription of random lasing mechanism. (c) The tapping mode AFM image of CdSe/CdS/ZnS CQDs films showing the clustered surface. (d) Large scale optical microimage of self-assembled CdSe/CdS/ZnS CQDs films with dense clusters.

According to the features of the lasing spectra from the CdSe/CdS/ZnS CQDs clusters, the lasing action could be classified into coherent random lasing. To further confirm the coherent random lasing mechanism from the CdSe/CdS/ZnS CQDs clusters, the excitation area dependent random lasing was carried out [152]. Based on the coherent random lasing theory, there should be a minimal area in order to form a

closed loop or ring cavity, and more ring cavities can be generated by scattering with the increasing of excitation area [151]. As a result, more and more sharp peaks will emerge as the excitation area increases under fixed excitation intensity. Here, the excitation area was altered by tuning the stripe length of the focus laser beam under a constant excitation intensity of 18.0 mJ/cm^2 . As is presented in Figure 4.9 (a), the sharp peaks or lasing action can only occur when the excitation area is larger than $4000 \text{ }\mu\text{m}^2$, and increased sharp peaks emerge as the excitation area increase, which further corroborates the coherent random lasing mechanism. Moreover, the cavity length of the closed loop from the sample can be estimated by performing the power Fourier transform (FT) of the lasing spectrum [151, 152]. Figure 4.9 (b) shows the spectrum after FT processing under pump intensity of 19.2 mJ/cm^2 . The length of the cavity, L , can be derived by formula: $L = 2\pi d/n$, where d is a parameter extracted from the peak positions in the spectrum. We can see that there are a series of peaks locating at 34, 70, 101, 132 and 174 μm in the FT-processed spectrum and the interval between the adjacent peaks are nearly identical, thus we can safely assign the 34 μm – peak to the basic cavity length and 70, 101, 132 and 174 μm -peaks to the high harmonics of the cavity due to multiple trips experienced by the light around the fundamental cavity. As a result, the cavity length is derived to be $L \sim 126 \mu\text{m}$, considering the $n \sim 1.7$ in our sample [6].

Figure 4.9 (a) Excitation area dependent PL spectra from self-assembled CdSe/CdS/ZnS CSS CQDs with rich clusters with fixed excitation intensity of 18.0 mJ/cm^2 . (b) Typical Fourier transform spectrum from self-assembled CdSe/CdS/ZnS CSS CQDs with rich clusters.

4.7 Summary

In this Chapter, by rationally employing the CdSe/CdS/ZnS CSS CQDs in order to

enhance the 3PAC, suppress the Auger process and improve the photostability, we successfully developed stimulated emission by direct three-photon absorption from CQDs. Furthermore, to demonstrate three-photon induced lasing action, we produced highly disordered active system of the CdSe/CdS/ZnS CQDs clusters, which behalf as both the active gain materials as well as the scattering centers. Finally, coherent random lasing via 3PA was realized.

Chapter 5

Low-threshold blue stimulated emission and lasing from ternary CdZnS/ZnS alloy quantum dots

5.1 Introduction and motivation

In previous Chapter, we show that stimulated emission and lasing from CQDs can be achieved by not only one- and two-photon absorption but also simultaneous three-photon absorption. However, almost all of the stimulated emission and lasing demonstrations from CdSe-based CQDs are only in spectral range of green to red region with wavelengths longer than ~ 500 nm [42, 158, 159]. To extend the stimulated emission and lasing wavelength to blue region, the size of the CQDs should be further reduced in order to generate stronger quantum confinement effect [9, 160]. However, with the decreasing of the dot size, the nonradiative Auger recombination, known as the main channel that depletes the population inversion [40, 161, 162], will be highly accelerated. Furthermore, the reduced dot size will increase the surface-to-volume ratio of CQDs, hence, more surface defects tend to form and more excited carriers will be trapped [160]. As a result, blue stimulated emission or lasing from CdSe-based CQDs is extremely challenging. Whilst, the blue lasers are known to hold diverse important applications including the development of high-density photomemories and full-color laser displays [1, 163]. Therefore, it is imperative to explore the blue stimulated emission and lasing from CQDs. In this chapter, we employ the newly engineered blue-emitting CdZnS/ZnS alloy QDs replacing CdSe-based ones in order to develop the blue-CQD lasers. As is known that

lasers can be divided into gas, liquid and solid lasers based on the state of the gain media. Each of these lasers hold their own advantages over others. For example, solid-state lasers are usually more compact compared to liquid and gas ones [1]. On the other hand, liquid lasers are favorable for the development of high power lasers by virtue of the facilities of thermal dissipation through recycling of the liquid gain media [32, 164, 165]. In addition, the optofluidic lasers, an emerging liquid laser, have drawn great research interests by virtue of their potential applications in biology and biophotonics [166, 167]. However, most of the CQD-lasers are based on the close-packed solid films of CQDs due to the high packing density of CQDs in the films in order to satisfy the predicted critical loading factor of CQDs for the development of lasing action [6, 9, 164]. In this work, we find that lasing action can be easily achieved from the dilute solution of these CdZnS/ZnS alloy CQDs, where the loading factor of these CQDs is far below the critical value for CdSe-based CQDs. Importantly, the thresholds of the stimulated emission and lasing action from these CdZnS/ZnS alloy CQDs are so low that quasi-continuous wave pumping using compact Q-switched nanosecond laser is accessible. Detailed steady state and ultrafast dynamics spectroscopy studies reveal the underlying mechanisms for the low stimulated emission thresholds to the low density of trapping defect and slow nonradiative Auger recombination of CdZnS/ZnS alloyed-core/shell CQDs, which are further confirmed by comparatively optical study on a series of CdZnS-based CQDs, namely, CdZnS cores, CdZnS/ZnS alloyed-core/sharp-shell and CdZnS/ZnS alloyed-core/alloyed-shell in the following part. Furthermore, the feasibility of lasing

action with low thresholds from the dilute solution is made possible by the high gain cross-section of these CQDs and the employment of high Q-factor whispering gallery mode resonators.

5.2 Sample fabrication

The samples were provided by our collaborators. The CdZnS/ZnS alloyed-core/alloyed shell CQDs emitting at ~435 nm and the series of CdZnS-based CQDs emitting at ~460 nm, namely, CdZnS cores, CdZnS/ZnS alloyed-core/sharp-shell and CdZnS/ZnS alloyed-core/alloyed-shell, investigated here were all synthesized by one-pot hot-injection method adopted from the literature [163, 168, 169].

For the growth of CdZnS/ZnS alloyed-core/alloyed shell CQDs emitting at ~435 nm, cadmium oxide (CdO) (1 mmol) and Zn(acet)₂ (10 mmol) were mingled into oleic acid (OA) (7 mmol) and stored in a flask with volume of 100 mL. Then, the mixture was air exhausted for 20 min and the temperature was elevated to 150 °C by heating under nitrogen condition. Next, 1-octadecene (1-ODE) (15 mL) was introduced into the above mixture and further heated up to 300 °C. After that, the S-precursor, which was prepared by slowly mixing S powder (2 mmol) into solvent of 1-ODE (3 mL), was rapidly added into the mixture at elevated temperature of 300 °C. Then, the reaction was kept for 8 min, during which the temperature was kept at 300 °C. Following that, S powder (8 mmol) dissolving in tributylphosphine (TPBS) was introduced into the above mixture. Finally, the CQDs were dissolved in toluene after purification and was kept at 4 °C in dark until further use.

For the synthesis of CdZnS cores, a clear transparent solution of cadmium- and zinc-oleate was first acquired from a stirring mixture of 128.4 mg (1 mmol) of CdO, 1.8349 g (10 mmol) of Zn(ace)₂ and 9.5 mL (30 mmol) of OA, which were heated to 150 °C in a 3-necked 50mL round-bottom flask. Subsequently, 12.5mL non-coordinating solvent of 1-ODE was added to the metal-oleate precursors, and the air as well as the moisture was further removed. Thereafter, the solution was brought to 310 °C under inert gas purging. Upon reaching this temperature, 51.3mg (1.6 mmol) of sulfur powder pre-dissolved in 2.4mL of ODE at 130 °C was quickly added into the hot solution to initiate the nucleation. Then, the reaction volume was held for 12 min before cooling down to a warm temperature of ~70 °C. The nanocrystals were purified by repeated acetone/methanol precipitation and toluene redispersion, and the final CdZnS solution was kept at 4 °C in dark until further use.

For the synthesis of CdZnS/ZnS alloyed-core/sharp-shell CQDs, the above developed CdZnS cores were adopted. 128.3 mg (4 mmol) of sulfur powder pre-dissolved in 5 mL of oleic acid at 130 °C was injected into the CdZnS-core solution in a drop-wise manner into the flask within ~10 min to stimulate the growth of ZnS shell. The reaction was aged for another 20min followed by rapid cooling to a mild temperature ~70 °C. The nanocrystals were purified by repeated acetone/methanol precipitation and toluene redispersion, and the final CdZnS/ZnS alloyed-core/sharp-shell CQDs solution was kept at 4 °C in dark until further use.

For the synthesis of CdZnS/ZnS alloyed-core/alloyed-shell CQDs, the same procedures for the fabrication of CdZnS/ZnS alloyed-core/sharp-shell CQDs was

employed but with additional annealing processing for 3 hours at 310 °C. The nanocrystal reaction volume, after cooled to gently hot temperature, was purified by repeated acetone/methanol precipitation and toluene redispersion, and the final CdZnS/ZnS alloyed-core/alloyed-shell CQDs solution was kept at 4 °C in dark until further use.

