Modulation of excitonic response in colloidal low-dimensional nanomaterials

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2020

Yu, J. (2020). Modulation of excitonic response in colloidal low-dimensional nanomaterials.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/137766>

<https://doi.org/10.32657/10356/137766>

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**Modulation of Excitonic Response in Colloidal Low-
Dimensional Nanomaterials**

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SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

April 2020

Modulation of Excitonic Response in Colloidal Low-Dimensional Nanomaterials

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A thesis submitted to the Nanyang Technological University in
partial fulfillment of the requirement for the degree of Doctor
of Philosophy

April 2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Yu Junhong

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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(Steve) Cuong Dang

Authorship Attribution Statement

This thesis contains material from three papers published in the following peer-reviewed journals in which I am listed as the first author.

The first part of Chapter 2 (Chapter 2.2) is published as Yu, J.; Sharma, M.; Li, M.; Hernandez-Martinez, P. L.; Delikanli, S.; Sarma, A.; Altintas, Y.; Hettiarachchi, C.; Sum, T.; Demir, H. V.; Dang, C. Sustained biexciton emission in colloidal quantum wells assisted by dopant-host interaction. 2019, *arXiv*:**1905.11571**.

The contributions of the co-authors are as follows:

- Asst Prof. Cuong Dang and Prof. Hilmi Volkan Demir supervised and contributed to all aspects of the research.
- I, Dr. Manoj Sharma, Prof. Hilmi Volkan Demir and Asst Prof. Cuong Dang wrote the manuscript.
- I conducted the spectroscopy measurement and proposed the coupled kinetic model.
- I and Chathuranga Hettiarachchi conducted low-temperature emission spectroscopy measurement.
- Dr. Manoj Sharma performed the material synthesis and designed them to achieve the best Biexciton lasing performance.
- Dr. Savas Delikanli and Ashma Sharma helped in material synthesis and characterizations.

- Dr. Mingjie Li performed lifetime and transient absorption measurement. Dr. Mingjie Li and Prof. TzeChien Sum supervised the ultrafast dynamic analysis.
- Dr. Pedro Ludwig Hernández-Martínez conducted the Hamiltonian calculation to predict the biexciton binding energy.
- Dr. Yemliha Altintas conducted the material characterization.
- All authors analysed the data, discussed the results, commented on the manuscript and participated in manuscript revision.

The second part of Chapter 3 (Chapter 3.3) is published as Yu, J.; Sharma, M.; Delikanli, S.; Birowosuto, M. D.; Demir, H. V.; Dang, C. Mutual Energy Transfer in a Binary Colloidal Quantum Well Complex. *J. Phys. Chem. Lett.* **10**, 17, 5193-5199 (2019). DOI: 10.1021/acs.jpcclett.9b01939.

The contributions of the co-authors are as follows:

- Asst Prof. Cuong Dang and Prof. Hilmi Volkan Demir led and supervised all aspects of the research.
- I and Asst Prof. Cuong Dang initiated the idea.
- I, Prof. Hilmi Volkan Demir and Asst Prof. Cuong Dang wrote the manuscript.
- I and Dr. Muhammad Danang Birowosuto performed the PL dynamics measurement;
- I conducted the PLE measurement.
- I and Asst Prof. Cuong Dang built up the model to characterize FRET from PLE spectroscopy.

- Dr. Manoj Sharma performed the d-CQW and u-CQW synthesis and optimized them to achieve the best performance. Dr. Savas Delikanli helped in material synthesis and characterizations.
- All authors analyzed the data, discussed the results, commented on the manuscript, and participated in manuscript revision.

The Chapter 5 is published as Yu, J.; Shendre, S.; Koh, W.-K.; Liu, B.; Li, M.; Hou, S.; Hettiarachchi, C.; Delikanli, S.; Hernandez-Martinez, P. L.; Birowosuto, M. D.; Wang, H.; Sum, T.; Demir, H. V.; Dang, C. Electrically control amplified spontaneous emission in colloidal quantum dots. *Sci. Adv.* **5** : eaav3140 (2019). DOI: 10.1126/sciadv.aav3140.

The contributions of the co-authors are as follows:

- Asst Prof. Cuong Dang initiated the idea and led, supervised, and contributed to all aspects of the research.
- Prof. Hilmi Volkan Demir initiated and supervised the CQD synthesis and capacitor device fabrication.
- I, Prof. Hilmi Volkan Demir and Asst Prof. Cuong Dang wrote the manuscript.
- I, Dr. Sushant Shendre and Dr. Baiquan Liu fabricated the device;
- I performed the ASE measurements and the steady-state absorbance measurement.
- I, Songyan Hou, and Dr. Muhammad Danang Birowosuto performed the PL dynamics measurement.
- Dr. Mingjie Li conducted the fluence-dependent lifetime measurement.
- I and Cuong Dang conducted the kinetic model simulation.

- Dr. Sushant Shendre and Dr. Savas Delikanli synthesized the CdSe/CdS/ZnS CQDs.
- Dr. Pedro Ludwig Hernández-Martínez conducted the COMSOL simulation.
- Chathuranga Hettiarachchi, Dr. Weon-kyu Koh, and I performed the SEM and TEM measurements.
- Prof. TzeChien Sum and Prof. Hong Wang discussed the results and provided the technical advice.
- All authors discussed the results, commented on the manuscript, and participated in the manuscript revision.

25-10-2019

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Date

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Yu Junhong

Stay humble, stay confident, and moving on

To those who are suffering from peer pressure

New York is 3 hours ahead of California, but it does not mean that California is slow, or that New York is fast. Both are working based on their own time zone.

Someone graduated at the age of 22 but waited for 5 years before securing a good job. And there is another who graduated at 27 and secured employment immediately.

Someone is still single. Someone got married and 'waited' 10 years before having a child. While there is another who had a baby within a year of marriage.

Steve Jobs became CEO at 25, while Ren Zhengfei established HUAWEI at 50. Barack Obama retired at 55, but Donald Trump started the presidency at year of 70.

Absolutely, everyone in this world works based on their own time zone. Your colleagues, friends, younger ones might "seem" to go ahead of you. Don't envy them, they are in their 'Time Zone' and you are in yours. Life is about waiting for the right moment to act and God has a different plan for everybody.

So, relax, hold on, be strong, and stay true to yourself.

All things shall work together for your good.

You are not late.

You are not early.

You are very much on time.

To my beloved family

Acknowledgements

To my supervisor, colleagues, collaborators and friends who made this thesis possible:

First and foremost, I would like to express the greatest gratitude to my supervisor, Assistant Professor (Steve) Cuong Dang, for his immeasurable and invaluable guidance during my PhD study. I will never take your support and encouragement for granted. Every single moment that we went through together is buried in my mind forever: I still remember when I joined the group, I knew nothing about the nanomaterials and how patient you are to explain those terms and mechanisms to me; I still remember how much I struggled during my first year, it is you accompanying me and working together in the optical lab until midnight; I still remember those laughter and tears when we submitted our work and waited for the response. I am entirely lucky to finish this journey with you, THANK YOU, Man!!!

I give my special acknowledgement to Prof. Hilmi Volkan Demir and Dr. Muhammad Danang Birowosuto, who have been phenomenal collaborators and mentors. Prof. Volkan's scientific insights and expertise on colloidal nanomaterials really enhanced the quality of my research work. Those fruitful discussions with Dr. Danang enabled me to have a deeper understanding about photonic and plasmonic physics.

Sincere appreciations are given to Dr. Manoj Sharma and Dr. Shendre Sushant. Dr. Manoj provided the high-quality nanomaterials, and more importantly, he broadened my understanding of materials science from a variety of different perspectives. Dr. Sushant taught and trained me from device fabrication to operation. Even though we only worked together for half of a year, his outstanding experimental skills and shining personality inspired me a lot.

I would like to thank all my past and present group mates and collaborators; without the help and valuable discussion from your guys, all of my research works would not have been

possible. I thank Dr. Mingjie Li, Dr. Dongliang Tang and Dr. Baiquan Liu for always being “elder brothers”. Mr. Aozhen Xie, Dr. Yuan Gao, Dr. Dong Wang, Mr. Songyan Hou and Mr. Chathuranga Hettiarachchi for their friendship. Dr. Vijay Sharma, Dr. Fei Yan, Dr. Pedro Martinez, Dr. Weon-Kyu Koh, Dr. Yiping Zhang, Dr. Emek Durmusoglu, Dr. Landobasa Tobing, Dr. Savas Delikanli, Dr. Zhenwei Xie, Ms. Ashma Manoj, Dr. Yimeng Wang, Dr. Lin Wang, Dr. Philip Anthony Surman and Dr. Francesco Maddalena for your kindly help and sharing fun.

I also would like to thank the technical staffs at *LUMINOUS!*: Ms. Vino Prabakaran and Mr. Ng Yong Chiang, for making those paper-works and admin procedures easier.

Abstract

Colloidal low-dimensional nanomaterials (CLDNMs), benefitting from the solution-processability, quantum-confinement effect and high quantum efficiency, are prominent candidates to prevent the end of Moore's law and maintain the ever-accelerating progress in the field of optoelectronics. In the last two decades, tremendous research efforts have been concentrated on monitoring, understanding the photophysics in CLDNMs and uncovering that confined excitons are responsible for these extraordinary properties. Therefore, the daunting challenge to realize the potential of these CLDNMs in practical applications is to control, manipulate and eventually modulate the excitons. Considering the limitation of extensively investigated quantum confinement engineering based- or chemical structure engineering based-modulation, how to master intra- and inter-particle excitonic processes in CLDNMs via newly-developed technologies are crucial for future innovation.

This thesis is devoted to the study of excitonic modulation of CLDNMs beyond the conventional quantum confinement engineering based- or chemical composition based-methods, through both synthesis modification and post-synthesis treatment. Specifically, for excitonic modulation during synthesis process, we proposed that doped transition metal ions (e.g., Cu, Ag or Mn) can be utilized to generate an anisotropic Coulomb environment in the CLDNM host and thus, modulate the intrinsic properties of excitonic carriers. For excitonic modulation under post-synthesis condition, we first explored the usage of Förster resonance energy transfer (FRET) as a tool-kit to modulate the inter-particle excitonic processes in the assembly of two distinct CLDNMs. We then studied the interaction between excitons in CLDNMs and localized surface plasmon (LSP) sustained in metallic nanostructures to convert the energy stored in excitons into the bosonic quasi-particles (polaritons). Finally, we

investigated the effect of excess electrons in the conduction band on the excitonic gain performance of CLDNMs.

For synthesis modification, our key achievements include demonstration of room-temperature biexciton emission under continuous-wave excitation enabled by dopant-host interaction and ultra-low threshold biexciton lasing resulted from reduced Coulomb screening; For post-synthesis treatment, our main contributions are reflected in: i). Designing an all-optical strategy to manipulate the exciton flow between the donor-acceptor pair through stimulated emission mediated FRET and breaking the limitation of unidirectional exciton flow in conventional binary FRET scheme by utilizing the d orbital electrons in dopants; ii). For the first time, demonstrating that the ultrastrong exciton-plasmon coupling (Rabi energy larger than 400 meV) and high cooperativity (exceeding 11) can be achieved using Wannier-Mott excitons; iii). In a long-sought practical device, revealing that the negative Trion can be utilized to tune the excitonic gain performance.

Our works have proposed and demonstrated several new ways to modulate the excitonic processes in CLDNMs. The developed concepts, mechanisms and methods can be readily applied to other quantum-confined systems (e.g., perovskites and 2D transition metal dichalcogenides). We hope that these works can play the role of throwing out a minnow to catch a whale, in the development of excitonic or optoelectronic devices.

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Chapter 1: Introduction

Since the first semiconductor transistor was introduced in 1947, our world has been dramatically changed by the development of semiconductor optoelectronics in the last century^[1]. Through decades of researches' painstaking efforts, nowadays, conventional semiconductor optoelectronics, which suffers from the limitation of large device dimension (the size is restricted by the diffraction limit of photon wavelength) and interconnection delay (the interconnection between electronic processing and optical communication slows down the operation speed), is approaching the end of Moore's law^[2-4]. Utilizing the exciton, an optically active medium, instead of electron, an optically inactive medium, is of particular interest to maintain the contribution of semiconductor devices to the third industrial revolution, considering that excitons can directly link to photons to eliminate the delay^[5] and excitons with De Broglie wavelength of ~ 10 nm at room temperature can effectively improve the compactness^[6].