5.3 Steady state absorption and emission

Figure 5.1 shows the room temperature absorption and photoluminescence spectra of the CdZnS/ZnS alloyed-core/alloyed-shell CQDs, whose emission peak locates at 435 nm, dispersed in toluene. The FWHM of the PL spectra is as narrow as 18 nm, which indicates the excellent composition homogeneity and size uniformity [163]. The PL QY measurement reveals a high value of up to 80% according to the method described in Chapter 3, suggesting the low carrier trapping effect in these CdZnS/ZnS alloyed-core/alloyed-shell CQDs [170]. The physical mechanisms for the high PL QY or the minimal defect states in these CdZnS/ZnS CQDs is attributed to reduced lattice mismatch between CdZnS alloyed-core and ZnS-shell, minimizing the defects in the interface and surface [171, 172]. Direct experimental evidence will be presented in the next part. The TEM image of these CdZnS/ZnS CQDs is displayed in the inset of Figure 5.1. The size of these CQDs is revealed to be as large as ~8.5 nm, therefore, these CQDs belong to the weak confinement regime. The photograph of the solution of CdZnS/ZnS CQDs under UV-lamp is shown in the inset of Figure 5.2.

Figure 5.1 Linear UV-visible absorption and photoluminescence spectra of the CdZnS/ZnS alloyed-core/alloyed-shell CQDs. The corresponding TEM image is presented as the inset, and the schematic structure of these CQDs is also portrayed in the inset.

The temperature-dependent PL measurements, which can offer more information on the PL properties [173-176], were also performed on these CdZnS/ZnS alloyed-core/alloyed-shell CQDs. To do so, the CQDs were dispersed into PMMA so as to suppress the influence of energy transfer between the CQDs with slightly different sizes in the CQDs ensemble [175]. In addition, to eliminate any over illumination impact, the excitation intensity from the Xenon lamp was kept low. Figure 5.2 displays the temperature-dependent PL spectra of CdZnS/ZnS CQDs under excitation wavelength of 395 nm, where the temperature was changed from 10 K to

300 K. The spectrally integrated PL intensity with respect to temperature is illustrated in Figure 5.3, which unravels an anti-quenching followed by quenching process. In particular, the spectrally integrated PL intensity increases with the rising of temperature from 10 K to 150 K, which is due to contribution in PL from the thermally released carriers which are shallowly localized in surfaces/interfaces to the radiant CdSe-cores [173, 177]. Then, the PL intensity exhibits thermal quenching effect from 150 K to 300 K, which should be attributed to the carrier trapped into the residual deep-level surface/interface defects and the nonradiative thermal escape of carriers with help of multi-phonon interaction [178, 179]. It is noted that almost 90% of the initial PL intensity at 10 K can be retained as the temperature varies from 10 K up to room temperature, suggesting that the carrier trapping effect in these CdZnS/ZnS alloyed-core/alloyed-shell CQDs is nearly negligible [177]. As a result, both the room temperature PL and the temperature dependent PL measurements indicate the high quality of these CdZnS/ZnS CQDs.

Figure 5.2 Photoluminescence spectra of CdZnS/ZnS CQDs with varied temperature from 10 K to 300 K. The photograph of CdZnS/ZnS CQDs solution under UV-lamp excitation is presented in the inset.

Furthermore, the information about the band gap change with temperature and exciton-acoustic/optical-phonon interaction in these ternary CdZnS/ZnS CQDs can be derived from the temperature dependent PL spectra [175, 180]. The PL peak shifts towards longer wavelength, which is similar to the trend in conventional II-VI binary CQDs, such as CdSe, CdTe and InP CQDs [173, 174, 180]. The redshift of the PL peak is attributed to the thermal lattice expansion and the interaction between excitons and phonons [181, 182]. Empirically, the temperature-dependent PL peak energy can be fitted by the Varshni expression, given by [183]:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}$$

where $E_g(0)$ represents the band gap emission energy at 0 K, α denotes the temperature coefficient and β is the fitting parameter. From the best-fitting of the data shown in Figure 5.3, $E_g(0)$ is derived to be 2.929 eV, α is derived to be $(4.49 \pm 0.06) \times 10^{-4}$ eV/K and β is derived to be (268 ± 8) K.

The FWHM of the PL spectra is found to broaden with the increase of temperature. This phenomenon is very common in semiconductors and can be ascribed to the scattering between excitons and optical/acoustic phonons within the targeted material [86, 181]. The curve of the temperature-dependent FWHM of the PL spectra can be well-reproduced by the formula [178]:

$$\Gamma(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO} / (e^{E_{LO} / k_B T} - 1)$$

where Γ_{inh} describes the contribution to the broadening of FWHM from size inhomogeneity, σT describes the broadening from the interaction between the exciton and the acoustic-phonon and σ denotes the interaction coefficient, the term $\Gamma_{LO} / (e^{E_{LO} / k_B T} - 1)$ describes the broadening from the interaction between the exciton and the LO-phonon, Γ_{LO} denotes the interaction strength and E_{LO} represents the energy of LO-phonon. From the best-fit of the data, Γ_{inh} is extracted to be (93.7 ± 0.2) meV, σ to be (33.8 ± 5.2) μ eV/K, Γ_{LO} to be (29.3 ± 3.6) meV and E_{LO} to be (30.2 ± 3.6) meV. These results are comparable to those for the binary CQDs, namely, CdSe, CdTe and InP CQDs [173-175].

Figure 5.3 The spectrally integrated emission intensity of ternary alloy CdZnS/ZnS CQDs with respect to temperature (the above) and the corresponding peak energy and FWHM (the bottom) as a function of temperature are presented.

5.4 Ultralow-threshold stimulated emission and liquid microlasers

To investigate the stimulated emission properties of these CdZnS/ZnS alloyed-core/alloyed-shell CQDs, the close-packed solid film of CdZnS/ZnS CQDs prepared by spin-coating method was pumped employing the stripe configuration, as described in Chapter 4, under excitation wavelength of 395 nm. Note that the pulse-width of the excitation laser source is 5 ns, far longer than the time constant

(~350 ps) of the Auger process in CdZnS/ZnS CQDs (see later for detailed discussion). Therefore, the CdZnS/ZnS CQDs were excited in the quasi-continuous wave regime, which is much more desired referring to practical applications [61, 184, 185]. Figure 5.4 displays the PL spectra with respect to excitation intensity of CdZnS/ZnS CQDs. The PL spectra are found to be dominated by the broad spontaneous emission (FWHM: 18 nm). As the excitation intensity increase, a sharp peak with FWHM of ~5 nm appears, indicating the development of stimulated emission [186, 187]. The plot of the integrated PL intensity from 435 nm to 445 nm exhibits a nonlinear increase behavior, further confirming the achievement of stimulated emission [188]. The threshold is extracted to be 22 $\mu\text{J/pulse}$, which corresponding to $\sim 14.7 \text{ mJ/cm}^2$ calculated based on the size of the excitation spot of $\sim 300 \mu\text{m} \times 400 \mu\text{m}$. Noticeably, the emerging amplified spontaneous emission peak lies on the lower energy side of the excitonic emission peak, which agrees with the well-established biexciton lasing in conventional type-I CQDs [6].

Figure 5.4 Pump pulse energy dependent PL spectra from self-assembled close-packed film of CdZnS/ZnS CQDs. The spectrally integrated PL intensity (435~445 nm) as a function of pump pulse energy are presented as the inset.

Although liquid lasers hold various important applications, it is extremely difficult to achieve lasing from CQDs in solution, which is mainly due to the low loading factor of CQD in solution and the photo-induced absorption related to the surface/interface defects of CQDs [164, 189]. The ultra-low lasing threshold from the solid film of CdZnS/ZnS CQDs offers the opportunity to achieve lasing from CQDs solution with a low loading fraction, and the minimal surface/interface defects could effectively suppress the optical gain loss from photo-induced absorption. As a result, the challenges towards lasing from CQDs solution would be possibly resolved by

employing the CdZnS/ZnS CQDs as the gain media. To investigate the lasing action from the solution of CdZnS/ZnS CQDs, the silica capillary tube was used serving as both the holders for the CQD solution and the resonant cavity since the circular cross-section of the capillary tube was naturally a whispering gallery mode resonator [190]. To produce the liquid CQD-laser, the CdZnS/ZnS CQDs solution was filled into the hollow capillary tube with the help of capillary action. After that, the two ends of the capillary tube were sealed by wax to avoid evaporation. Figure 5.5 (a) and (b) show the optical images of CdZnS/ZnS CQDs solution infiltrated into the fiber under halogen illumination and the boundary of CdZnS/ZnS CQDs solution in the fiber. To study the optical properties of the individual capillary tube filling with CdZnS/ZnS CQDs solution, a home-built micro-photoluminescence system was utilized as schematically portrayed in Figure 5.6.

Figure 5.5 (a) Optical image of the hollow fiber filled with ternary alloy CdZnS/ZnS

CQDs solution under excitation by halogen lamp. (b) Optical image showing the boundary of the infiltrated ternary alloy CdZnS/ZnS CQDs solution. (c) The PL image of the hollow fiber infiltrated with ternary alloy CdZnS/ZnS CQDs solution under low excitation intensity below the lasing threshold. (d) The PL image of the hollow fiber infiltrated with ternary alloy CdZnS/ZnS CQDs solution under excitation intensity above the lasing threshold. The scale bars denotes 50 μm .

Figure 5.6 The schematic experimental setup for the micro-PL measurement.

The laser beam (wavelength: 395 nm, pulsewidth: 5 ns, repetition rate: 20 Hz) was guided and focused onto the capillary tube with spot size of $\sim 300 \times 400 \mu\text{m}^2$, and

the emission signal from the sample was collected by an objective (NA = 0.42, 50 $\times$). A portion of the emission signal was directed to a camera for imaging, and the other comes into a monochromator and recorded by a CCD for spectra recording. Suitable filters were introduced to block the scattering of the excitation laser and protect the imaging camera and CCD.

Figure 5.7 displays the μ -PL spectra of an individual CQD-filled capillary tube with respect to excitation pulse energy. It is found that the μ -PL spectra are dominated by the excitonic emission spectra (FWHM: 18 nm) when the excitation pulse energy is lower than 30.2 μ J/pulse. As the excitation pulse energy keeps increasing, sharp spikes emerge whose spectral position is nearly identical to that of the stimulated emission peak, indicating the occurrence of the lasing [185]. The plot of sharp peak intensities versus excitation pulse energy shows a sharp increase, a typical threshold behavior, thus further confirming the achievement of lasing action from the solution of CdZnS/ZnS CQDs [9, 191]. The lasing threshold is extracted to be as low as 30.2 μ J/pulse, corresponding to ~ 25.2 mJ/cm². It is also worth mentioning that the liquid CQD-laser is working under quasi-continuous wave pumping regime, which is strongly desired towards a variety of practical applications, where the optical gain time scale is much longer than the typically short Auger time constant [192].

Figure 5.7 Pump pulse energy dependent PL spectra from ternary alloy CdZnS/ZnS CQDs infiltrated into the hollow fiber with inner diameter of $\sim 54 \mu\text{m}$. The spectrally integrated PL intensity (435 ~ 445 nm) versus pump pulse energy is presented as the left inset. The right inset portrays the simplified excitation and signal collection configuration in this measurements.

The lasing mechanism is tentatively assigned to the whispering gallery mode lasing around the inner walls of the capillary tube (inset of Figure 4b) due to higher refractive index of the solvent (~ 1.51 at 450 nm) than that of the silica capillary tube [193]. To check our assumption, the lasing peaks are attempted to be fitted based on WGM model [74]. Given that only the first radial mode order works ($q=1$), the spectral condition for the resonant oscillation is determined by [72]:

$$m\lambda_m = \pi nD$$

where m is the angular mode number and λ_m is the corresponding resonant wavelength at specific angular mode number, m , D is the inner diameter of the capillary tube, which is derived to be $\sim 54 \mu\text{m}$ from the optical microscope image of the cross-section, shown in Figure 5.8 (a). Based on the method developed by Duong *et al.* [74], the lasing peaks can be well reproduced with mode numbers from 597 to 603, supporting the assignment of the WGM lasing. Moreover, to further confirm the WGM lasing mechanism from our laser system, we performed the optical studied of capillary tube with varied sizes filled by CdZnS/ZnS CQDs solution. The $\mu\text{-PL}$ spectra versus excitation pulse energy for different sized capillary tubes are shown in Figure 5.10-5.12. Similarly, the inner wall diameter of the individual capillary tube was determined from the optical microscope images displayed in Figure 5.8 (b), (c) and (d).

Figure 5.8 Cross-sections of the hollow fibers used in the experiments with different diameters. The scale bar denotes $50 \mu\text{m}$.

It is found that the free spectral range (FSR) of the lasing spectra decreases with the increase of the size of the capillary tube. Quantitatively, the FSR is revealed to be in reverse proportion to the inner diameter of the capillary tube, as illustrated in Figure 5.9 (b). From the theoretical analysis according to WGM model, the relationship between the FSR and the resonator diameter is given by [72, 193]: $FSR = \lambda^2 / \pi n D$, which indicates that the FSR is indeed proportional to the inverse of the inner wall diameter of the capillary tubes. The agreement between experimental data and theory further confirms the WGM lasing mechanism of the liquid CQD-laser. In addition, the electric field distribution at resonant wavelength was investigated by numerical simulation based on finite element method (FEM). Figure 5.9 (c) shows the electric field distribution of the capillary tube with inner wall diameter of 54 μm in radial direction by setting solution refractive index to be 1.56, which is determined from the best-fitting of the lasing peaks, and that of the silica capillary tube to be 1.47 [190]. We can see that the electric field is strongly confined within the CQD-solution part and concentrated close to the inner wall boundary. The normalized electric field profile is also shown in Figure 5.9 (d), which again reveals that the electric field is localized within the CQD-solution and only a tiny part of the evanescent wave leaks out from the CQD-solution part. The low loss of the liquid CQD-laser structure leads to the low lasing threshold and the high Q-factor of up to ~ 3000 , which is determined by: $Q = \lambda / \Delta\lambda$, where λ is the lasing peak wavelength and $\Delta\lambda$ is the corresponding linewidth of the lasing peak [72, 74].

Figure 5.9 (a) Assignment of the lasing spikes based on WGM model. (b) The plot of FSR as a function of the inner diameter of the hollow fibers. The proposed WGM lasing mechanism of these fiber lasers is presented as the inset. (c) Electric field distribution for mode of $p=1$ and $m=600$ of the fiber laser. (d) The corresponding normalized electric field profile for mode of $p=1$ and $m=600$.

Figure 5.10 Pump pulse energy dependent PL spectra from ternary alloy CdZnS/ZnS CQDs infiltrated into the hollow fiber with inner diameter of $\sim 106\ \mu\text{m}$. The PL image of the fiber under excitation above the threshold is presented as the right inset. The plot of the wavelength separation between the neighbor lasing spikes as a function of the number of the lasing spikes is shown as the left inset. The scale bar denotes $50\ \mu\text{m}$.

Figure 5.11 Pump pulse energy dependent PL spectra from ternary alloy CdZnS/ZnS CQDs infiltrated into the hollow fiber with inner diameter of $\sim 160\ \mu\text{m}$. The PL image of the fiber under excitation above the threshold is presented as the right inset. The plot of the wavelength separation between the neighbor lasing spikes as a function of the number of the lasing spikes is shown as the left inset. The scale bar denotes $50\ \mu\text{m}$.

Figure 5.12 Pump pulse energy dependent PL spectra from ternary alloy CdZnS/ZnS CQDs infiltrated into the hollow fiber with inner diameter of $\sim 210 \mu\text{m}$. The PL image of the fiber under excitation above the threshold is presented as the right inset. The plot of the wavelength separation between the neighbor lasing spikes as a function of the number of the lasing spikes is shown as the left inset. The scale bar denotes $50 \mu\text{m}$.

The exciton dynamics of the CdZnS/ZnS alloyed-core/shell CQDs and the liquid laser device was investigated to better understand the lasing action in this system by time-resolved spectroscopy. In doing so, the CQDs solution was filled in a 1-mm-thick quartz cuvette, which was excited by femtosecond laser pulse (wavelength: 395 nm, pulsewidth: 100 fs, repetition rate: 1000 Hz). The time-resolved

PL signal was accessed by a streak camera system with temporal resolution of ~50 ps. Figure 5.13 (a) shows the variation of the PL decay of CdZnS/ZnS CQDs solution under varied excitation intensities. It is found that the shapes of PL decay curves are nearly identical when the excitation intensities are low than $\sim 85 \mu\text{J}/\text{cm}^2$, which agrees with the characteristic of excitonic recombination [194]. The decay curve can be well-reproduced by the two-exponential function, given by [170]:

$$I_t = A_1 \exp^{-t/\tau_1} + A_2 \exp^{-t/\tau_2}$$

where τ_1 and A_1 denotes the Auger lifetime and the corresponding amplitude, and τ_2 and A_2 denotes the single exciton lifetime and the corresponding amplitude. The results by well-fitting of the curve are listed in Table 3. The double-exponential decay of the single exciton recombination is common for CQDs and indicates two radiative decay channels relating to the surface state, responsible for the long time decay of 9.9 ns, and core state, responsible for the short time decay of 2.1 ns [170]. With the increase of excitation intensity, an apparent rapid recombination process with lifetime of ~350 ps appears, which corresponds to the nonradiative Auger recombination [36]. Although the Auger recombination with lifetime of ~350 ps is much faster with respect to the spontaneous emission process, it is actually relatively slow compared to those in conventional CQDs, especially those of the blue-emitting CdSe CQDs with typical Auger lifetime of several tens of ps [36]. The slow Auger recombination rate or long Auger lifetime of these CdZnS/ZnS alloyed-core/shell CQDs should be responsible for the low threshold stimulated emission and lasing from these CQDs, and the underlying reasons are speculated to [171, 189, 195]: 1) the big dot size of

these CdZnS/ZnS CQDs makes them locate in the weak confinement region, where the quantum confinement effect is not that strong as for the blue-emitting CdSe CQDs;

2) the gradual transition in composition from the core to the shell lead to a soft core-shell potential profile, which further suppress the Auger recombination. To verify the above assumption, we have performed comprehensive study on a series of CdZnS-based CQDs, as will be shown in detail in the next part. The transient dynamics of the liquid CQD-laser was also investigated. By changing the excitation intensity from far below threshold, just below the threshold to just above the threshold, we can clearly observe the variation of the decay dynamics of the laser device. As shown in Figure 5.13 (d), under low excitation intensity of $12 \mu\text{J}/\text{cm}^2$, far below the threshold, the emission is dominated by the single exciton recombination. When the excitation intensity increases approaching the lasing threshold, the fast Auger recombination emerges. As the excitation intensity exceeds the threshold, the emission is dominated by the ultrafast lasing action with narrow spectrum. Figure 5.13 (c) displays the dynamic transition of the laser device from just below the threshold excitation to just above the threshold excitation in linear curves. We can see that although the fast nonradiative Auger recombination can deplete the population inversion effectively, the development of the ultrafast lasing action with timescale less than 50 ps, which is restricted by the time resolution of our system, will thoroughly defeat the Auger recombination.