Meanwhile, quantum technology, which has been predicted to be the main driving force to trigger the fourth industrial revolution^[7], is also having all kinds of connection to excitonics. For instance, one of the fundamental difficulties of quantum computing is to overcome the decoherence of quantum qubits since quantum states are dramatically sensitive to the surroundings^[8]. Degenerate excitons, which can condense into the lowest quantum state and form a Bose-Einstein condensate (BEC), are the most practical way to stabilize those quantum states considering that quantum effects in BEC are visible on a macroscopic level rather than an extremely microscopic level for engineer to operate^{[9][10]}. Furthermore, the radiative decay of biexcitons is the most efficient and reliable way to generate the interdependent photon pairs (entanglement), which is the cornerstone of quantum technology^{[11][12]}.

Consequently, semiconductors which support stable, efficient and accessible excitons at room temperature are essentially needed and have strategic importance. Thanks to their quantum confinement environment (supporting the exciton with binding energy up to ~ 100 meV to avoid thermal disassociation)^[13], high quantum yield (significantly reducing the non-radiative loss caused by traps and defects enabled by room-temperature colloidal epitaxy synthesis)^[14] and solution processability (permitting upscaling capability on arbitrary substrates with high uniformity and low cost)^[15], colloidal low-dimensional nanomaterials (CLDNMs) are undoubtedly prominent testbed to design, examine, optimize and understand the next-generation devices.

Before the discussions of excitonic works on CLDNMs, chapter one as the introduction part will cover the following content: i). The basic concepts of excitons needed throughout the thesis, including the steady-state (energy band) and dynamical properties of excitons in CLDNMs; ii). The most representative progress in excitonic research in recent years; iii). An overview of the thesis, including our motivation and objectives according to the on-going research focus in the field of excitonics, major achievements and the outline.

1.1 Excitonic properties

One of the most important consequences of low dimensions in semiconductor is the significantly enhanced Coulomb interaction between the hole in valence band and the electron in conduction band because of a forced overlap of wavefunction overlap between the electron-hole pair and reduced dielectric screening^{[16][17]}. The enhanced wavefunction overlap is easy to understand due to the finite potential boundary and the reduced screening is resulting from the leakage of the electric field of the low-dimensional semiconductor into the surrounding medium (e.g., organic ligands, solvent or air), which typically has a smaller dielectric constant compared to semiconductor materials^[18]. As a consequence of the strong Coulomb interaction,

the electron/hole pair in low-dimensional semiconductor, instead of moving freely, is bounded together and form a hydrogen-like quasi-particle called an exciton^[19]. The formation of the bounded states will lower the energy of free electron/hole pairs, which is described by the exciton binding energy: $E_{exciton} = E_{free\ electron/hole\ pair} - E_{binding}$.

The steady-state properties of excitons (i.e., the transition energy), which are determined by the energy band of CLDNMs, is directly linked to the photoluminescence-related application (e.g., display, lighting, optical communication and biological labelling); and the dynamic properties of excitons, which resolves the accumulation/disassociation ability of excitons, is significantly crucial to those transient-based application (e.g., optical gain, light harvesting, photon-matter interaction and single photon emission). These two properties will be discussed in detail in this part.

1.1.1 Steady-state properties

The steady-state properties of excitons in semiconductor is determined by the energy band: the energy dispersion inside the empty conduction band and the occupied valence band^[20]. In bulk semiconductors, the energy band is fixed and determined by the composition and lattice structure; While, CLDNMs, which fall within a regime intermediate of microscopic atoms/molecules and macroscopic bulk, provides entirely new avenues to reshape the energy band structure in semiconductors.

In CLDNMs, when the of the particle is comparable or even smaller than the free motion length of electron/hole pair (the Bohr radius), the motion of energetically low-lying carriers will be bounded and accordingly, the structure of energy band will be tailored^{[16][17]}. This so-called ‘quantum confinement effect’ can be used to control the steady-state properties of excitons and its physical meaning will be discussed. In bulk semiconductors, an electron is affected by an effective periodic lattice potential ($V(\vec{r})$) given by the surrounding electrons

and the positively charged protons in the nuclei. Using the Bloch theory, the wavefunction of electrons can be expressed by^[21]:

$$\psi_e(\vec{k}, \vec{r}) = e^{i\vec{k} \cdot \vec{r}} u_\lambda(\vec{k}, \vec{r}) \quad (1.1)$$

where $\vec{k}$ and $\vec{r}$ are the wave-vector and space vector, respectively. $u(\vec{k}, \vec{r})$ is the Bloch function and satisfied the lattice periodicity in real space: $u(\vec{k}, \vec{r}) = u(\vec{k}, \vec{r} + \vec{R})$. $\vec{R}$ is the lattice cycle vector. λ is the energy eigenvalue.

Assuming the size is infinite in bulk, a plane wave ($e^{i\vec{k} \cdot \vec{r}}$) can be used as the envelop function. However, in CLDNMs, due to the confinement, the envelop function must vanish at the boundary of the particle. As a result, a quantized standing wave (ζ_λ^ν , ν is the quantum number) is utilized to replace the plane wave and the wavefunction of electrons in CLDNMs is shown as^{[21][22]}.

$$\psi_e(\vec{k}, \vec{r}) = \begin{cases} \zeta_\lambda^n(z) e^{i(k_x x + k_y y)} L_z^{-1} u_\lambda(\vec{k}, \vec{r}) & \text{for 2D} \\ \zeta_\lambda^m(x) \zeta_\lambda^p(y) e^{i(k_z z)} L_x^{-\frac{1}{4}} L_y^{-\frac{1}{4}} u_\lambda(\vec{k}, \vec{r}) & \text{for 1D} \\ \zeta_\lambda^n(z) \zeta_\lambda^m(x) \zeta_\lambda^p(y) u_\lambda(\vec{k}, \vec{r}) & \text{for 0D} \end{cases} \quad (1.2)$$

where, 2D, 1D and 0D means the confinement in z-direction (e.g., quantum wells), the confinement in x- and y-direction (e.g., quantum wires), the confinement in all three directions (e.g., quantum dots), respectively.

Plugging these wavefunction into the time-dependent Schrodinger equation with the effective mass approximation:

$$H(t)\psi_e = \left[\frac{p^2}{2m^*} + V(t) \right] \psi_e = i\hbar \frac{\partial \psi}{\partial t} \quad (1.3)$$

where p is the electron momentum and m^* is the effective mass of electron.

Then we can solve the density of states (ρ , DOS) which is close to the conduction band^{[21][22]}:

$$\rho \propto \begin{cases} (E - E_g^{bulk})^{\frac{1}{2}} & \text{for bulk} \\ H(E - E_n) & \text{for 2D} \\ (\frac{1}{E - E_n})^{\frac{1}{2}} & \text{for 1D} \\ \delta(E - E_n) & \text{for 0D} \end{cases} \quad (1.4)$$

where E_n is the energy Eigenvalue of permitted transition for n_{th} quantum number. E_g^{bulk} is the energy band gap of bulk semiconductor. H is the Heaviside step function and δ is the delta function.

Also, the energy band gap in CLDNMs (when $n=1$) can be resolved^{[22][23]}:

$$E_g = E_g^{bulk} + \begin{cases} \frac{\hbar^2 \pi^2}{m^* L^2} & \text{for 2D} \\ \frac{\alpha \hbar^2 \pi^2}{m^* L^2} & \text{for 1D} \\ \frac{\beta \hbar^2 \pi^2}{m^* L^2} & \text{for 0D} \end{cases} \quad (1.5)$$

where L is the smallest dimension size in the low-dimension semiconductors. α and β are the experimental determined factors which satisfied: $\beta > \alpha > 1$.

These calculation results are visualized in **Figure 1.1** and the energy band in CLDNMs is strongly modified by the quantum confinement effect in two aspects: i). The DOS in bulk is continuous and proportional to the square root of energy; Whereas in CLDNMs, the DOS is strongly quantized: for 2D materials, the DOS is a step function; and for 1D materials, singularity appears in the DOS distribution; while for 0D materials, the DOS is a delta

function which is quite similar to the behaviours of single atom/molecule; ii). At the same time, the band gap in CLDNMs is enlarged with a confinement-related factor.

Figure 1.1 Modification of energy band in CLDNMs due to the quantum confinement effect. ρ is the DOS; CB: conduction band; VB: valence band; n : quantum number. The figure is reproduced from reference^[22].

According to the discussion above, besides the chemical composition and lattice structure, the transition energy of excitons in CLDNMs is dramatically modified by the quantum confinement. This is significantly attractive for those applications based on photon absorption and photoluminescence since researchers only need to develop one synthesis method and then, the size or shape can be used to widely and precisely tune the optical transitions (i.e., absorption and emission spectra). **Figure 1.2** utilize CdSe (bulk band gap: 1.76 eV, Bohr radius: 9.6 nm)^[24] as an example to exhibit how versatile it can be in terms of controlling fluorescence/absorption using the quantum-confinement effect. The emission colour can span throughout the entire visible range, making them suitable for various biological imaging and light-emitting applications. Furthermore, the quantized DOS offers a controllable extinction

coefficient and broad absorption spectra that are unavailable in bulk counterpart or organic chromophores.

Figure 1.2 Impact of shape and size on the absorption/emission properties of CdSe low-dimensional semiconductors. **(a)** Quantum dots (3D confinement): the upper panel is the transmission electron micrograph and the bottom panel shows the effect of size on the absorption/emission properties. The figure is reproduced from reference^[24]. **(b)** Quantum rods (2D confinement): the upper panel is the transmission electron micrograph and the bottom panel shows the effect of rod volume on the absorption/emission properties. The figure is reproduced from reference^[25]. **(c)** Quantum tetrapods (1.5D confinement): the upper panel is the transmission electron micrograph and the bottom panel shows the effect of arm diameter and arm length on the absorption/emission properties (1: 6.3 ± 0.5 nm and 24.8 ± 2.3 nm; 2: 10.9 ± 0.8 nm and 27.6 ± 2.9 nm; 3: 8.2 ± 1.3 nm and 40.7 ± 3.8 nm; 4: 10.6 ± 2.4 nm and 41.3 ± 4.6 nm). The figure is reproduced from reference^[26]. **(d)** Quantum wells (1D confinement): the upper panel is the Transmission electron micrograph and the bottom panel shows the effect of thickness in z-direction (the number of monolayer) on the absorption/emission properties. The figure is reproduced from reference^{[24][27]}.

1.1.2 Dynamical properties

Figure 1.3 Excitonic dynamics-related applications. (a) Optical amplification: when population inversion is achieved, CLDNMs can exhibit optical gain (top panel). However, the gain process is dramatically hindered by the Auger loss (bottom panel). The figure is reproduced from reference^{[28][29][30]}. (b) Single photon emission: if only exciton is generated at one time in CLDNMs, the emitted photons will be anticorrelated (top panel), yielding a sub-Poissonian photon statistics. However, Auger-caused blinking is a considerable drawback: the ON state is related to the emission of a neutral exciton, and the OFF state is due to the charged exciton and emission is quenched by Auger loss (bottom panel). The figure is reproduced from reference^{[31][32]}. (c) Energy harvesting: in CLDNMs, the harvesting efficiency can be several times enhanced when exciton multiplication occurs. In traditional photon-excitation (top panel): the pumping photon with energy larger than the exciton generates a hot electron, the excess energy of hot electron will dissipate as heat. While for exciton multiplication (bottom panel): due to the enhanced electron-electron interactions in CLDNMs, the excess energy of this hot electron can transfer to a valence band electron via the Coulomb interaction and thus multiple excitons are generated. The figure is reproduced from reference^[29]. (d) Light-matter interaction: if the interaction between cavity photons and excitons in CLDNMs can be faster than any loss or decoherent mechanisms, polariton (a hybrid light and matter quasiparticle) is formed. Radiative decay of excitons (the conversion process from exciton to photon) is critical for interaction strength and coherent energy exchange. The figure is reproduced from reference^{[33][34]}.

Excitonic dynamics in CLDNMs are important for number of applications, as shown in **Figure 1.3:** i). Optical amplification is a result of multiexciton stimulated emission (i.e., the

accumulation of excitons) and it is strongly stymied by the Auger recombination which leads to an ultrashort lifetime of optical gain^[28]. Auger recombination is considerably efficient in CLDNMs;

ii) CLDNMs has great potential to become a nonclassical light source that emits antibunching photons (i.e., single photon emission). Again, Auger process which causes the random fluctuation in the emission intensity (i.e., PL intermittency or blinking) is the biggest obstacle for antibunching application since it requires a stable photon stream with no interruptions^[32]. iii). The enhanced Coulomb interaction in CLDNMs can enable the exciton multiplication: the process that absorbs a single photon with high energy and produces multiple excitons^[29]. It is extremely attractive for energy harvesting and leads to the internal quantum efficiency exceeding 100%. Understanding transient absorption properties is crucial to achieve high exciton multiplication efficiency in CLDNMs; iv). Light-matter interaction is a result of coherent energy exchange between photons/excitons and the radiative decay of excitons determines the interaction strength^[33]. The radiative decay of excitons is significantly modified in CLDNMs. Therefore, to conceive novel excitonic design using CLDNMs for practical applications, understanding the Auger recombination, transient absorption and radiative decay of excitons is required.

1.1.2.1 Auger recombination

Auger recombination is the process that the energy of exciton recombination is not released as photons (radiatively) but is used to excite a third carrier (hole or electron) to a higher energy state (non-radiatively)^{[35][36]}. In bulk semiconductors, as shown in **Figure 1.4a**, assuming that thermal energy is not involved, all three carriers in the continuous energy band (bulk semiconductors) have zero transition momentum. If Auger recombination occurs, the carrier that receives the recombination energy will gain a transition momentum and the whole system

violates the law of translational momentum conservation^{[30][37]}. As a result, Auger recombination is less efficient in bulk semiconductors.

However, in CLDNMs, as shown in **Figure 1.4b**, the quantum confinement effect quantizes the energy band (i.e., converting the parabolic momentum dispersion to discrete states) and the translational momentum conservation becomes less stringent. Thus, the relaxed momentum conservation, combining with the enhanced carrier interaction and reduced dielectric screening in CLDNMs, makes the Auger recombination becoming one of the determining factors in the excitonic dynamics.

Figure 1.4 Auger recombination. The figure is reproduced from reference^[30]. (a) Auger recombination is violating the translational momentum conservation in bulk semiconductor. (b) Auger recombination is more efficient in CLDNMs due to the relaxed translational momentum conservation. (c) Universal volume scaling of Auger lifetime in CdSe quantum dots. (d) Universal volume scaling of Auger lifetime in other quantum dots. (e) The energy released routine of negative trion (top panel), positive trion (middle panel) and biexciton (bottom panel) in Auger recombination.

As discussed above, the Auger lifetime should be expected to vary with the quantum confinement (e.g., size or shape of semiconductor particles). Actually, this trend is true and known as a ‘volume scaling’^[38]. Here, we use quantum dots (3D confinement) as a representative example, as illustrated in **Figure 1.4c and 1.4d**. For almost all quantum dots, the size dependence of Auger lifetime for biexciton, negative trion and positive trion can be described as scaling with the cube of the radius of quantum dots: $\tau_{Auger} \propto R^3$.

Besides the dependence on geometry, the Auger lifetime should also scale with the numbers of carriers since the efficiency of Auger process is linked to the numbers of all possible recombination pathways. This so-called ‘statistics scaling’^[36] is described in **Figure 1.4e**, if the conduction band and valence band is mirror symmetric, the biexciton (XX) Auger recombination rate should be as twice the sum of Auger decay rate of positive trion (X^+) and negative trion (X^-): $k_{Auger}^{XX} = 2(k_{Auger}^{X^-} + k_{Auger}^{X^+})$. And this relationship is experimentally demonstrated in CdSe and PbSe quantum dots.

More generally, considering the multiple exciton scenario (the number of excitons is N), the Auger decay rate can be expressed as: $k_{Auger}^{NX} = \frac{N^2(N-1)k_{Auger}^{XX}}{4}$ and we can see that the Auger rate increases rapidly with N , which results in the quench of emission in the multiple exciton scenario.

1.1.2.2 Transient absorption

Transient absorption in CLDNMs which describes the absorption change in both time and energy domains using the pump-probe technique is mainly a result of two effects: state filling and transition variation^{[29][39]}. For state filling, due to the Pauli exclusion principle, the occupation of the quantized states in conduction band of CLDNMs will lead to the optical bleaching. This bleaching signal in transient absorption can only give the information about

the occupied states and are useful in quantitative studies of exciton properties (e.g., population and dynamics).

Figure 1.5 A simplified description of absorption change ($\Delta\alpha$) CLDNMs (using quantum dots as an example). The figure is reproduced from reference^[29]. (a-c) State filling. Left panel: the nonlinear absorption ($\alpha = \alpha_0 + \Delta\alpha$, α_0 : linear absorption) under different state occupation, the red solid line is for $1S_L-1S_e$ transition, the blue solid line is for $1S_U-1S_e$ transition, and the black dashed line is the overall spectrum. Right panel: the absorption change under different state occupation. (d-e) Transition variation. Left panel: the nonlinear absorption before and after the intra-band relaxation, the red solid line is the excited absorption spectrum, and the black dashed line is the ground absorption spectrum (which is similar to the spectrum in Figure 1.5a). Right panel: the absorption change before and after the intra-band relaxation.

For transition variation, the absorption change is due to the variation of optical transition energy (e.g., shift, broadening or narrowing of the spectra) or oscillator strength (e.g., the modification of amplitude)^{[29][40]}. Transition variation can be caused by the Coulomb interactions among excitons (e.g., Stark effect) or the thermal assisted relaxation (e.g., phonon

broadening). In contrast to state filling, which is only the response of populated states, transition variation will give information about all possible optical transitions.

To illustrate absorption change in CLDNMs, here, we still use the CdSe quantum dots as a representative example and assume all states are twofold spin degenerate. Two optical transitions that involve the same $1S$ electron state in conduction band and two different $1S$ hole states in valence band are considered: $1S_L-1S_e$ (low energy transition) and $1S_U-1S_e$ (high energy transition).

In the state filling only scenario, when quantum dot is in the ground state (**Figure 1.5a**), weak $1S_L-1S_e$ and strong $1S_U-1S_e$ transition can be observed in the nonlinear absorption spectrum; Then, if one electron in $1S_L$ state is excited into the $1S_e$ state (**Figure 1.5b**), the complete bleaching of $1S_L-1S_e$ transition (the emission and absorption are cancelled out) and 50% bleaching of $1S_U-1S_e$ transition are shown in the nonlinear absorption spectrum; While in the absorption change spectrum, two bleaching bands corresponding to both $1S_L-1S_e$ and $1S_U-1S_e$ transitions can be observed; finally, if two electrons in $1S_L$ state are excited into the $1S_e$ state (**Figure 1.5c**), in nonlinear absorption spectrum, the absorption of $1S_U-1S_e$ transition is completely bleached and optical gain related to $1S_L-1S_e$ transition is developed. While in the absorption change spectrum, the amplitude of two bleaching bands will be doubled compared to the case in **Figure 1.5b**.

If transition variation is taken into account (we use spectrum shift to illustrate and only consider the strong transition: $1S_U-1S_e$), in the initial stage after excitation (i.e., before the hot carrier relaxes into the band edge), as shown in **Figure 1.5d**, $1S_U-1S_e$ transition is only affected by the spectrum shift and no bleaching is exhibited in the nonlinear absorption spectrum. While in the absorption change spectrum, a derivative-like shape is observed due to the energy shift. After the hot carrier fully relaxes into the edge of conduction band (**Figure**

1.5e), the bleaching signal overwhelms the energy shift. This means that transition variation should be detected at the initial stage before carrier relaxation.

1.1.2.3 Radiative decay

In semiconductors, due to the crystal field, the lowest-energy hole state will be split into two levels with $|J_m| = 1/2$ and $3/2$ that correspond to light and heavy holes, respectively^[29]. However, the enhanced Coulomb interaction in CLDNMs will lead to additional splitting of excitonic states (**Figure 1.6a**). A combination of the hole with $\pm 1/2$ spin and the electron with $\pm 1/2$ spin generates three excitonic states with the projection of the total angular momentum $|N_m| = 0$ (denotes as 0^U and 0^L , U means high energy transition and L means low energy transition) and $|N_m| = 1$ (denotes as 1^U)^[30]. On the other hand, a combination of the hole with $\pm 3/2$ spin and the electron with $\pm 1/2$ spin generates two excitonic states with the projection of the total angular momentum $|N_m| = 1$ (denotes as 1^L) and $|N_m| = 2$. When $|N_m| = 2$, this exciton is referred to dark exciton since it is optical forbidden. For 1^L , this exciton is optically active and called bright exciton. The energy separation between $|N_m| = 2$ and $|N_m| = 1^L$ is defined as the dark-bright exciton splitting (Δ_{db}).

As a result, in CLDNMs, radiative decay of excitons is significantly depending on the populations in bright and dark states^[19]. Here, we assume that the probability of finding excitons in bright and dark states (p_d and p_b : the probability for the bright and the dark states, respectively) follows the Boltzmann distribution^[30]:

$$p_d = \frac{1}{1 + e^{-\frac{\Delta_{db}}{k_B T}}}; p_b = \frac{1}{1 + e^{\frac{\Delta_{db}}{k_B T}}} \quad (1.6)$$

where T is the temperature (K) and k_B is the Boltzmann constant.

Then, the total recombination rate can be expressed as:

$$k_{tot} = k_{non-rad} + k_{rad} = \frac{k_d}{1 + e^{\frac{\Delta_{db}}{k_B T}}} + \frac{k_b}{1 + e^{\frac{\Delta_{db}}{k_B T}}} \quad (1.7)$$

where k_d and k_b are the recombination rate for dark and bright excitons, respectively.

Figure 1.6 Radiative decay in CLDNMs. The figure is reproduced from reference^[30]. **(a)** Schematic illustration of the fine-structure of band-edge excitons. The two lowest energy states which dominates the radiative decay of excitons are referred as bright excitons ($|N_m| = 1^L$) and dark excitons ($|N_m| = 2$). **(b)** The calculated exciton lifetime using the dark-bright exciton splitting model. The arrows indicate the temperature threshold (defined as the temperature at which exciton lifetime drops by 10% compared to the value when T is close to 0 K).

Thus, we find that the dark-bright exciton splitting energy (Δ_{db}) which is related to the quantum confinement and temperature can be used to control the radiative decay rate of excitons in CLDNMs. To visualize this relationship, we have selected three specific values of Δ_{db} to calculate the exciton lifetime ($k_d = 1/(1 \text{ } \mu\text{s})$ and $k_b = 1/(8 \text{ ns})$ are used). As shown in **Figure 1.6b**, at low temperature, all excitons are primarily in the dark states. After certain

temperature (the so-called temperature threshold), the dark excitons can be activated as bright excitons. This temperature threshold will be larger for higher Δ_{db} .

This behavior of radiative decay rate of excitons in CLDNMs is extremely useful for light-matter interaction or the study of high-order excitonic states since it allows researchers to find a balance between photon conversion (the radiative decay rate is larger, then the energy exchange between photon and exciton or the generation of correlated photons from high-order states will be more efficient) and excitonic loss (more excitons in dark state will slow down the recombination of exciton, the long-lived exciton status will offer more chance to observe the interaction or high-order states).

1.2 Recent advances

Attracted by the extraordinary excitonic properties in CLDNMs and driven by the desire to realize the potential of excitonics in practical applications, tremendous research efforts have been devoted to modulating the excitons in CLDNMs. In this section, the most representative progress in recent years will be overviewed and discussed.