Table 3. PL decay dynamics of CdZnS/ZnS QDs

τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{Auger} (ps)	τ_{SE} (ps)
2.1	28	9.9	72	350	< 50

Figure 5.13 (a) Excitation intensity dependent PL decay of ternary alloy CdZnS/ZnS CQDs. (b) The plot of PL intensity of ternary alloy CdZnS/ZnS CQDs after 1.2 ns upon photoexcitation as a function of excitation intensity. (c) PL decay of the laser device with excitation intensities of just below and above the threshold. (d) The spectrograms showing the PL decay dynamics of the laser device with excitation intensity far below the lasing threshold (the upper one), approaching the lasing threshold (the middle one) and above the lasing threshold (the bottom one).

Furthermore, the concentration of the CdZnS/ZnS CQDs solution adopted here could be derived from the excitation dependent PL intensity from the single exciton recombination [194]. In particular, since the Auger process is very rapid, all the CQDs following photoexcitation will relax to no more than one exciton after long enough time with respect to the timescale of Auger recombination. As a result, PL intensity at decay time of 1.2 ns, where the Auger recombination has already come to an end, is in proportion to the probability of the photoexcited CQDs, described by [194]:

$$P = 1 - P_0 = 1 - e^{-\langle N \rangle}$$

where P denotes the likelihood of the photoexcited CQDs in the ensemble and $P_0 = e^{-\langle N \rangle}$ represents the probability of the nonexcited CQDs in the ensemble. From the best-fit of the data illustrated in Figure 5.13 (c), the absorption cross-section is extracted to be $\sim 2.1 \times 10^{-15} \text{ cm}^2$. Thus, the concentration is derived to be $\sim 2.0 \times 10^{-5} \text{ mol/L}$. Surprisingly, it is almost impossible for CdSe-based CQDs to achieve lasing with such a low CQD concentration. An effective loading fraction of as low as 0.079% of CdZnS/ZnS CQDs is obtained taking into account the CdZnS-core size of $\sim 5 \text{ nm}$, which stays far below the critical loading factor (0.2%) for CdSe-based CQDs [9, 164]. This incongruity should be attributed the different gain properties of these CdZnS/ZnS CQDs compared to those of the CdSe-based CQDs. To measure the gain cross-sections of these CdZnS/ZnS CQDs, the femtosecond pump-probe spectroscopy was employed [165, 191]. In doing so, the CdZnS/ZnS CQDs solution was filled into a quartz cuvette with thickness of 1 mm. The pump beam with optical wavelength of 400 nm was slightly focused onto the sample with spot size of $\sim 1 \text{ mm}$ in diameter.

The probe beam offered by the optical parameter amplifier with wavelength tunable from 260 nm to 2.6 μm was focused onto the sample (spot size: ~ 0.5 mm) and was made almost concentric with the pump beam. The transient absorption ($\Delta\alpha$) was obtained by tuning the delay between the pump and probe beam. The inset of Figure 5.14 (b) schematically shows the principle of the pump-probe technique. The achievement of optical gain is represented by $-\Delta\alpha/\alpha_0 > 1$, in which α_0 denotes the linear absorbance at the probe wavelength [9]. Figure 5.14 (a) shows the time dependent $-\Delta\alpha/\alpha_0$ of these CdZnS/ZnS CQDs solution with increased excitation intensities at probe wavelength of 440 nm, which is resonant with the lasing peaks, and pump wavelength of 400 nm. We can see that the optical gain is clearly achieved in these CdZnS/ZnS CQDs solution when the excitation intensity exceeds 0.52 mJ/cm^2 . Besides, the optical gain could be sustained more than 50 ps under high excitation intensities, which benefits from the suppressed Auger recombination in these CQDs. However, when the probe wavelength is not resonant with lasing peaks, $-\Delta\alpha/\alpha_0$ will never exceeds 1, as shown in Figure 5.14 (b). In addition, the maximum net gain of the sample could be derived from the above data according to the formula [191]: $I_p = I_0 e^{gd}$, in which I_p denotes the transmitted probe beam intensity following the excitation of pump beam, I_0 denotes the probe beam intensity before it passed through the sample, d denotes the optical path and g denoted the net gain of the sample. The best-fit of the data gives a net gain of CdZnS/ZnS CQDs solution as high as 0.53 cm^{-1} . As a result, the gain cross-section of these CQDs is extracted to be $5 \times 10^{-17} \text{ cm}^2$, which is much larger than that of the CdSe CQDs for the critical loading

fraction calculation [9], thus rationalizing the achievement of lasing action from these CdZnS/ZnS CQDs with such a low concentration.

Figure 5.14 (a) The excitation intensity dependent decay of transient absorption changes with pump and probe wavelength of 400 nm and 440 nm, respectively. (b) Transient absorption changes under pump wavelength of 400 nm and probe wavelengths of 430 nm and 440 nm, respectively, with respect to pump intensity.

5.5 Unraveling the high photoluminescence quantum yield

Figure 5.15 (a) Linear UV-visible absorption spectra of CdZnS/ZnS AS CQDs, CdZnS/ZnS SS CQDs and CdZnS core. The zoom-in of the absorption spectra near band edge is presented as the inset. (b) The PL spectra of CdZnS/ZnS AS CQDs, CdZnS/ZnS SS CQDs and CdZnS core.

Although the PL QY of the ternary alloyed CdZnS/ZnS core/shell CQDs could unprecedentedly achieve up to 90%, the underlying mechanisms, which, in turn, would offer guidelines for designing high quality CQDs, have not yet been explored so far [163]. In this part, we performed systematic steady state and time-resolved optical studies on a series of CdZnS-based CQDs, namely, CdZnS alloyed-core,

CdZnS/ZnS alloyed-core/sharp-shell (SS) and CdZnS/ZnS alloyed-core/alloyed-shell (AS) CQDs, aiming at revealing the corresponding physical reasons. The absorption spectra of the solutions of CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs with similar concentrations at room temperature are displayed in Figure 5.15. We can see that extra absorption at shorter wavelength of less than ~ 400 nm emerges for CdZnS/ZnS SS CQDs, corresponding to the absorption of ZnS shell, and the extra absorption increases for CdZnS/ZnS AS CQDs [196], suggesting the thickness of the ZnS shell grows during the long time annealing process, which is further confirmed by the size measurement via TEM. Figure 5.16 (a), (b) and (c) shows the TEM images of the CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs, from which the sizes are determined to be 6.8 nm, 9.4 nm and 11.4 nm for CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs, respectively.

Figure 5.17 (a) The schematic structure of CdZnS core, the corresponding TEM image is presented. (b) The schematic structure of CdZnS/ZnS SS CQDs, the

corresponding TEM image is presented. (c) The schematic structure of CdZnS/ZnS AS CQDs, the corresponding TEM image is presented.

The close-up of the absorption spectra around the band edge are presented in the inset of Figure 5.16 (a). The smearing out of the band edge exciton absorption peak after the coating of the ZnS shell is attributed to the deteriorated homogeneity in composition or size. The increased FWHM of the PL spectra of the CdZnS/ZnS SS and CdZnS/ZnS/AS CQDs further confirms the deterioration in size or composition uniformity. The blue-shift of the near band edge absorption of CdZnS/ZnS AS CQDs with respect to that of the CdZnS/ZnS SS CQDs indicates the inter-diffusion of Zn ions into the core or the interfacial alloying during the long time annealing process [163, 168]. The schematical illustrations of the structure of CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs are presented in Figures 5.17 (a), (b) and (c). The PL QY of the CdZnS core, CdZnS/ZnS SS and CdZnS/AS CQDs are measured to be ~10%, ~47% and ~90%, respectively, based on the same method using in Chapter 2. Importantly, for normal core-shell CQDs, such as the CdSe/CdS and CdSe/ZnS CQDs [34, 163, 172], the PL QY tends to be low with relatively thick shell due to the defect formation by the release of stress in the core-shell interface. In our case, the shell thickness of the CdZnS/ZnS AS CQDs, corresponding to ~7.5 monolayers, is exceptional large. However, the PL QY is abnormally high. It is firmly revealed that the low PL QY arises from the nonradiative recombination of the excited carriers related to the defect trapping [177]. As a result, the PL QY of CQDs could be enhanced by either reducing the surface/interface defects or/and separating the carries