1.2.1 Chemical structure engineering

From the perspective of material science, modifying the chemical structure (e.g., chemical element or chemical composition ratio) of CLDNMs is an intrinsic way to modulate the excitonic properties in CLDNMs^{[41][42]}. Four most representative works in terms of chemical structure engineering in the past five years are shown in **Figure 1.7** and **Figure 1.8: i)**^[43]. In order to solve the blinking problem at the single-particle level, a single CdSe quantum dot encapsulated in a silica shell coated with a continuous gold nano-shell was synthesized (**Figure 1.7a**). Due to the coupling between the plasmon in gold nano-shell and the excitons in quantum dots, the radiative recombination of multiple excitons has been enhanced (i.e., the

Auger loss is suppressed). Hence, the PL of this hybrid quantum dot exhibits non-blinking property and long-term photon-stability under high-power excitation;

Figure 1.7 Recent advances of excitonic modulation in CLDNMs using chemical structure engineering. **(a)** A hybrid quantum dot structure with CdSe/CdS/SiO₂/Au is used to suppress the blinking process. The figure is reproduced from reference^[43]. The upper panel is the principle of synthesis and corresponding TEM images. The lower panel is the fluorescence intensity as a function of time (time bin: 10 ms), due to the enhanced recombination rate in the multi-exciton environment, the PL intensity of the hybrid quantum dot is stable and continuous. **(b)** A multi-shell quantum dots with optimized component ratio is used to equalize the brightness of each emission colour. The figure is reproduced from reference^[44]. The upper panel is the structure of the brightness-equal quantum dots, in which the core size is fixed and the chemical composition or thickness of the core is modified to control the emission colour and brightness. The middle panel exhibits the converged extinction coefficient for different colours at 400 nm. The lower panel shows the equalized fluorescence brightness.

ii)^[44]. For bio-imaging application, the similar intensity of multi-color emission in CLDNMs is preferred to conduct quantitative analysis. In **Figure 1.7b**, Andrew M. Smith and co-workers have reported the quantum dots with equalized brightness in multicolor emission

channels. Through varying the chemical composition of quantum dot shell, the quantum yield and extinction coefficient can be controlled and equalized since the different emission colors are arising from different structure domains in the quantum dots;

Figure 1.8 Recent advances of excitonic modulation in CLDNMs using chemical structure engineering (continued). (a) A core-shell structure quantum dot with different core-shell geometry is used to modulate the Auger process. The figure is reproduced from reference^[45]. The upper panel is the charge density of the conduction band minimum, valence band maximum, and averaged e_n and h_n states for four different core-shell quantum dots, which implying different dielectric screening for negative or positive trions. The middle and lower panels are the experimental recombination rates in two different core-shell quantum dots, which demonstrates that the Auger rate through positive trion and negative trion pathways can be inverted. (b) A ternary I-III-VI₂ semiconductor quantum dot is used to fabricate the luminescent solar concentrators. The figure is reproduced from reference^[46]. The upper panel illustrates the band-edge electronic structure of CISES quantum dots. Compared to CdSe quantum dots, smaller band gap which is closer to the solar spectrum is presented. Moreover, absorption in CISES is dominated by the quantized states while the emission is related to the intragap hole state, thus, a large Stokes shift is observed (~ 0.53 eV). The middle panel exhibits the spectra overlap between the CISES absorption and solar radiation. The lower panel shows the optical intensity loss due to the reabsorption in the luminescent solar concentrators with 12 cm length.

iii)^[45]. Xiaogang Peng and co-workers have demonstrated that the Auger recombination in CLDNMs are controllable through changing the core/shell geometries in quantum dots. As shown in **Figure 1.8a**, benefitting from the geometry-dependent dielectric screening, the Auger recombination rate via positive trion, negative trion and biexciton pathways can be modulated by simply changing the shell thickness; iv)^[46]. In order to maximize the coverage of the absorption spectrum in CLDNMs with the solar spectrum to enhance the light-harvesting ability, quantum dots of ternary I–III–VI₂ semiconductors (CuInSe_xS_{2-x}) with large Stokes-shift and lower band gap are utilized for luminescent solar concentrators (**Figure 1.8b**). Due to the suppressed reabsorption and the large overlapping with the solar spectrum, an optical power conversion efficiency of up to 3.27% is demonstrated.

1.2.2 Quantum confinement engineering

Considering that almost all the attractive properties of excitons in CLDNMs arises from the quantum confinement effect, engineering the quantum confinement environment for electrons and holes possibly is the second idea that reflects in researchers' mind to modulate the excitonic properties in CLDNMs. Similarly, we have also chosen the four most representative works to illustrate the progress in the field of excitonic modulation using quantum confinement engineering. As shown in **Figure 1.9** and **Figure 1.10**: i)^[47]. In order to suppress the emission fluctuation including both emission energy and linewidth variation, a large, directionally anisotropic lattice mismatch between the core and shell in quantum dots has been utilized to engineer the quantum confinement (**Figure 1.9a**). As a result, the reduced exciton-phonon interaction and suppressed Auger process enables the quantum dots exhibiting stable emission energy (<1 meV standard deviation) and narrow emission linewidth (~20 meV) at room temperature; ii)^[48]. Edward H. Sargent and co-workers have demonstrated that uniform biaxial lattice strain can be used to change the fine structure splitting in quantum dots, and

thus, to make the population inversion much easier (**Figure 1.9b**). Using this biaxially strained quantum dots, room temperature continuous wave pumped lasing is achieved;

Figure 1.9 Recent advances of excitonic modulation in CLDNMs using quantum confinement engineering. **(a)** A core-shell quantum dot structure with anisotropic lattice mismatch is used to suppress the fluctuation of emission energy and emission linewidth. The figure is reproduced from reference^[47]. The upper panel is a schematic illustration of the CdSe/Cd_xZn_{1-x}Se quantum dots. The asymmetric lattice strain engineers the conduction- and valence-band confinement potentials and leads to the localization of both electron and hole wavefunction in the core region. Thus exciton-phonon interaction and exciton transition energy are restricted. The lower panel shows the ultra-narrow emission linewidth and ultra-small emission energy fluctuation in the CdSe/Cd_xZn_{1-x}Se quantum dots. **(b)** A facet-selective epitaxy synthesized quantum dot with uniform biaxial strain is used to decrease the band-edge degeneracy and lower the optical gain threshold. The figure is reproduced from reference^[48]. The upper panel shows the fine-structure splitting in hydrostatically strained (conventional) and biaxially strained (engineered) quantum dots. In conventional quantum dots, the hole energy state splitting is comparable to the thermal energy, resulting in low state filling and difficult population inversion. While in engineered quantum dots, the hole energy state splitting is enhanced by the biaxial strain. Thus, the hole is concentrated into the lowest energy level and population inversion is much easier to be achieved. The lower panel shows the lasing in the biaxial strained quantum dots-DFB device under continuous-wave excitation.

Figure 1.10 Recent advances of excitonic modulation in CLDNMs using quantum confinement engineering (continued). **(a)** A continuously graded quantum dots with suppressed Auger recombination is used to demonstrate the optical gain with directly electrical pumping. The figure is reproduced from reference^[49]. The upper panel shows the compositional profile along the radial direction in the engineered quantum dots. The middle panel exhibits the confinement potential in the engineered quantum dots. Due to the smoothed potential at the interface, Auger loss is significantly suppressed. The lower panel shows the electroluminescence from the $1P(e)$ to $1S_{3/2}(h)$ transition which is the evidence for optical gain. **(b)** A core-shell quantum dots with giant shell is used to fabricate luminescent solar concentrator with high optical efficiency. The figure is reproduced from reference^[50]. The upper panel is a schematic representation of the giant quantum dots. The middle panel exhibits the confinement potential in the giant quantum dots. Due to the localization of hole wavefunction in the core domain, the absorption and emission process have been separated in the giant quantum dots. The lower panel shows that thick shell enables larger Stokes shift.

iii)^[49]. Fast Auger loss is the main obstacle that prevents the realization of lasing with electrical injection. Victor I. Klimov and co-workers have demonstrated that population inversion and optical gain can be observed in continuously graded quantum dots with direct-current electrical pumping (**Figure 1.10a**). The continuously graded $\text{CdSe/Cd}_x\text{Zn}_{1-x}\text{Se}$

quantum dots are type-I structure and due to smoothed quantum confinement in the alloyed interface, Auger decay through both hole and electron pathways is efficient suppressed; iv)^[50]. In order to reduce the reabsorption loss in luminescent solar concentrators, CdSe/CdS quantum dots with giant shells is demonstrated to enable huge Stokes shift and reduce the reabsorption loss by 100 times compared to the conventional CdSe quantum dots (**Figure 1.10b**). Due to the localized confinement of holes in the CdSe core, the giant shell (served as a light-harvesting antenna) with thin core (behaved as a lower-energy emitter) structure has separated the absorption process and emission process and results in large Stokes-shift. Optical efficiencies >10% is demonstrated in the luminescent solar concentrator with this engineered quantum dots.

1.3 Thesis overview

This thesis covers the main research works conducted in my PhD study which are concentrated on the investigation of new-developed methods to modulate the excitonic properties in CLDNMs. After introducing the basic properties and recent research progress in the field of excitonic modulation in CLDNMs, now we have the capacity to evaluate the motivation, objectives and major contributions of this thesis.

1.3.1 Motivation and objectives

After enormous research efforts in the last three decades, the research status of excitonics in CLDNMs has successfully completed the transition from knowledge accumulation (i.e., monitoring and explaining the special and extraordinary properties of excitons) into knowledge utilization (i.e., controlling and modulating the excitonic properties for practical applications). Even though tremendous research progress has been made in excitonic modulation, as described and discussed in the '**Recent advances**' part, it is still a long journey

to fully realize the potential of excitonic modulation in practical applications (i.e., solid-state devices) due to the following challenges:

So far, research efforts aiming to modulate the excitonic properties in CLDNMs are mainly focusing on new-developed synthetic methods, such as, control over stoichiometry and geometry in the nanomaterials, incorporation of novel ligands, seeking new chemical elements or employing new treatments to passivate the surface of CLDNMs. There is no doubt that these excitonic modulations in CLDNMs through different synthetic routes are robust, straightforward and efficient. However, these types of **passive** modulation (i.e., all properties of excitons are set in the synthesis process and fixed at the stage of device fabrication) have difficulty in meeting the operation requirement of excitonic devices and guaranteeing the functionality in solid-state devices.

Solid-state devices, no matter whether they are electronic-, spintronic-, photonic-, or excitonic-based devices, all rely on manipulation of the different degree of freedom in corresponding carriers (e.g., the sign or the amount of charge in electronics, the spin number in spintronics, the polarization and orbital angular momentum in photonics, exciton energy, recombination and flow in excitonics) to store and process information. Typically, integrating CLDNMs with nanophotonic or nanoelectronic structures under **active** operation (i.e., excitonic properties in CLDNMs which can be modulated using post-synthesis treatments, such as optical, electric, magnetic or pressure stimuli) is required to achieve the device functionality.

Consequently, the works conducted in this thesis are driven by two types of motivation, both synthetic and post-synthetic, to develop new insights into the excitonic modulation in CLDNMs. From a synthetic perspective, it is still passive modulation which we cannot change, however, the thing that we do have ability to change is that: instead of modulating the

excitonic properties through changing the intrinsic energy structures in CLDNMs, is it possible to add additional energy states to change the exciton environment during synthesis, for example, by introducing foreign atoms into the host CLDNMs? This strategy is of great interest since it adds more degrees of freedom for the excitons which may benefit the active operation. From post-synthetic perspective, to aim for the active operation, our works dedicate to seeking device-preferable methods to modulate the excitonic properties, including applying an electric field, controlling Förster resonance energy transfer in donor-acceptor system and interacting with plasmons.

1.3.2 Outline and contributions

Besides the introduction chapter, there are another five chapters included in this thesis and they are organized as follows:

- i). Chapter two is about the excitonic modulation in synthesis process. Copper ions, as an example of transition metal ions, are introduced into the CdSe colloidal quantum well (CQW) host. Benefitting from the additional energy states added by the copper ions, we have successfully demonstrated the room temperature biexciton emission with huge binding energy (doubles the value compared to the biexciton binding energy in other undoped inorganic nanomaterials) under continuous-wave excitations. Moreover, utilizing the sustainable biexciton states enabled by the dopant-host interaction, a biexciton lasing device with ultralow threshold is developed.
- ii). Chapter three is about the excitonic modulation under post-synthesis treatment using Förster resonance energy transfer (FRET). The first part of chapter three is an example to show how the one more degree of freedom added by copper ions can be beneficial for active modulation. Through utilizing the d orbital electrons in copper ions, for the first time, a unique mutual FRET process, which breaks the unidirectional limitation in FRET, is demonstrated in

a binary inorganic nanomaterial complex. The second part of chapter three is about controlling the exciton flow between donor and acceptor. An all optical method based on the population overlap between the acceptors' ground states and the donors' excited states is developed.

iii). Chapter four is about the excitonic modulation under post-synthesis treatment through applying electric field. Controllable threshold of optical gain in the CLDNMs is demonstrated in a device platform by excess electron injection. We have observed that singly charged exciton can low down the threshold while doubly charged exciton will stymie the optical amplification process.

iv). Chapter five is about the excitonic modulation under post-synthesis treatment via interacting with localized plasmon. Due to the highly in-plane dipole orientation, non-stacking and enhanced exciton binding energy in high aspect ration CQWs, we have demonstrated that ultrafast coherent energy exchange and high cooperativity is also possible in Wannier Mott exciton-plasmon interaction.

v). In chapter six, we will summarize the thesis. According to the obtained results and uncovered aspects of the finished works, several ideas for future research will also be discussed.

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Chapter 2: Dopant-host interaction enables sustainable biexcitons

2.1 Motivation and Introduction

Entangled photon pairs are natural candidates for basic entities (‘qubits’) in quantum information and quantum computation^[1-3]. Commonly, parametric down conversion (PDC) in nonlinear optics is utilized to create entangled photon pairs^[4]. However, PDC mechanism suffers from non-guaranteed single photon pair as well as extremely low non-linear efficiency^[5]. Utilizing biexciton states in quantum emitters is a promising strategy to circumvent the limitations since the radiative decay of a biexciton has two channels: either emit a horizontally (H) polarized photon or a vertically (V) polarized photon^{[1-3],[6]}. If fine-structure splitting (FSS) is negligible, the generated two photons are indistinguishable in any other properties except the polarization: $\sqrt{2}|\phi\rangle = |H\rangle|H\rangle + |V\rangle|V\rangle$ ^[7]. Benefiting from the strong many-body interaction in atomically thin transition metal dichalcogenides (TMDs), the first observation of biexciton emission at 10 K using femtosecond pulse excitation was achieved 3 years ago^[8]. Since then, lots of investigations have been conducted to demonstrate continuous-wave pumped biexciton states at room temperature in TMDs^{[7],[9-11]}⁴. However, the synthesis (i.e. mechanical exfoliation, chemical exfoliation, and chemical vapor deposition) of high quality TMDs is still suffering from various issues^[15-17] such as synthesizing cost, upscaling capability (curbed by flake size and film uniformity), emission efficiency (quantum yield: < 5%) or limited spectral tunability (constrained by the valley band). The use of colloidal nanomaterials offers an avenue for fully solution-processed, highly efficient, bottom-up biexciton sources, which in turn enable the easy integration of quantum emitters into a wide variety of optoelectronic quantum architectures^{[18][19]}.

Till now, the demonstration of biexciton states in colloidal nanomaterials, which is also beneficial to light-emitting diodes and optical gain, can only be achieved under intense excitation with ultrashort pulsed lasers and cryogenic condition due to the two key challenges: very fast non-radiative process^{[20][21]}, and small biexciton binding energy^{[22][23]}. The former relates to efficient Auger/traps introduced non-radiative recombination in colloidal nanomaterials with a typical time constant of tens to hundred picoseconds, which leads to ultrafast deactivation of the high-order correlated excitonic states. The latter relates to Coulomb interaction to form a bounded four-body complex from two excitons. The biexciton binding energy in colloidal nanomaterials^[22] is typically smaller than 30 meV, comparable to the thermal energy at room temperature and much smaller than the inhomogeneous broadening of exciton emission. Insufficient binding energy causes the thermal dissociation of biexciton states at room temperature and makes biexcitonic transition inseparable from exciton states. Suppression of Auger recombination has been investigated extensively for colloidal nanocrystals to achieve optical gain practically. Large-volume nanocrystals leveraging the well-known ‘volume scaling’^{[21][24]} or interfacial alloying core/shell nanocrystals^{[20][25]} utilizing the smoothed confinement potential exhibit relatively long Auger recombination (nanosecond timescales). Unfortunately, large-size nanomaterials which lose the benefits of strong quantum confinement (i.e. large binding energy and reduced dielectric screening)^{[24][26]} and smooth interface nanocrystals which associate with broad photoluminescence (PL) spectrum (FWHM: > 30 nm, caused by the interface composition gradient)^{[20][27]} are hard to be ideal biexciton sources.

The requirements for colloidal nanomaterials which reconcile suppressed Auger recombination, quantum confinement and narrow emission spectrum can be satisfied with colloidal quantum wells (CQWs)^{[18][28][29]}. In this quasi-2D system, the exciton wave functions are quantized only in vertical direction, which makes Auger process harder to meet the

momentum conservation compared with the situation in colloidal quantum dots^{[18][22]}. Also, the exciton emission in CQWs exhibits extremely narrow linewidth at room temperature (FWHM of 4-monolayer CdSe CQWs: ~40 meV) due to vertical thickness control at the single atomic layer level and weak phonon coupling^[30-34]. However, the highest biexciton binding energy reported for CQWs (~ 34 meV) is still smaller than their emission bandwidth, and thus the biexciton emission peak is only resolved at cryogenic temperature^{[22][31][33]}.

Brovelli and colleagues^[35] have shown that in Ag doped CdSe colloidal quantum dots (CQDs), by exploiting the effect of excitonic carriers in host nanomaterials on dopant ions, the nonmagnetic dopants can exhibit optically switchable magnetism. Ag^+ dopants are not magnetic ([Kr]4d¹⁰, there is no unpaired electron spin in full 4d shell), after capturing the photo-generated hole in host CdSe, Ag^+ is oxidized to Ag^{2+} ([Kr]4d⁹) and the unpaired electron spin can exhibit paramagnetic behaviour. Reversibly, we propose that in doped CdSe CQWs, through utilizing the effect of dopant ions on the excitonic carriers in host nanomaterials, the biexciton binding energy can be enhanced. The dopants strongly capture the photo-generated holes and change the Coulomb interactions among carriers in the host nanomaterial, thus increases biexciton binding energy^[36-38]. In the first part of chapter 2, we have demonstrated Cu dopants in CQWs enhances the biexciton binding energy up to 64 meV, a factor of 2 greater than the values reported in undoped counterparts. The boosted biexciton binding energy, suppressed Auger, and narrow emission spectrum enable continuous-wave biexciton emission at room temperature. A comprehensive analysis of this sustainable biexciton emission in Cu-doped CdSe CQWs (Cu:CdSe CQWs) is presented via the carrier dynamics (time-resolved photoluminescence and transient absorption) with temperature and excitation dependent emission spectra.

After the observation of the robust biexciton states, another motivation is utilizing the biexcitons to enhance the optical gain performance. Transition metal doped colloidal

nanomaterials (TMDCNMs), including Cu, Ag and Mn, have recently attracted broad interest for optoelectronic applications^[35,36-38]. Compared with their undoped counterparts, TMDCNMs not only retain all the advantages of the host colloidal nanomaterials but also exhibit emergent optical/electronic properties introduced by transition metal ions, such as a broadband Stokes-shifted emission^[39], p-type conductivity^[40] and photoinduced magnetism resulting from spin-exchange interaction^[41-43]. Extensive progress about TMDCNMs have been reported over the past several years. From the perspective of understanding, the role of dopants in the bandgap modulation, steady-state/transient photoluminescence (PL) has been investigated into great depth^[35,44-49]. From the perspective of application, benefiting from the nearly zero self-absorption in the dopant related emission, Sharma et al. have demonstrated near-unity photo-luminescence quantum yields in the luminescent solar concentrators using copper-doped colloidal quantum wells (CQWs)^[50].

To date, majority of the works on TMDCNMs are conducted with low pump fluence/intensity (i.e., stay in the sub-single/single exciton regime) and the potential of TMDCNMs as optical gain materials has not arouse much attention. There is a current belief that TMDCNMs are awful emitters to achieve the stimulated emission since dopants typically behaves as the hole-trappers which severely hinders the built-up of population inversion in the host^[51-55]. However, this argument has completely ignored the effect of dopants on the excitonic dynamics of the host. For example, dopants can enhance the quantum yield to near unity in colloidal nanomaterials via suppressing the intrinsic defects^[50,51]; Also, dopants localize the holes and offer the chance to form the trapped excitons in the host. The trapped excitons with higher oscillator strength can interact with each other heavily to form the high-order excitonic states and facilitate the population inversion^[53]; Moreover, trapping holes also change the Coulomb environment in the host compared to the situation in undoped counterparts. It is possible that

the suppressed Coulomb screening effect^[54,55] can help the onset of stimulated emission. Therefore, it is worthwhile to investigate the optical gain performance in TMDCNMs.

In the second part of chapter 2, through analysing the amplified spontaneous emission (ASE) spectra in copper-doped CdSe CQWs with varying amount of copper dopants, we observe that copper dopants enable the CQWs exhibiting biexciton emission with strong biexciton binding energy (~ 64 meV) under extremely low pump fluence ($< 1 \mu\text{J}/\text{cm}^2$). As a result, the ASE threshold in copper-doped CQWs is the result of a competition between two opposite effects: biexciton formation which facilitates the population inversion and hole trapping which stymies the population inversion. At the copper dopant level of ~ 40 per CQW, the ASE threshold in copper-doped CQWs has been reduced by eight times compared to the value in undoped CQWs ($\sim 7 \mu\text{J}/\text{cm}^2$ versus $\sim 58 \mu\text{J}/\text{cm}^2$). To further access the biexcitonic gain potential of copper-doped CQWs, we have demonstrated a vertical cavity surface emitting laser (VCSEL) and an ultralow threshold of $\sim 4 \mu\text{J}/\text{cm}^2$ is achieved under sub-nanosecond excitation, a value comparable to or lower than those reported colloidal nanomaterial based lasing devices^[17-19].

2.2 Sustainable biexciton emission

Biexcitons have been considered as one of the fundamental building blocks for quantum technology because of its overwhelming advantages in generating entangled photon pairs. Although many-body complexes have been demonstrated recently in mono-layer transition metal dichalcogenides (TMDs), the low emission efficiency and scale up capability hinder their applications. Colloidal nanomaterials, with high quantum efficiency and ease of synthesis/processing, are regarded to be an appealing complement to TMDs for biexciton sources. However, a progress towards biexciton emission in colloidal nanomaterials has been challenging largely by small binding energy and ultrafast non-radiative process. Here, we

demonstrate room-temperature biexciton emission in Cu-doped CdSe colloidal quantum wells (CQWs) under continuous-wave excitation with intensity as low as $\sim 10 \text{ W/cm}^2$. The characteristics of radiative biexciton states are investigated by their super linear emission with respect to excitation power, thermal stability and transient photophysics. The interaction between the quantum confined host carriers and the dopant ions increases biexciton binding energy by two folds compared to the undoped CQWs. Such strong binding energy together with suppressed non-radiative process and efficient, spectrally narrow photoluminescence in a quasi-2D semiconductor enables sustainable biexciton emission at room temperature, providing a potential solution for efficient, scalable and stand-alone quantum devices.

2.2.1 Cu:CdSe CQWs as a dopant-host system

Figure 2.1 Structural information of 4 ML Cu:CdSe CQWs. For the TEM image, we can extract the lateral size of Cu:CdSe CQWs is $(36 \pm 1.9) \text{ nm} \times (15.0 \pm 1.5) \text{ nm}$.

We prepared Cu-doped CdSe CQWs according to the existing recipe^[50] and optimized the procedures to achieve highly efficient and reproducible synthesis (details of the synthesis are described in **Appendix 1.1**). The structure information of Cu:CdSe CQWs is shown in **Figure 2.1**: the four-monolayer (4 ML) CQWs are 1.2 nm thick¹⁸ and tens of nanometres along each side laterally. The PL quantum yield (PLQY, see **Appendix 1.2**) of Cu:CdSe CQWs is in the range of 40% to 80% depends on the amount of Copper precursor added in the synthesis.

Figure 2.2 The dopant-host system in a Cu: CdSe CQW. CE: copper-related emission; BE: band edge emission. (a) Schematic of carrier dynamics in the Cu-doped CQWs with photo excitation. After capturing of a VB hole (process 1), Cu^+ is changed to Cu^{2+} , activating the CE through recombining with a CB electron (process 3). (b) Optical absorption and steady-state PL spectrum of Cu-doped CQWs in solution under Xeon lamp illumination, green color region indicates the BE and red color region indicates the CE. (c) Normalized decay curves of CE for Cu-doped CQWs under the pump fluence of $0.4 \mu\text{J}/\text{cm}^2$. The PL dynamics is probed at $\sim 700 \text{ nm}$. (d) Normalized decay curves of BE for undoped CQWs and Cu-doped CQWs under the pump fluence of $0.4 \mu\text{J}/\text{cm}^2$. The PL dynamics of both doped and undoped CQWs are probed at 514 nm . The difference in dynamics sheds light on the suppressed intrinsic traps and the hole capture rate of Cu-dopants. (e) Time-resolved photoluminescence of BE and CE in Cu-doped CQWs with the pump fluence of $0.4 \mu\text{J}/\text{cm}^2$. The black circles show the excitonic dynamics (514 nm) and the red squares presents the copper ML_{CBCT} dynamics (integrated between 650 and 750 nm). Fitting the CE dynamics (blue solid line) yields the time constant of hole capture process ($\sim 1 \text{ ns}$), which is much slower compared with the Cu-doped quantum dots^[54].

The copper dopants in CQW host behave like a hole-trapper^[50-52], as illustrated in **Figure 2.2a**. After excitation, copper dopants irreversibly localize the photo-generated holes in CQW host, Cu^+ is promoted to Cu^{2+} and therefore activated as a radiative acceptor for the conduction

band (CB) electrons, which can be expressed as^[35]: $[\text{Ar}]3d9 + e \rightarrow [\text{Ar}]3d10 + h\nu$ ($h\nu$ is the photon energy of Cu-related emission and e denotes an electron in CB).