from the surface/interface defects [197, 198]. In these CdZnS/ZnS AS CQDs, the sharp interface between the core and shell will get “soft” or alloyed owing to the inter-diffusion of Zn ion during the long time annealing process. As a result, the lattice mismatch existing between the Cd-rich core and the ZnS shell, thus the interface defects can be effectively released by interfacial alloying in these CdZnS/ZnS AS CQDs, which is further confirmed by the temperature-dependent PL measurements. Figures 5.18, 5.19 and 5.20 show the temperature dependent PL spectra of CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs from 10 K to 300 K, and the corresponding spectrally integrated PL intensities with respect to temperature is presented in Figure 5.21. We can see that the PL intensity of CdZnS cores decreases rapidly and only 8.5% of the PL intensity could be maintained as the temperature increases from 10 K to 300 K. While for CdZnS/ZnS SS CQDs, 36% of the initial PL intensity at 10 K can be sustained as the temperature increases to 300 K. In contrast, up to 82% of the initial PL intensity is able to be maintained for CdZnS/ZnS AS CQDs. As is known that surface or interface defects will act as the carrier trapping centers, where the nonradiative recombination happens, and more and more excited carriers will be trapped as the temperature increase. Therefore, the much decreased dropping of PL intensity in CdZnS/ZnS AS CQDs indicates that the surface or interface defects are greatly reduced compared to CdZnS core and CdZnS/ZnS SS CQDs. The absence of defect emission at around 620 nm of CdZnS/ZnS SS and CdZnS/ZnS AS CQDs at 10 K as shown in the inset of Figure 5.19 and 5.20 further suggests the reduction of interface and surface defects in CdZnS/ZnS AS CQDs. It is

worth noting that in contrast to the CdZnS core which shows monotonic decrease in PL intensity with the increase of temperature, the PL intensities of CdZnS/ZnS SS and CdZnS/ZnS AS CQDs both exhibit an anti-quenching behavior before quenching. This phenomenon was also previously observed in CdSe/CdS/ZnS core/multi-shell CQDs [199] and can be ascribed to the interplay between the nonradiative carrier trapping by the residual surface or interface defects and the thermal release of shallowly localized carriers in the interface into the radiative CdZnS-core, thus leading to the increase of the PL intensity. Moreover, it is found that the PL intensity of the CdZnS/ZnS SS CQDs increases faster than that of CdZnS/ZnS AS CQDs and achieves its maximum at 50 K, much earlier than that of CdZnS/ZnS AS CQDs (150 K), which suggests that less excited carriers are localized at the surface or interface defects in CdZnS/ZnS AS CQDs, thus further confirming the reduced surface/interface defects in CdZnS/ZnS AS CQDs.

Figure 5.18 PL spectra of CdZnS core with varied temperature from 10 K to 300 K.

The broad range PL spectrum at 10 K is presented as the inset.

Figure 5.19 PL spectra of CdZnS/ZnS SS CQDs with varied temperature from 10 K to 300 K. The broad range PL spectrum at 10 K is presented as the inset.

Figure 5.20 PL spectra of CdZnS/ZnS AS CQDs with varied temperature from 10 K to 300 K.

to 300 K. The broad range PL spectrum at 10 K is presented as the inset.

Figure 5.21 Plot of the spectrally integrated PL intensity of CdZnS/ZnS AS CQDs, CdZnS/ZnS SS CQDs and CdZnS core as a function of temperature from 10 K to 300 K.

The PL decay dynamics of the CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs were also shown in Figure 5.22. A rapid decay pathway is clearly observed in CdZnS core, which corresponds to the carrier trapping process [146, 197], and this rapid decay process is effectively mitigated in CdZnS/ZnS SS CQDs and is nearly negligible in CdZnS/ZnS AS CQDs, which again confirms that the CdZnS core could be well-passivated by the ZnS-shell and the interfacial alloying by long time annealing could further reduce the surface and interface defects.

Figure 5.22 Single exciton decay dynamics of CdZnS/ZnS AS CQDs, CdZnS/ZnS SS CQDs and CdZnS core.

5.6 Achieving ultralow-threshold stimulated emission and revealing the underlying mechanisms

To study the stimulated emission of the CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs, the self-assembled close-packed films of these CQDs were pumped using the stripe pumping configuration. The laser pulses with repetition rate of 1000 Hz, pulse-width of 100 fs and optical wavelength of 400 nm was employed as the laser source. Figures 5.23, 5.24 and 5.25 show the PL spectra of CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs, respectively, under gradually increased excitation intensities. We can see that all the samples can show spectral narrowing with the increasing of excitation intensity, indicating the occurrence of stimulated emission [9].

The plot of PL intensity versus excitation intensity are presented in the inset of

Figures 5.23, 5.24 and 5.25 shows an abrupt increase, which is the signature of the stimulated emission, thus further confirming the achievement of stimulated emission [200]. The stimulated emission thresholds are measured for dozens of films for individual of CdZnS core, CdZnS/ZnS SS and CdZnS/ZnS AS CQDs, shown in Figure 5.26, which demonstrates the reproducibility of the stimulated emission thresholds. Importantly, although the PL QY of CdZnS core is as low as ~10%, indicating the poor surface quality, it is still able to achieve stimulated emission, which indicates the carrier trapping is not the deadly obstacle towards stimulated emission for CQDs. Due to the better surface passivation by ZnS-shell, the stimulated emission threshold decreases to $\sim 160 \mu\text{J}/\text{cm}^2$ for CdZnS/ZnS SS CQDs compared to that ($\sim 260 \mu\text{J}/\text{cm}^2$) of the naked CdZnS core. Surprisingly, by virtue of the interfacial alloying through the long time annealing process, the record low stimulated emission threshold of $\sim 55 \mu\text{J}/\text{cm}^2$ in blue spectral range is achieved in CdZnS/ZnS AS CQDs.

Such a low threshold is one order of magnitude lower than that of the deliberately designed blue-emitting CdSe/ZnCdS CQDs [6]. The rapidly reduced stimulated emission threshold in these CdZnS/ZnS AS CQDs can be ascribed to the optimized surface passivation by interface alloying and, most importantly, to the further suppressed Auger recombination, the main optical loss under high excitation intensities, since the interfacial alloying has been theoretically and experimentally demonstrated to suppress Auger recombination in core-shell CQDs [50, 171] as will

be shown later.

Figure 5.23 Excitation intensity dependent PL spectra of CdZnS core, indicating the achievement of stimulated emission under high excitation intensities. The plot of PL intensity versus excitation intensity is presented in the inset, further confirming the development of stimulated emission.

Figure 5.24 Excitation intensity dependent PL spectra of CdZnS/ZnS SS CQDs, indicating the achievement of stimulated emission under high excitation intensities. The plot of PL intensity versus of excitation intensity is presented in the inset, further confirming the development of stimulated emission.

Figure 5.25 Excitation intensity dependent PL spectra of CdZnS/ZnS AS CQDs, indicating the achievement of stimulated emission under high excitation intensities.

The plot of PL intensity versus excitation intensity is presented in the inset, further confirming the development of stimulated emission.

Figure 5.26 The plot of the stimulated emission thresholds measured from dozens of films of CdZnS/ZnS AS CQDs, CdZnS/ZnS SS CQDs and CdZnS core.

To confirm the above assumption, the Auger recombination in the samples is investigated by streak camera system. Figure 5.27 (a) displays the exciton decay dynamics of CdZnS/ZnS SS CQDs under gradually increased excitation intensity. Under low excitation intensities, the PL decay is dominated by the single exciton recombination. With the increase of excitation intensity, an apparent rapid decay process appears, corresponding to the nonradiative Auger recombination [32]. Based on the subtraction procedure developed by Klimov *et al* [36, 38], the Auger lifetime of CdZnS/ZnS SS CQDs is extracted to be ~ 320 ps (inset in Figure 5.27 (a)), which is one order of magnitude longer than that of blue-emitting CdSe-based CQDs and

comparable to those of deliberately designed red-emitting CdSe-based CQDs. In doing the subtraction, the first step is to normalize the time transients to make the long-time decay values match for those under different excitation intensities, and then the low excitation intensity trace corresponding to the single exciton recombination was subtracted from the high excitation intensity decay trace to extract the Auger recombination path [36, 38]. The efficient carrier trapping process in CdZnS core makes the extraction of the Auger lifetime complicated. Nevertheless, we can treat the Auger recombination in CdZnS core the same as that in CdZnS/ZnS SS CQDs [9]. The exceptionally slow Auger recombination in CdZnS core and CdZnS/ZnS SS CQDs is attributed to the huge dot sizes, which makes them locate in the weak confinement regime [169]. As a result, the Auger recombination is not as efficient as that in blue-emitting CdSe-based CQDs. As shown in Figure 5.27 (b) and the inset in Figure 5.27 (b), similar to the variation of PL decay in CdZnS/ZnS SS CQDs, the fast Auger decay process, corresponding to the Auger recombination [32], appears as the excitation intensity increases in the CdZnS/ZnS AS CQDs, and the Auger lifetime is extracted to be ~650 ps, which is two times longer than that of CdZnS/ZnS SS CQDs. The suppressed Auger recombination in these CdZnS/ZnS AS CQDs compared to that in CdZnS/ZnS SS CQDs is ascribed to the gradient potential profile between the core and shell formed by the interfacial alloying effect, which suppresses the Auger recombination through the more strict momentum conservation than that in CdZnS/ZnS SS CQDs [51, 171]. By virtue of the further suppressed Auger recombination, the CdZnS/ZnS AS CQDs exhibit much lower stimulated emission

threshold than CdZnS/ZnS SS QDs, thus confirming the better optical gain properties than those of CdZnS core and CdZnS/ZnS SS CQDs.