As a result, the photoluminescence (PL) spectrum (**Figure 2.1b and 2.2b**) of Cu:CdSe CQWs is composed of two emission bands: (1) a narrow band-edge emission (BE) at ~514 nm with a full-width at half-maximum (FWHM) of ~40 meV, which is not affected by copper dopants; (2) a broad Cu-related emission (CE) peaking at ~700 nm with a very large FWHM of ~350 meV, the broad emission linewidth is arising from a wide distribution of copper energy level rather than size/doping inhomogeneity within an ensemble of Cu:CdSe CQWs, as detailed previously^{[50][55]}.

The absorption spectrum (**Figure 2.2b**) of Cu:CdSe CQWs is also consistent with the scenario presented in **Figure 2.1a**: two clear excitonic features associated with electron to heavy-hole (512 nm) and electron to light-hole (480 nm) transitions, remain unchanged compared with undoped CdSe CQWs (absorption spectra of undoped and doped CQWs with different copper doping levels are presented in **Figure 2.1b**). Notably, there exists a weak and broad absorption tail on the red side of the first CQW excitonic maximum (low energy tail in **Figure 2.1b**), which can be assigned as the direct transition of d orbital electrons in Cu^+ to the CB of CdSe CQWs^{[54][55]}. However, the contribution of this transition to BE and CE is eliminated since the extinction coefficient of this tail at its maximum^{[54][55]} is smaller than $1000 \text{ M}_{\text{Cu}}^{-1} \text{ cm}^{-1}$ and without the hole-capture process, the extremely low recombination rate (0.002 ns^{-1} , **Figure 2.2c**) between Cu^{2+} and CB electron cannot compete with the band-edge recombination.

In view of this host-dopant system, the diluted hole concentration in CQW host is suggested by strong CE (**Figure 2.2b**). It is important to ensure the hole-capture dynamics can support the radiative band edge recombination since the ultrafast hole consumption leads to insufficient constituent (holes) for many-body complexes in host. To figure out the kinetics of

hole capturing in Cu:CdSe CQWs, **Figure 2.2d** presents the BE dynamics of undoped and doped CQWs in the sub-nanosecond time scale, which shows that the ultrafast recombination channel (~ 31 ps) is absent in doped CQWs. The single exponential decay behaviour of Cu:CdSe CQWs in a short time window is consistent with the theoretical calculation conducted by Nelson^[61], in which highly localized covalent $[\text{CuSe}_4]$ cluster can suppress or deactivate intrinsic traps and thus, enhance the quantum efficiency of Cu-doped nanocrystals (**Figure 2.1b**). Therefore, in doped CQWs, the eliminated ultrafast non-radiative process is highly preferred for the observation of high-order excitonic states. Here, we can assume that Auger can be negligible in low pumping regime ($\langle N \rangle$ is smaller than 0.1), only hole capture process is responsible for the difference in BE dynamics between undoped and doped CQWs. Thus, we can extract^[62] the time constant of hole capture process (τ_{hc}) from exciton lifetime of doped (τ_{doped}) and undoped ($\tau_{undoped}$) CQWs using $1/\tau_{undoped} + 1/\tau_{hc} = 1/\tau_{doped}$, which is around 1.1 ns.

Furthermore, since the prerequisite of CE is Cu^+ localizes a hole, hole-capturing time can be calculated from the rising part of CE^[54]. As shown in **Figure 2.2e**, in a nanosecond time window, a slow rising process in CE indicating a time constant of 977 ± 45 ps is in good agreement with hole-capture dynamics extracted from **Figure 2.2d**. It is worth to mention that, the onset of CE is significantly delayed compared to BE, emphasizing again the proposed carrier dynamics in **Figure 2.2a**. Compared with the ultrafast hole-capture process (an averaged lifetime of ~ 25 ps) in Cu:CdSe CQDs^[54], we attribute the slow dynamics in CQWs to the larger spatial separation of band-edge excitons and copper dopants due to large lateral size of the structure. The 2D morphology can slow down the hole localization, suppress the Auger recombination and lengthen the lifetime of multiple-exciton, as four-exciton states observed in CdSe/CdTe CQWs using transient absorption spectroscopy^{[63][64]}.

2.2.2 Continuous-wave excited biexcitons

We have therefore obtained a colloidal nanomaterial that may support radiative many-body complexes considering that the host excitons are strongly perturbed by the dopants and traps induced non-radiative process is suppressed. To explore the excitonic properties in Cu:CdSe CQWs, PL of the drop-cast film under continuous-wave excitation with different intensity at room temperature has been studied (**Figure 2.3a and 2.3b**). With low pump intensity ($< 6 \text{ W/cm}^2$, the bottom spectrum in **Figure 2.3b**), the BE shows single symmetric peak located at $\sim 514 \text{ nm}$, which is assigned to typical single exciton emission^{[18][22]}.

With gradually increased excitation intensity, a new emission feature appears at the low-energy side (peaking at $\sim 528 \text{ nm}$) and the intensity of this new feature grows much faster than the intensity of exciton emission with increasing excitation intensity. Beyond the excitation intensity of $\sim 10 \text{ W/cm}^2$, the new feature emerges as the strongest emission channel (see **Figure 2.3c**, the maximum intensity of BE shifts from 514 to 528 nm with higher excitation intensity). To quantitatively analyse the properties of the emerging emission feature, BE is fitted by two separately symmetric emissions using Voigt function^{[22][65]}, as shown in **Figure 2.3b**. The fitting profiles are in good agreement with the experimental spectra with different excitation intensities.

After spectrally separating the exciton emission and the new emission feature, **Figure 2.3d** presents the integrated emission intensities as a function of the excitation intensity. The excitation intensity dependence of these two features can be described adequately by the power-law equation^[8-12]: $I_{\text{emission}} \propto I_{\text{Intensity}}^k$. The exciton emission exhibits a slightly sublinear fluence dependence ($k = 0.91$), due to the hole capturing process from host CQWs to Cu^+ sites^{[8][54]}. However, the integrated intensity of the new emerged emission displays a super-linear growth with excitation intensity ($k = 1.68$).

Figure 2.3 Photoluminescence spectra of Cu-doped CQWs at room temperature with varied continuous-wave excitation intensities. (a) Normalized BE map of Cu: CdSe CQWs under different excitation intensities. The white dashed lines indicate different excitation intensities and the ordered numbers correlate to the BE spectra in Fig. 2b. (b) BE spectra recorded for different excitation intensities. Black dots: measurement; green line: the fitting of exciton; blue line: the fitting of biexciton; red line: the overall fitting. (c) Wavelength of the maximum BE intensity as a function of the excitation intensity. Beyond ~ 10 W/cm², the intensity of biexciton emission (peaking at ~ 528 nm) exceeds the exciton emission (peaking at ~ 514 nm). (d) Logarithmic plot of the integrated emission intensity for exciton (red stars) and biexciton (blue circles) as a function of the excitation intensities. The green and blue solid lines are the power-law fitting for exciton and biexciton, respectively.

On the basis of nearly quadratic (our case is ~ 1.85) intensity dependence of the new emission feature with respect to the exciton emission, the new feature peaked at ~ 528 nm can only be assigned to biexcitons formed from two excitons, the population of single exciton growing almost linearly (~ 0.91) with excitation intensity^[12]. This is similar to the case of biexcitons in

other systems, providing a first evidence that Cu:CdSe CQWs support radiative biexcitons at room temperature with extraordinary low excitation intensity ($\sim 10 \text{ W/cm}^2$).

Furthermore, the biexciton binding energy can be extracted based on the energy difference between exciton and biexciton emissions assuming that the radiative decay of a biexciton will generate one photon and an exciton (see the derivation in **Appendix 2.1**)^{[8][12]}. The value of $\sim 64 \text{ meV}$ derived here is two-fold of the biexciton binding energy in undoped CdSe CQWs^[22] (see PL spectra of undoped CdSe CQWs in **Figure 2.4**). This is also higher than that of inorganic colloidal perovskites^[65] and surprisingly comparable to the value in monolayer WSe_2 ^[8].

Figure 2.4 Emission spectra of undoped CdSe CQW film under continuous-wave laser excitation (a) and 500 ps laser pulse excitation (b). Under continuous-wave pumping, even the pump intensity go to 100 W/cm^2 , the band edge emission still exhibits a symmetry profile (peaked at $\sim 514 \text{ nm}$) and only exciton emission is observed (note that in Cu:CdSe CQWs, when pump intensity is beyond $\sim 10 \text{ W/cm}^2$, the biexciton will become the strongest emission channel). Under 500 ps laser pulse excitation, when the pump fluence is increasing, we can observe the biexciton emission feature located at $\sim 522.7 \text{ nm}$, which is matching the results from Moreels et al^[22]. And the binding energy of biexciton in undoped CdSe CQWs is $\sim 30 \text{ meV}$. If fluence is furtherly increasing, we can observe the onset of ASE peaked at 530.1 nm and the threshold is around $160 \mu\text{J/cm}^2$.

To probe the biexciton states in more detail, we have investigated the thermal stability of biexcitons in Cu:CdSe CQWs at the excitation intensity of 10 W/cm^2 . As temperature

decreases from 298 to 125 K, besides the expected spectra change and increased emission intensity (**Figure 2.5a and 2.5b**), biexciton emission displays a lower intensity increasing rate when $T < 100$ K (**Figure 2.5c**).

Figure 2.5 Photoluminescence spectra of Cu-doped CQWs with fixed excitation intensity of 10 W/cm^2 at different temperatures. **(a)** BE map of Cu:CdSe CQWs at different temperatures. The white dashed lines correspond to different temperatures and the ordered numbers correlate to the BE spectra in Figure 2.6b. **(b)** BE spectra recorded at different temperatures. Black dots and red/green/blue lines have the same denotations as expressed in Figure 2.4. **(c)** Integrated biexciton emission intensity (blue stars) as a function of $1/T$. The red line is the Boltzmann distribution fitting, which yields an activation energy of $\sim 60 \text{ meV}$. **(d)** Normalized CE map as a function of the temperature. the suppressed CE suggests the weaker hole capture ability of copper sites at low temperature.

This trend can be explained by the assumption^[8] that the formation rate of biexciton is roughly constant with varied T , while the dissociation rate (γ_{biex}) is enhanced by the thermal energy:

$\gamma_{biex} = \gamma_{const} + a \cdot \exp(-E_a/k_B T)$, where γ_{const} is a fixed recombination rate, a is a ratio factor and E_a is the activation energy.

Meanwhile, the integrated emission intensity of biexciton could be well fitted by the Boltzmann distribution (see **Appendix 2.2**)^{[6][8][66]} with an activation energy E_a of ~60 meV (**Figure 2.5c**), for which $\exp(-E_a/k_B T)$ will have a negligible effect on γ_{biex} and the integrated intensity of biexciton emission will show a plateau when T is lower than 100 K. The E_a value of ~60 meV is almost equal to the biexciton binding energy derived from steady-state PL analysis (**Figure 2.3**). This agreement emphasizes again the peak located at ~528 nm arises from biexcitons, in which the dissociation rate can be tuned by the thermal energy. Moreover, with decreased temperature, CE exhibits barely blue-shifted and narrowing spectra, accompanying with decreased emission intensity (**Figure 2.5d**). This trend is another supporting evidence of the spatial separation of dopant ions and host carriers (see the discussion in **Figure 2.2**): with gradually decreased temperature, thermally assisted carrier movement will be suppressed, weakening the hole capture probability and resulting in reduced CE intensity^[52].

2.2.3 Transient photophysics of biexcitons

To furtherly justify our assignment of biexcitons, we have investigated the transient photophysics in Cu:CdSe CQWs. Firstly, we conducted time-resolved PL measurement in Cu:CdSe CQW film with varying excitation fluences (see **Appendix 1.4**). In the bottom panel of **Figure 2.6a**, a narrow PL spectrum is observed with low excitation fluence ($0.4 \mu\text{J}/\text{cm}^2$, the bottom panel); while with high fluence ($0.4 \mu\text{J}/\text{cm}^2$, the top panel), biexciton emission appears and locates exactly at the wavelength observed in continuous-wave excited PL (**Figure 2.3 and 2.5**). Following the white and black dashed lines in **Figure 2.6a**, we compare the PL decay trace for X (located at 514 nm) and XX (located at 528 nm). With low fluence in which

biexciton emission is absent, the dynamics of X and XX are almost identical (single-decay process with similar lifetime of ~ 234 ps and ~ 245 ps for X and XX, respectively), and their onsets are at the same time (see **Figure 2.6b**).

Figure 2.6 Time-resolved photoluminescence of Cu-doped CQWs. (a) Streak camera images of Cu: CdSe CQWs under excitation of 100 fs pulsed laser. Top panel: at high excitation fluence ($40 \mu\text{J}/\text{cm}^2$) in which biexciton emission is observed. Bottom panel: at low excitation fluence ($0.4 \mu\text{J}/\text{cm}^2$) in which biexciton emission is absent. Black dashed line is located at 514 nm (X: exciton) and white dashed line is located at 528 nm (XX: biexciton). (b) Decay traces probed at 514 nm and 528 nm and corresponding fitting curves when the excitation fluence is $0.4 \mu\text{J}/\text{cm}^2$. 514 nm (measurement: black squares, fitting: black solid line), 528 nm (measurement: red circles, fitting: red solid line). (c) Decay traces probed at 514 nm and 528 nm and corresponding fitting curves when the excitation fluence is $40 \mu\text{J}/\text{cm}^2$. Same color and shape coding as in (b). (d) Normalized PL intensity decay map of BE in Cu: CdSe CQWs (probed at 514 nm) as a function of the time and the excitation fluence. With low excitation fluence, the lifetime of X increases due to the filling of copper sites. Further increasing the excitation fluence, multiple carriers dominate the recombination dynamics of X. (e) Excitation fluence dependent lifetimes probed at 514 nm which is extracted from the 2D contour map shown in **Figure 2.6d**. The red solid line is the fitting based on the coupled kinetic-equation model (see **Appendix 2.3**).

In contrast, with high fluence and thus high exciton density (**Figure 2.6c**), the onset of XX is significantly delayed compared with X, accompanying a fast recombination process with the lifetime of 128 ± 27 ps while the lifetime of X is 201 ± 32 ps. This delayed and accelerated decay provides another strong evidence of the biexciton emission^{[6][67]} at XX. Note that the lifetime ratio between exciton and biexciton is ~ 1.57 , which is close to the value reported in traditional epitaxial quantum wells (GaAs or CdS)^{[68][69]}. The result strongly suggests a suppressed Auger recombination in Cu:CdSe CQWs compared to that in type-I CdSe CQDs^{[20][21]}, where biexciton lifetime is typically two order of magnitude shorter than exciton lifetime. Moreover, according to the statistics of carrier recombination, the radiative recombination rate of the biexciton should be one quarter of the value in exciton, here, our ratio is smaller than 4^[21], excluding the efficient Auger recombination in Cu:CdSe CQWs, as discussed in previous studies^{[22][24][25]}.

Figure 2.7 Calculated biexciton states. (a) Simulated biexciton dynamics. The red solid line is the fitting based on the coupled kinetic-equation model and blue solid line is the biexciton dynamics which holds the thermal equilibrium. (b) Simulated biexciton emission as a function of pump fluence. Hollow square is the simulation result and red solid line is the power law fitting. And extracted $k = 1.77$ is slight larger than what we observed in continuous-wave excitation^[8].

To shed more light on the effect of copper dopants on band edge emission in host CQWs, we have analysed the fluence dependent dynamics of exciton (probed at 514 nm). As shown in **Figure 2.6d**, initially increasing fluence results in a slower dynamic and the exciton lifetime will be close to the value in undoped CQWs (293 ps, see **Figure 2.2d**), indicating saturated copper sites. This trend validates the proposed carrier mechanism in **Figure 2.2a** and our method to extract the hole capture lifetime from host CQW to the Cu^+ sites (**Figure 2.2d**). With even higher excitation fluence, in addition to the Cu^+ saturation, multiple-exciton interaction process is occurring with high excitation fluence and accelerates the exciton dynamics (two-exciton interaction process to promote into biexciton)^{[21][70]}. We furtherly verify our interpretation by reproducing the fluence dependent exciton dynamics using a copper-perturbed coupled kinetic-equations^{[8][71]}. Briefly, exciton dynamics is controlled by the interplay between dopant-related exciton decay rate and fluence dependent exciton-exciton interaction process while biexciton formation rate is related to the thermal equilibrium status (see the model in **Appendix 2.3** for details). The quality of the fitting (see **Figure 2.6e**) confirms the validity of our model: with low fluence, exciton dynamics is changing following the filling of Cu^+ site; Whereas with high fluence, multiple carrier interaction takes control the decay channel.

Moreover, we can also predict the biexciton dynamics and fluence dependent biexciton intensity based on the proposed model, which is consistent with the experimental results, as shown in **Figure 2.7a**. The blue curve is the calculated biexciton decay, using the biexciton formation rate under the full thermal equilibrium, which clearly deviates from the experiment result. **Figure 2.7b** shows the biexciton emission intensity plotted logarithmically against the pump fluence. After doing the power fit for simulation results, $k = 1.77$ is extracted which is slightly larger compared with the experimental result shown in **Figure 2.3d** (main text, continuous-wave excitation).

A most striking observation is the stimulated emission in dispersions of Cu:CdSe CQWs at high excitation fluence in transient-absorption spectra (see **Appendix 1.5**), arising from the radiative recombination of biexcitons.

Figure 2.8 Transient absorption spectra of Cu:CdSe CQWs, excitation laser: 100 fs @ 400 nm. (a) 2D transient absorption change (ΔA) images of Cu:CdSe CQWs (see the ΔA data with the full wavelength range in Fig. S6b). The measurement was obtained at a fluence of $40 \mu\text{J}/\text{cm}^2$. Also the negative ΔA beyond the PIA band is only observed in Cu:CdSe CQWs (see the ΔA images of undoped CQWs in **Figure 2.9a and 2.9d**). (b) ΔA spectra as a function of wavelength using different delay time at a fluence of $40 \mu\text{J}/\text{cm}^2$. The negative band around 528 nm exhibits a delayed formation. (c) 2D transient absorption (A) images of Cu:CdSe CQWs at a fluence of $40 \mu\text{J}/\text{cm}^2$. The red color-coded region indicates the stimulated emission ($A < 0$) around 528 nm. (d) Time-resolved A spectra (probed at 528 nm) with different fluences. At a fluence of $40 \mu\text{J}/\text{cm}^2$, the gain can last over a period of >200 ps. The inset shows the dynamics of $-A$ at a fluence of $40 \mu\text{J}/\text{cm}^2$ which yields a lifetime of 187 ± 5 ps.

As expected, in the ΔA spectra of Cu:CdSe CQWs, we observe a weak absorption bleach (the transition of d orbital electrons in Cu^+ to the CB of CdSe CQWs, $\text{ML}_{\text{CB}}\text{CT}$, which is also discussed in **Figure 2.2**) covering the whole spectrum beyond the red side of the positive

photo-induced absorption (PIA) band, as shown in **Figure 2.8a and 2.8b**. This weak absorption bleach exhibits nearly invariant dynamics within the measured time window ($> 3\text{ ns}$) which is consistent with the slow recombination between CB electrons and copper-trapped holes (lifetime: $\sim 450\text{ ns}$, **Figure 2.2c**). Notably, after several picoseconds delay, we unambiguously observe the appearance of a strong negative signal (the saturated red region in **Figure 2.8a**) peaked at $\sim 528\text{ nm}$ below the PIA band. Here, we can assign the emerged negative signal around 528 nm to a stimulated emission process, because of three reasons as follows. (i) This does not arise from $\text{ML}_{\text{CB}}\text{CT}$ since this process induced bleaching should occur simultaneously with the heavy-hole bleaching (see the curve in **Figure 2.8b** with a delay time of 10 fs)^[54].

Moreover, the strong negative signal exhibits much faster decay than the absorption bleaching of $\text{ML}_{\text{CB}}\text{CT}$, implying that the negative signal around 528 nm is related to the dynamics of band edge carriers^[50]. (ii) The negative signal peaking at 528 nm shows a delay formation and only appears after several picosecond (**Figure 2.8b**) with respect to the linear absorption bleaching band^{[71][72]}. (iii) The negative signal can only be observed under high pump fluence (see the images of ΔA in Cu:CdSe CQWs with different pump fluences in **Figure 2.9e**) and the energy location is exactly matching our biexciton emission spectra^{[63][71][72]}.

The stimulated emission from biexcitons is further verified by the absolute absorbance $A(\lambda, t) = \Delta A(\lambda, t) + A_0(\lambda)$, where $A_0(\lambda)$ is the linear absorption with the same measurement condition^{[72][73]}. **Figure 2.8c** presents the contour map of absolute absorbance at a pump fluence of $40\text{ }\mu\text{J}/\text{cm}^2$ which codes the positive absorbance with blue colour and gain ($A < 0$) with red colour. The optical gain region is exactly matching the biexciton emission resolved in previous part (dashed black rectangle) and can last more than 100 ps . The dynamics of stimulated emission with different pump fluences probed at the wavelength of 528 nm is shown in **Figure 2.8d**. with low fluence, no gain can be achieved. With increasing fluence ($>$

$10 \mu\text{J}/\text{cm}^2$), the value of A turns negative after the initial short-lived (< 1 ps) positive feature caused by hot carriers.

Figure 2.9 Supplementary TA spectra (ΔA , absorbance change) of doped and undoped CQWs. **(a)** Undoped CQWs with the pump fluence of $40 \mu\text{J}/\text{cm}^2$. **(b)** Doped CQWs with the pump fluence of $40 \mu\text{J}/\text{cm}^2$, white dashed square indicates the biexciton gain region which is missing in undoped sample; **(c)** ΔA of doped and undoped CQWs probed at the delay time of 25 ps with the pump fluence of $40 \mu\text{J}/\text{cm}^2$; **(d)** 2D transient absorption change (ΔA) images of undoped CQWs which emphasizes the long wavelength range. **(e)** ΔA of doped CQWs as a function of pump fluence (delay time: 25 ps).

At the fluence of $40 \mu\text{J}/\text{cm}^2$, the optical gain relaxation is fitted to a bi-exponential decay. The slow decay component with a lifetime of ~ 187 ps matches well with the PL decay probed at 528 nm (~ 128 ps, **Figure 2.6c**), confirming again the long-lived biexciton states support the observation of sustainable biexciton emission in Cu:CdSe CQWs. Interestingly, the gain dynamics shows a fast component (with a lifetime of 8.67 ± 0.2 ps) which is absent in the trPL measurement. This fast decay in absorbance is likely to be assigned to multi-exciton recombination.

2.3 Low-threshold biexciton lasing

Transition metal doped colloidal nanomaterials (TMDCNMs) have recently attracted attention as promising nano-emitters due to the dopant-induced properties. However, despite ample investigations on the steady-state and dynamic spectroscopy of TMDCNMs, experimental understandings of their performance in stimulated emission regime are still elusive. Here, the dopant-amount-dependent optical gain properties of copper-doped CdSe colloidal quantum wells (CQWs) are systematically studied for the first time. We have demonstrated that the amplified spontaneous emission (ASE) threshold in copper-doped CQWs is a competing result between the biexciton formation (which is preferred to achieve population inversion) and the hole trapping (which hinders the population inversion). An optimum amount of copper dopants enables a lower ASE threshold of $\sim 7 \mu\text{J}/\text{cm}^2$ compared to the value ($\sim 58 \mu\text{J}/\text{cm}^2$) in undoped CQWs under sub-nanosecond pulse excitation. Based on it, a copper-doped CQW film embedded in the vertical cavity surface-emitting laser (VCSEL) structure yields an ultralow lasing threshold of $4.1 \mu\text{J}/\text{cm}^2$. Exploiting optical gain from TMDCNMs may help to further boost the performance of colloidal-based lasers.

2.3.1 Optical properties of undoped and copper-doped CQWs

We prepare the copper-doped and undoped 4 mono-layer CdSe CQWs according to the existing recipes^[50,51] and optimize the procedures to achieve copper-doped CQWs with high aspect ratio to avoid stacking. For the optical gain study, the amount of copper dopants is controlled by modifying the volume of copper precursor added and the averaged copper dopants per CQW is determined by the coupled plasma mass spectrometry (ICP:MS, see details in **Appendix 1.3**).

Figure 2.10 Optical properties of undoped and copper-doped CQWs. (a) The steady-state optical properties of undoped (bottom) and copper-doped (top) CQWs. The insets are the HAADF-STEM images (scale bar: 30 nm). The copper-doped CQWs display two emission bands: band-edge emission (BE) and copper-related emission (CE). (b) The schematics to illustrate the carrier transitions and radiative recombination in copper-doped CQWs. (c) Normalized decay curves of BE for undoped CQWs (measurement: black square; fitting: black solid line) and copper-doped CQWs (measurement: green circle; fitting: green solid line) with the low pump fluence, the PL dynamics of both doped and undoped CQWs are probed at 514 nm in hexane.

An example of the steady-state optical properties of doped and undoped CQWs under UV illumination is shown in **Figure 2.10a** (the spectra of other doping level are shown in **Figure 2.11**), the similar absorption spectra indicate that excitonic resonance in CQW host is not affected by copper dopants. Notably, besides showing a narrow band edge emission (BE), doped CQWs display a broad PL band at the low energy side, which is called the copper-related emission (CE). As shown in **Figure 2.10b**, CE is attributed to the recombination between the captured holes in copper dopants and the electrons in the conduction band (CB) of the host CQWs: $\text{Cu}^{2+} + e \rightarrow \text{Cu}^{1+} + h\nu$ ($h\nu$ is the photon energy of CE and e denotes an electron in CB)^[4,5,20].