Figure 5.27 (a) PL decay traces of CdZnS/ZnS SS CQDs with varied excitation intensity. The corresponding Auger lifetime extracted by the subtraction method is presented as the inset. (b) PL decay traces of CdZnS/ZnS AS CQDs with varied excitation intensity. The corresponding Auger lifetime extracted by the subtraction method is presented as the inset.

5.7 Solid-state external cavity-free high-Q quasi-toroid microlasers

As is well-known that CQD-lasers have many irreplaceable advantages over

traditional lasers, such as epitaxial semiconductor lasers, dye lasers, polymer lasers and so on [9]. Nevertheless, until now, almost all the CQD-based lasers are fabricated by incorporating CQDs into or coating onto deliberately designed external resonators with only a few exceptions, in which external cavity-free CQD-lasers were demonstrated [40, 129, 133, 201, 202]. However, all of these external cavity-free CQD-lasers possess relatively poor Q-factors [40, 159], thus limiting their practical applications. Herein, we produced external cavity-free quasi-toroid lasers with high Q-factors from self-assembly of CdZnS/ZnS AS CQDs by simple one-step inkjet printing technique, in which the CdZnS/ZnS AS CQDs serve as the optical gain media and, on the other hand, provide optical feedback by the total internal reflection around the ring wall formed by coffee stain effect [65, 72, 203]. The photograph of the microplotter as the fabrication setup is shown in Figure 5.28.

Figure 5.28 Photograph of the inkjet microplotter used for the laser device fabrication.

Figure 5.29 (a) Schematic drawing of the inkjet technique employed for the fabrication of CQD-microlasers. (b) Optical image of typical the CQD-disk array fabricated by the inkjet method. (c) High resolution SEM image showing the close-up of the CQD-disk. (c) Higher resolution SEM image showing the morphology of the edge of the CQD-disks.

For the laser device fabrication, the solution of CdZnS/ZnS AS CQDs (concentration: ~5 mg/mL) was firstly infiltrated into the nozzle of the microplotter through capillary effect. After that, the CQDs droplets were deposited onto the distributed Bragg reflector substrate via piezoelectric action [204]. After the evaporation of solvent, self-assembled solid-state CQD-disks were formed. Figure 5.29 (a) schematically portrayed the laser device fabrication process. The position and the size of the disks can be well-controlled by the microplotter system. The optical micro-image of the CQD-disk array with diameter of ~80 μm is shown in Figure 5.29 (b). By virtue of the coffee stain effect during the evaporation of the solvent, a ring

wall around the disk boundary was obtained. The scanning electron microscopy (SEM) in Figure 5.29 (c) clearly reveals the quasi-toroid structure. Importantly, the quasi-toroid structure is known to have better optical field confinement compared to that of the conventional disk with flat edge [65, 205]. Therefore, a high Q-factor is expected. Moreover, the surface of toroid is unraveled to be optically smooth as shown in Figure 5.29 (d) thanks to the hydrophobic ligands of the CQDs. As a result, the scattering loss can be effectively suppressed [205].

Figure 5.30 (a) Pump pulse energy dependent PL spectra from the self-assembled CQD-quasi-toroid. (b) Plot of the spectrally integrated PL intensity from the

self-assembled CQD-quasi-toroid as a function of pump pulse energy. (c) Optical image of individual self-assembled CQD-quasi-toroid illuminated by halogen lamp. (d) PL image of the individual self-assembled CQD-quasi-toroid. (e) Zoom-in of the lasing spectra from the individual self-assembled CQD-quasi-toroid, showing discrete and evenly spaced spikes.

To investigate the optical properties of the individual CQD-quasi-toroid, a micro-PL system as was described in Chapter 4 was employed. Figure 5.30 (a) shows the PL spectra of an individual quasi-toroid with diameter of $\sim 80 \text{ }\mu\text{m}$, whose optical image under halogen lamp is presented in Figure 5.30 (d), under gradually increased excitation pulse energies. We can see that sharp comb-like spikes emerges under high excitation energies, whose spectral position is nearly identical to that of the stimulated emission peak, suggesting the development of lasing action [129]. Further valid evidence of the occurrence of the lasing action is threshold behavior of the plot of the integrated PL intensity versus the excitation pulse energy. The zoom-in of the lasing spectra with excitation pulse energy of $9.5 \text{ }\mu\text{J/pulse}$ is displayed in Figure 5.30 (e), revealing the discrete evenly spaced spikes, from which the Q-factor is determined to be ~ 2500 [74]. The ring-shaped PL image above the lasing threshold of the quasi-toroid as shown in Figure 5.30 (c) indicates the whispering gallery mode lasing mechanism [74, 129]. Furthermore, by investigating the lasing spectra of the individual quasi-toroid with different size (Figure 5.31 (a)), the free spectral range is found to decrease with the increase of the size (Figure 5.31 (b)) and is unraveled to be in reverse proportion to the diameter of the quasi-toroid (Figure 5.31 (c)), thus

unambiguously validating the WGM lasing mechanism of these quasi-toroid lasers.

Figure 5.31 (a) Different sized self-assembled CQD-quasi-toroids fabricated by the inkjet technique. (b) The change of the free spectra range of the lasing spectra as the diameter of these self-assembled CQD-quasi-toroid increases. (c) Plot of the free spectral range as a function of the diameter of the CQD-quasi-toroid.

5.8. Summary

Through steady state and ultrafast spectroscopy studies, we reveal that the ternary alloy CdZnS/ZnS CQDs are intrinsic superior optical gain materials in blue spectral range thanks to the inborn slow Auger recombination. Based on the optimized CdZnS/ZnS alloyed-shell/alloyed-shell CQDs with further suppressed Auger recombination and minimized carrier trapping defects, we achieved ultralow-threshold stimulated emission from close-packed CQD thin films. Besides

manifesting the superior gain properties of ternary alloy CdZnS/ZnS CQDs, we realized liquid blue lasers by infiltrating the CQD solution into capillary tubes with such low thresholds that quasi-continuous pumping is accessible. We further adopted the novel and facile inkjet printing method to fabricate an external cavity-free quasi-toroid laser in solid state. We believe these results will attract wide range of attention and trigger more research on CQD-based microlasers.

Chapter 6

Green stimulated emission from quaternary CdZnSSe/ZnS alloy quantum dots

6.1 Introduction

In last chapter, we employed the ternary alloy blue-emitting CdZnS/ZnS CQDs, alternative to the conventional CdSe-based CQDs, to achieve ultra-low threshold stimulated emission and lasing. However, the spectral tunability of CdZnS/ZnS CQDs is merely limited in blue spectral region, roughly from 410 nm to 470 nm. On the other hand, green lasers are known to hold various of applications, ranging from illumination to display [1]. However, the ubiquitous epitaxial semiconductor lasers are still experiencing difficulties accessing the green regime due to the challenges in materials, known as “the green valley of death” [1, 2]. The emergence of CQD-lasers promises the addressing of the “green gap” issue. Unfortunately, the size of the conventional CdSe-based CQDs have to be reduced to ~2 nm in diameter to reach green emission [196], where the nonradiative Auger recombination is highly activated [36]. As a result, very few stimulated emission demonstrations are reported in green spectral range, and the thresholds are usually one order of magnitude higher than those of the red ones [6, 133]. Therefore, searching suitable green-emitting CQDs as the optical gain media turns to be imperative. Recently, the quaternary alloy CdZnSeS/ZnS core/shell CQDs are shown to be able to exhibit finely tunable emission across the green regime with high PL QY of up to ~80% by facile composition control. Moreover, based on these CdZnSeS/ZnS core/shell CQDs, the

best-performed green LED with the record high efficiency of 46.4 cd/A has been achieved. Nevertheless, the stimulated emission and lasing properties of these quaternary alloy CdZnSeS/ZnS core/shell CQDs have not yet been investigated. Herein, we, for the first time, study the optical gain properties of these CQDs, and achieved ultra-low threshold stimulated emission, which is attributed to the suppressed Auger recombination, minimal carrier trapping defects and the high absorption cross-section of these CdZnSeS/ZnS core/shell CQDs. Furthermore, high-quality organic/inorganic hybrid whispering gallery mode microlasers are realized by coating the CdZnSeS/ZnS CQDs onto the self-assembled polymer hemispheres.

6.2 Sample fabrication

The samples were provided by our collaborators. As a contrast experiment, the naked ternary alloy CdZnSeS CQDs is also fabricated and investigated. To grow CdZnSeS and CdZnSeS/ZnS core/shell CQDs, zinc oxide (ZnO) (3.41 mmol) and Cadmium acetate (Cd(ace)_2) (0.14 mmol) were dissolved in oleic acid (OA) (7 mL) in a round-bottom flask with three necks, whose temperature was increased to 150 °C under Argon (Ar) atmosphere. After that, 1-octadecene (ODE) (15 mL) was introduced into the solution and, then, the temperature was increased up to 310 °C. Subsequently, the anionic solution (1.9 mL) made by merging Selenide (Se) (5 mmol) and sulfur (S) (5 mmol) in trioctylphosphine (TOP) (5 mL) was quickly added into the prepared cationic mixture under high temperature of 310 °C. After that, the reaction was kept for 10 minutes for the growth CdZnSeS CQDs. To grow the quaternary alloy

CdZnSeS/ZnS core/shell CQDs, S (1.6 mmol) dispersed in ODE (2.4 mL) was introduced into the CdZnSeS CQDs at temperature of 310 °C. After reaction of 12 minutes, the Zn stock mixture prepared by dispersing Zn acetate dehydrate ($\text{Zn}(\text{ace})_2$) (2.86 mmol) into the mixture of OA (1 mL) and ODE (4 mL) was added into the above solution at temperature of 310 °C. After that, the solution was cooled down to 270 °C. At last, the S stock mixture prepared by dispersing S (9.65 mmol) into TOP (5 mL) was introduced into the prepared solution drop by drop and the reaction for the shell growth was kept for 20 minutes. The fabricated CdZnSeS and CdZnSeS/ZnS CQDs were cleaned for three cycles and re-dissolved in chloroform for the following experiments.

6.3 Steady state absorption and emission

Figure 6.1 (a) Room temperature absorption and emission spectra of CdZnSeS CQDs and CdZnSeS/ZnS core/shell CQDs. The schematic structures of CdZnSeS CQDs (left) and CdZnSeS/ZnS core/shell CQDs (right) are presented as the insets. (b) TEM image of CdZnSeS CQDs. (c) TEM image of CdZnSeS/ZnS core/shell CQDs.

Figure 6.1 (a) shows the linear absorption and emission spectra of CdZnSeS and CdZnSeS/ZnS CQDs at room temperature. The narrow PL emission FWHM and the sharp excitonic absorption peak suggest the fine uniformity in composition and size [206]. The PL QY of CdZnSeS and CdZnSeS/ZnS CQDs are measured to be ~40% and ~80%, respectively. The much increased PL QY of CdZnSeS/ZnS CQDs with respect to that of CdZnSeS CQDs is attributed to the improved surface passivation by the inorganic ZnS shell [207]. Noticeably, the excitonic absorption peak and the PL maximum wavelengths of CdZnSeS/ZnS CQDs are blueshifted compared to those of the CdZnSeS CQDs, indicating the interdiffusion of atoms between the core and shell, hence the interfacial alloying in the CdZnSeS/ZnS CQDs. Two beneficial effects can be provided by the interfacial alloying effect: 1) the lattice mismatch locating in the interface of the core and shell can be released, which leads to superior surface passivation for thick-shelled CQDs as was studied in detail in last Chapter, and the 2-fold increased PL QY with respect to that of the CdZnSeS CQDs; 2) the nonradiative Auger recombination can be potentially suppressed [50, 51]. Figure 6.1 (b) and (c) show the TEM images of CdZnSeS and CdZnSeS/ZnS CQDs, from which the sizes are determined to be ~9.6 nm and ~12.7 nm in diameter, respectively.

Importantly, the huge dot sizes makes these CQDs fall into the weak confinement regime, therefore the nonradiative Auger recombination is expected to be not efficient [208], thus facilitating the stimulated emission and lasing.

6.4 Photoluminescence decay dynamics

Figure 6.2 shows the single excitonic decay dynamics of CdZnSeS and CdZnSeS/ZnS CQDs monitored by the streak camera system. The solution of CdZnSeS and CdZnSeS/ZnS CQDs were filled in 1-mm-thick quartz cuvette, and the photographs of the samples under laser excitation are presented in the inset of Figure 6.2 (left: CdZnSeS CQDs; right: CdZnSeS/ZnS CQDs). It is found that the lifetime of CdZnSeS/ZnS CQDs (18.5 ns) is much increased compared to that of CdZnSeS CQDs (14.3 ns), which is attributed to the reduced nonradiative carrier trapping by the

Figure 6.2 PL decay of CdZnSeS and CdZnSeS/ZnS CQDs under low excitation intensity, corresponding to single exciton regime. The PL image of CdZnSeS (left) and

CdZnSeS/ZnS (right) CQDs storing in quartz cuvette are presented as the insets.

better surface passivation [146]. To access the Auger recombination in CdZnSeS and CdZnSeS/ZnS CQDs, the excitation intensity dependent PL decay dynamics were recorded. Figure 6.3 (a) displays the PL decay curves of CdZnSeS/ZnS CQDs monitored at the optical wavelength of PL maximum under gradually increased excitation intensities with excitation wavelength of 400 nm. It is found that the PL decay curve consists with the single exciton recombination when the excitation intensity is lower than $\sim 12 \mu\text{J}/\text{cm}^2$. With the further increase of excitation intensity, the rapid decay process emerges obviously, which corresponds to the nonradiative multi-exciton Auger recombination. Based on the subtraction procedure developed by Klimov *et al* [32, 36], the lifetime of Auger recombination is derived to be ~ 300 ps. As a comparison, the Auger recombination of CdZnSeS CQDs was also measured and displayed together with that of CdZnSeS/ZnS CQDs under the same excitation intensity of $46.7 \mu\text{J}/\text{cm}^2$. We can clearly see that the rate of the fast decay channel or the Auger recombination of CdZnSeS/ZnS CQDs is reduced with respect to that of CdZnSeS CQDs, which is derived to be ~ 230 ps. Importantly, the Auger lifetime of ~ 230 ps for CdZnSeS CQDs is dramatically higher than those of the conventional green-emitting CdSe-based CQDs and comparable to those of the conventional red ones [36]. Such a slow Auger recombination in CdZnSeS CQDs agrees with the above expectation and is ascribed to the extraordinarily big dot size, which makes the dots fall into the weak quantum confinement regime. The further increased Auger lifetime

of CdZnSeS/ZnS CQDs is attributed to the interfacial alloying effect as was experimentally demonstrated in last Chapter. The minimized carrier trapping defects and the suppressed Auger recombination by the alloyed shell could effectively reduce the optical loss, which benefits the achievement of low-threshold stimulated emission and lasing.

Figure 6.3 (a) The excitation intensity dependent PL decay curves of quaternary alloy

CdZnSeS/ZnS CQDs. (b) The PL decay curves of quaternary alloy CdZnSeS and CdZnSeS/ZnS CQDs under relatively high excitation intensity. (c) Plot of PL intensity of quaternary alloy CdZnSeS/ZnS CQDs after 1.2 ns upon photoexcitation as a function of excitation intensity.

6.5 Low threshold green stimulated emission via one- and two-photon pumping

To investigate the stimulated emission properties of CdZnSeS and CdZnSeS/ZnS CQDs, the thin films prepared by spin-coating the CQD solutions onto glass substrates were pumped with stripe configuration. The excitation source (optical wavelength: 400 nm, pulse-width: 100 fs and repetition rate: 1000 Hz) is provided by a femtosecond amplified pulse laser system. The PL spectra of CdZnSeS and CdZnSeS/ZnS CQDs under gradually increased excitation intensity are presented in Figure 6.4 and 6.5, respectively. We can see that the PL spectra of the samples are dictated by the relatively broad spontaneous emission. Whilst, as the excitation intensity keeps increasing, a sharp peak on the right side of the corresponding spontaneous emission appears, suggesting the achievement of stimulated emission [189]. The PL intensity of the emerging peak versus excitation intensity is plotted in the insets in Figure 6.4 and 6.5, which shows a threshold behavior, hence further validating the development of stimulated emission [9]. Moreover, the thresholds are determined to be ~ 180 and $\sim 80 \mu\text{J}/\text{cm}^2$ for CdZnSeS and CdZnSeS/ZnS CQDs, respectively. The decreased stimulated emission threshold of CdZnSeS/ZnS CQDs compared to that of CdZnSeS CQDs can be ascribed to the reduced optical loss by the

slower Auger recombination and better surface passivation. Importantly, the stimulated emission threshold of CdZnSeS/ZnS CQDs represents of the lowest value for green-emitting CQDs and is comparable to those of the best red-ones [6]. Besides the reduced optical gain loss, another possible reason for the ultra-low threshold can be the large absorption cross-section of CdZnSeS/ZnS CQDs owing to the huge dot size. In order to extract the absorption cross-section of CdZnSeS/ZnS CQDs at optical wavelength of 400 nm, we make full use of the features of the Auger recombination and the spontaneous emission. Thanks to the much faster Auger recombination compared to the radiative spontaneous emission, all of the excited CdZnSeS/ZnS CQDs will relax to single exciton state when the Auger recombination is completed. As a result, the PL intensity after decay of 1.2 ns is in proportion to the ratio of the excited CQDs in the ensemble, which is described by [194]: $1 - P_0$, where $P_0 = e^{-\langle N \rangle}$ denotes the portion of the non-excited CQDs. From the best-fit of the data, the absorption cross-section of CdZnSeS/ZnS CQDs at excitation wavelength of 400 nm is determined to be $\sim 8 \times 10^{-15} \text{ cm}^2$, which is much higher than those of the conventional binary green-emitting CdSe-based CQDs [209]. Furthermore, the model gain of the CdZnSeS/ZnS CQDs was extracted by the standard variable stripe length (VLS) technique. From the best-fitting (Figure 6.6) of the data by equation [44]:

$$I = (A/g)(e^{gL} - 1)$$

where A is the coefficient and g is the model gain, which is determined to be $\sim 96 \text{ cm}^{-1}$ at excitation intensity of $130 \text{ } \mu\text{J}/\text{cm}^2$. Such a high value is comparable to those of the best red-emitting CQDs [6].

The two-photon pumped stimulated emission property was also investigated on CdZnSeS/ZnS CQDs. To do so, the thin film of close-packed CdZnSeS/ZnS CQDs was pumped by the stripe configuration at optical wavelength of 800 nm. As shown in Figure 6.7, the appearance of spectral narrowing phenomenon and the nonlinear increase behavior of PL intensity versus the excitation intensity suggest the development of two-photon induced stimulated emission, and the corresponding threshold is determined to be $\sim 8.2 \text{ mJ/cm}^2$, which is even lower than those of the red ones [145], thus further confirming the superior optical gain performance of these CdZnSeS/ZnS CQDs.

Figure 6.4 PL spectra of CdZnSeS CQDs with gradually increased excitation intensity, indicating the achievement of stimulated emission. The PL intensity versus excitation intensity is presented as the inset, further confirming the development of stimulated emission.

Figure 6.5 PL spectra of CdZnSeS/ZnS CQDs with gradually increased excitation intensity, indicating the achievement of stimulated emission. The PL intensity versus excitation intensity is presented as the inset, further confirming the development of stimulated emission.

Figure 6.6 Plot of PL intensity as a function of excitation stripe length under fixed excitation intensity of $130 \mu\text{J}/\text{cm}^2$.

Figure 6.7 PL spectra of CdZnSeS/ZnS CQDs under excitation wavelength of 800 nm with gradually increased excitation intensity, indicating the achievement of stimulated emission induced by two-photon pumping. The PL intensity versus excitation intensity is presented as the inset, further confirming the development of two-photon

stimulated emission.

6.6 All solution processed micro-lasers

To directly demonstrate the potential of these CdZnSeS/ZnS CQDs as optical gain material, we produced a real laser device by coating these CQDs onto a self-assembled polymer hemisphere. Distributed Bragg reflector was employed to realize 3-dimensional optical confinement. Figure 6.8 (c) shows optical micro-image of the naked self-assembled polymer (mixture of epoxy resin and hardner (ratio 10:1)) hemispheres, and Figure 6.8 (d) displays the optical micro-image of a typical hemisphere covered with the CdZnSeS/ZnS CQDs. The structure of the prepared organic/inorganic hybrid micro-laser is schematically drawn in the inset of Figure 6.8 (a). To investigate the optical properties of individual laser device, the home-built micro-photoluminescence system is employed. As for the excitation source, a nanosecond laser system was adopted. The power dependent PL spectra of a typical laser device with size of $\sim 22\text{ }\mu\text{m}$ in diameter are presented in Figure 6.8 (a). We can see that the PL spectra under excitation intensities lower than $\sim 12.5\text{ }\mu\text{J/pulse}$ is dictated by the broad spontaneous emission. As the excitation intensity keeps increasing, sharp spikes appear, which are evenly spaced, suggesting the achievement of lasing action [61]. The plot of the PL intensity over these spikes show abrupt increase versus excitation intensity, further confirming the development of lasing [45], and the lasing threshold is determined to be as low as $\sim 12.5\text{ }\mu\text{J/pulse}$, corresponding to $\sim 10.4\text{ mJ/cm}^2$. The PL images of the micro-laser under pump intensity below and

above threshold are shown in Figures 6.8 (e) and (f), respectively. A clear bright corona-like emission pattern is observed during the development of lasing action, attributing the lasing mechanism to the whispering gallery mode lasing in these micro-lasers [74, 210]. Furthermore, the lasing spikes can be well assigned according to WGM model, thus validating the WGM origin of these micro-lasers [74].

Figure 6.8 (a) Excitation intensity dependent PL spectra from single CQD-coated hemisphere microlaser. The PL intensity versus excitation intensity is presented as the left inset. The right inset depicts the structure of the hemisphere laser. (b) The assignment of the lasing peaks based on the WGM model. (c) Optical image of a

typical self-assembled hemisphere illuminated by halogen lamp. (d) Optical image of a typical CQD-coated self-assembled hemisphere illuminated by halogen lamp. (e) PL image of the microlaser below lasing threshold. (f) PL image of the microlaser under excitation intensity exceeding the threshold. Scale bar denotes 10 μm .

6.7 Summary

By employing the quaternary alloy CdZnSeS/ZnS core/shell CQDs as the optical gain media in green spectral range, we observed ultra-low threshold stimulated emission upon both 1- and 2-photon excitation. Real laser devices were fabricated by coating these CQDs onto self-assembled polymer hemispheres. These results hold the potential for the overcoming the “green gap” issue experiencing in epitaxial semiconductor lasers.

Chapter 7

Conclusions and future work

7.1 Conclusions

In this thesis, the emission and optical gain properties upon one- and multi-photon excitation of CQDs have been investigated. In Chapter 3, the third-order nonlinear optical studies indicate the heavy metal-free InP/ZnS CQD to be promising fluorescent two-photon bio-probes. In Chapter 4, the direct three-photon induced stimulated emission and lasing have been achieved for the first from CQDs by employing the CdSe/CdS/ZnS core/shell/shell CQDs, which could offer new possibilities in a wide range of fields. In Chapter 5, record low threshold stimulated emission in blue region has been observed from ternary alloy CdZnS/ZnS core/shell CQDs, and liquid blue lasers under quasi-continuous wave pumping have been realized. Comprehensive steady state and ultra-fast optical studies have been performed on a series of CdZnS-based CQDs in order to reveal the underlying mechanism and exploring general rules for designing CQDs for low-threshold lasers. In Chapter 6, the optical gain properties of green-emitting quaternary alloy CdZnSeS/ZnS core/shell CQDs were investigated for the first time, revealing the great potential in overcoming the “green gap” seen in epitaxial semiconductor lasers. Our studies will facilitate the research in developing CQD-based emitters and lasers and provide new possibilities in photonics and optoelectronics.

7.2 Future work

1. Exploring novel heavy-metal-free CQDs

Until now, the most successfully fabricated and comprehensively studied CQDs are heavy-metal-contained [32]. The potential hazard of these CQDs greatly limits their practical applications, including bio-sensing and bio-imaging [127]. Therefore, it is imperative to explore novel heavy-metal-free CQDs to replace the conventional toxic Cd-contained CQDs. Recently, the environment-friendly carbon-based CQDs have attracted increasing attention due to the nontoxicity, facile and wide range wavelength tunability across the whole visible range and the bio-compatibility [211, 212]. However, up till now, detailed optical studies including the multi-photon absorption and emission, which are of crucial importance toward applications in biology, photonics and their interactions of biophotonics has been rarely investigated, thus leaving a plenty room for future study.

2. Continuous wave lasing in CQDs

Most of the stimulated emission and lasing demonstrations are based on the ultra-short optical pulse excitation, such as tens of femtosecond and a few picosecond pulses, while only a few reports are using the nanosecond or longer optical pulses [42, 44], where the lasers were operating in quasi-continuous wave regime. However, it is still extremely challenging toward continuous-wave (CW) lasing, which holds a wide range of applications. Recently, by employing the two-dimensional CdSe colloidal quantum well with greatly suppressed Auger recombination as the optical gain media, Moreels *et al.* have achieved CW lasing [213]. However, the photoluminescence wavelength of colloidal quantum wells can only be tuned in discrete steps due to the one-dimensional quantum confinement, in stark contrast to that in CQDs [213]. As a

result, exploring and developing CW lasing in CQDs, whose emission spectra can be finely tuned, becomes imperative in order to approach broadened practical applications.

3. Electrical pumping in CQD-lasers

Although optically pumped stimulated emission and lasing has been achieved from CQDs, it is extremely challenging to realize electrical pumping in CQD-laser because of the insulating organic ligands surrounding the CQDs [214], which blocks the electric injection. Although some ideas have been put forward, such as the indirect electric pumping by resonant energy transfer and electrically driven laser diodes excitation [214], they cannot radically solve the difficulty of direct electric injection. With the development in synthesis of CQDs, the previously inevitable organic ligands during the nucleation and growth of CQDs become not necessary. For example, Talapin *et al.* have successfully replaced the organic ligands by the inorganic ones including S^{2-} , Se^{2-} and Te^{2-} , thus acquiring the so-called all-inorganic CQDs, and efficient electric injection has been achieved from these CQDs [215, 216]. However, further efforts are required to reduce the surface defects and maintain the high-quality of the CQDs after ligand exchange [216], so as to reduce the optical loss and, eventually, approach the direct electric pumping CQD-lasers.

4. Miniaturizing CQD-lasers and developing novel-structured CQD-lasers

Nanophotonics has become an explosively developed area due to its fundamental interests and the wide range of potential applications. Miniaturized lasers with sizes at

sub-wavelength scale have been achieved leveraging on plasmonics, where semiconductor wires and disks are employed [217, 218]. However, the spectral tunability of these lasers is limited. Thanks to the facile emission color control by size and composition tailoring, the exploration of CQD-based plasmon lasers with minimized sizes turns out to be interesting in both fundamental and applied research. On the other hand, by virtue of the solution processibility, CQDs can be easily coated onto or incorporated into different kinds of cavities, and external cavity-free CQD-lasers have also been realized [6, 61]. Whilst, developing novel-structured CQD-lasers remains to be hot and promising research spot.

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Publications

A. Journal articles

1. **Y. Wang**, X. Yang, T. C. He, Y. Gao, H. V. Demir, X. W. Sun, H. D. Sun, [Applied Physics Letters](#) 102 (2), 021917 (2013)
2. **Y. Wang**, V. D. Ta, Y. Gao, T. C. He, R. Chen, E. Mutlugun, H. V. Demir, H. D. Sun, [Advanced Materials](#) 26 (18), 2954 (2014)
3. **Y. Wang**, K. S. Leck, V. D. Ta, R. Chen, V. Nalla, Y. Gao, T. He, H. V. Demir, H. D. Sun, [Advanced Materials](#) 27 (1), 169 (2015) (Selected as the Frontpiece image)
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