Figure 2.11 Absorption (black curve) and PL (red curve) for different copper doping level. The amount of copper per CQW and the quantum yield are also presented.

The BE dynamics of doped (green circles) and undoped (black squares) CQWs in solution with low pump fluence ($< 0.1 \mu\text{J}/\text{cm}^2$) is presented in **Figure 2.10c**. In the short-time window (up to 400 ps), the ultrafast recombination channel (~ 31 ps) in undoped CQWs is absent in copper-doped CQWs. The single exponential decay behaviour of copper-doped CQWs is consistent with theoretical calculation conducted by Nelson^[61], in which highly localized covalent $[\text{CuSe}_4]$ cluster can suppress intrinsic traps (structure defects) and thus, enhance the

PL quantum yield (PLQY) of copper-doped nanocrystals. Moreover, the reduced lifetime of copper-doped CQWs both in the short-time window and the long-time window (up to 4 ns) supports the argument that copper dopants are trapping the hole from the host.

2.3.2 ASE from copper-doped CQWs

To investigate the ASE behaviour of copper-doped CQWs, we prepare a close-packed solid film by drop-casting (stripe excitation geometry with sub-nanosecond pulse is used). We have compared the emission properties between undoped and copper-doped CQWs. A contour map of ASE spectra for undoped sample is presented **Figure 2.12a**, a narrowing emission spectrum is observed when the pump fluence is beyond the ASE threshold of $\sim 58 \mu\text{J}/\text{cm}^2$, which is typical as reported previously^[71-75]. For doped sample with ~ 40 copper dopants per CQW, as shown in the contour map of ASE spectra in **Figure 2.12b** (the corresponding 1D spectra is presented **Figure 2.13**), when excitation fluence is low ($< 0.1 \mu\text{J}/\text{cm}^2$), BE spectra are symmetric and peak at $\sim 514 \text{ nm}$. As the fluence increases but still below the ASE threshold, a new emission channel appears to broaden the BE spectra and is confirmed to be the biexciton emission because of the super-linear intensity increase compared to the exciton emission (see the left panel of **Figure 2.12c**, more evidences for the biexciton justification can be found in our previous publication)^[24,76,77]. With the fluence higher than $\sim 0.22 \mu\text{J}/\text{cm}^2$, biexciton emission becomes the strongest emission channel (indicating by the bottom white dashed line in **Figure 2.12b**). When the fluence is even stronger, beyond the fluence of $\sim 7.05 \mu\text{J}/\text{cm}^2$, ASE emerges following by a sharp increase of BE intensity (**Figure 2.12c**) and the narrowing of the BE spectra (FWHM: $\sim 8 \text{ nm}$, the right panel of **Figure 2.12c**).

Meanwhile, CE starts to saturate beyond the ASE threshold (as indicated by the top white dashed line in the right panel of Figure 2b). This observation is confirmed again that copper

dopants are consuming the excitation energy in the host via hole trapping and ASE can only happen when copper dopants are fulfilled.

Figure 2.12 Amplified spontaneous emission (ASE) in undoped (a) and copper-doped (b-c) CQWs under the excitation of sub-nanosecond laser pulses. (a) Left panel: 2D spectra map for undoped CQWs, the map is normalized by the maximum emission intensity with each fluence; Right panel: integrated emission intensity (magenta squares) and FWHM (red stars) for undoped CQWs. The ASE threshold of $\sim 58.4 \mu\text{J}/\text{cm}^2$ is extracted. (b) 2D spectra map for copper-doped CQWs. Left panel: BE normalized by the maximum BE intensity with each fluence; right panel: CE normalized by the maximum CE intensity with the highest fluence. X: exciton emission. XX: biexciton emission. The dashed white lines point out the onset of biexciton emission and ASE, respectively. (c) Left panel: integrated BE intensity (magenta squares) and FWHM (red stars) for copper-doped CQWs with

low pump fluence. Beyond $\sim 0.22 \mu\text{J}/\text{cm}^2$, biexcitons emission dominates the BE; Right panel: integrated BE intensity (magenta squares), CE intensity (blue circles) and FWHM (red stars) for copper-doped CQWs with high pump fluence. The ASE threshold of $\sim 7.05 \mu\text{J}/\text{cm}^2$ is extracted.

Therefore, according to the existing experimental data, we can summary that there are two opposite effects which can influence the ASE behavior in copper-doped CQWs: (1) the strong biexciton emission which is the easy to form population inversion due to the four-energy-level and can reduce the linear absorption losses because of the red-shift; (2) the hole trapping which becomes a dopant-induced loss channel and damages the population inversion in the host via fulfilling the valence band. And we speculate that the observed ASE threshold in copper-doped CQWs should be a competition between the biexciton formation and hole trapping.

Figure 2.13 Emission spectra of copper-doped CQWs (~ 40 copper dopants per CQW) under the strip excitation geometry (500 ps laser pulse, drop-cast film). We can observe the transition for exciton (X) to biexciton (XX) at very low pump fluence.

To verify our speculation, we have conducted ASE measurement in copper-doped CQWs with different amounts of dopants and the threshold result is summarized in **Figure 2.14** (for clarify, the CE fraction percentage calculated from the UV illuminated emission spectra of doped

samples in solution is also presented, and the UV illuminated emission spectra of doped samples is presented in **Figure 2.11**). Three zones have been observed for the copper-doped sample with different dopant amounts. In zone I (i.e., light doping: copper dopants per CQW is smaller than 10), copper-doped CQWs display a low PLQY ($\sim 30\%$, which is comparable with the undoped CQWs) associated with a small CE fraction percentage. In this zone, threshold is higher than the value in undoped CQWs since the biexciton is not observed in this regime and hole trapping degrades the ASE performance.

Figure 2.14 The effect of copper dopants on ASE threshold: variation of amplified spontaneous emission (ASE) thresholds for copper-doped CQWs with different amounts of dopants per CQW. CE fraction of the emission spectra under UV illumination with respect to total integrated emission ($I_{\text{CE}}/I_{\text{CE}}+I_{\text{BE}}$) has been co-plotted along with ASE thresholds. Quantum yield numbers are also listed.

With further increasing the dopant precursor amount (i.e., medium doping: copper dopants per CQW is in the range of 10 to 40), in Zone II, the PLQY becomes higher than the value in Zone I due to the suppression of defects as discussed in **Figure 2.10**. And the contribution from the biexciton and the moderate percentage of CE (i.e., copper dopants are easy to be saturated) start to low the ASE threshold. The lowest threshold of $\sim 7 \mu\text{J}/\text{cm}^2$ is achieved (as

shown in **Figure 2.12**) when copper dopants per CQW is around 40. While in Zone III (i.e., heavy doping: copper dopants per CQW is larger than 40), we have achieved the highest PLQY. However, the CE is overwhelming the emission spectrum (CE percentage > 99%), in this case, a huge portion of excitation energy is lost due to hole trapping, consequently the optical gain performance becomes poor again.

2.3.3 Copper-doped CQWs based VCSEL

A VCSEL is a good testbed for us to characterize the lasing performance in copper-doped CQWs^{[20][59][60]}. Structure of the VCSEL device is shown in **Figure 2.15a**: a spin-casted copper-doped CQW film is embedded in a planar cavity constructed from two Bragg mirrors (see the reflection spectra of Bragg mirrors in **Figure 2.16a**).

The copper-doped CQWs based VCSEL is excited by a focused laser spot with a diameter of 15 μm and the emission is collected coaxially on the reflection side at the normal direction. It is worth pointing out that the cavity length in our VCSEL is controlled by a differential micrometer drive (see **Appendix 1.7** for details) and that both single-mode (shown in **Figure 2.15**) and multiple-mode lasing (see **Figure 2.16b**) are demonstrated. **Figure 2.15b** depicts the logarithmic plot of emission intensities with different fluences. We notice that the spontaneous emission in VCSEL is red-shifted compared to the ASE measurement, which is probably due to density of states modification by a dielectric cavity^[60]. When fluence is high enough, a narrow single-mode lasing peak ($\sim 531\text{ nm}$) is observed, as shown in the pseudo-colour intensity map (**Figure 2.15c**). The lasing action is further demonstrated by the spectra analysis (**Figure 2.15d**): the integrated BE intensity clearly exhibits a S-shape nonlinear dependence and FWHM of BE shrinks from ~ 12 down to $\sim 0.3\text{ nm}$ when the fluence exceeds $\sim 4.13\text{ }\mu\text{J}/\text{cm}^2$, suggesting the transition from spontaneous emission to lasing. In addition, after crossing the lasing threshold, a high-brightness spot (**Figure 2.17e**) without dim and diffusion emission of

spontaneous emission indicates the well-defined spatial coherence in our VCSEL device^{[20][59][60]}.

Figure 2.15 VCSEL lasing in copper-doped CQWs under the excitation of sub-nanosecond laser pulse. (a) Schematic of the VCSEL with two distributed Bragg reflectors (DBR, reflectivity at 525~535 nm > 99%). (b) Emission spectra of BE in VCSEL with varied fluences on a semi-logarithmic plot. Single-mode lasing is achieved beyond the laser threshold. (c) The normalized spectral map of BE in VCSEL, showing the transition from a broad spontaneous emission to a sharp lasing peak. (d) The integrated BE intensity (red asterisk) with increasing fluence in a log-log scale, showing a clear knee behaviour. Blue lines are the log-log fitting of BE intensity, extracting a lasing threshold of $\sim 4.1 \mu\text{J}/\text{cm}^2$. Blue squares show the change of FWHM of BE as a function of the fluence. (e) Near-field emission images of VCSEL when the excitation fluence is below, near and beyond the lasing threshold.

Figure 2.16 VCSEL laser device. (a) Reflection spectrum of a single distributed Bragg reflector (13.5 pairs: red curve; 5.5 pairs: blue curve). The distributed Bragg reflector (DBR) is fabricated using alternating $\lambda/4$ layers of Nb_2O_5 and SiO_2 deposited onto a soda-lime glass substrate by ion beam sputter deposition (IBSD). The design of the DBR leads to a stop-band width >140 nm (with $R > 90\%$) around the emission wavelength and a maximum reflectivity $R_{\text{max}} > 99\%$. (b) Multi-mode lasing in copper-doped CQW VCSEL device. Left panel is the emission spectra. Right panel is the 2d image recorded in our spectrometer. In our VCSEL device, we can actively control the optical length of the cavity. Thus, besides the single-mode lasing presented in **Figure 2.15**, multiple-mode lasing is also observed when the pump fluence is above the threshold. In addition, the threshold variation throughout the different optical length of cavity is minimal.

2.4 Summary

In the first part of this chapter, we have discovered the four-particle neutral biexciton in Cu-doped CdSe CQWs, which is unambiguously identified by its transient photophysical properties, super-linear emission intensity, and thermal stability. Further studies are necessary to understand formation mechanism and constituent of biexciton, where the roles of a dark exciton was not observed in our Cu:CdSe CQWs. This is in contrast with the biexciton

mechanism in WSe_2 where slow dark excitons enable biexciton states with continuous-wave excitation^[12]. It is also worth to explore whether biexcitons in Cu-doped CQWs could have a more significant fine structure splitting since the energy difference between photon pair generated from biexciton can reduce the pure polarization entanglement substantially^[13]. More evidences to characterize the electron-hole exchange interaction and optical selection rules could further check the potential of biexciton in Cu-doped CQWs as practical entanglement photon sources.

Nevertheless, we have demonstrated biexciton emission in Cu-doped CdSe CQWs under continuous-wave excitation at room temperature. The achievement is attributed to the signatures of the material: enhanced biexciton binding energy and suppressed non-radiative recombination in this host-dopant system. The observation of spectrally separable, radiative biexciton states is a key to study coherent many-body physics, such as condensation and superfluidity. Further, such sustainable biexciton emission at room temperature, using fully solution-processed colloidal assemblies of nanomaterials, offers broad potential applications in practical quantum optoelectronics, including quantum logic gates and high-order correlated photon emission.

In the second part of this chapter, we have studied the optical gain performance of copper-doped CdSe CQWs with varying amount of copper dopants. The pump-fluence-dependent spectra of the solid film indicate that an optimum copper amount (~ 40 dopants per CQW) can facilitate the biexciton formation and significantly lower the ASE threshold in CdSe CQWs despite the dopants are consuming the excitonic energy in the host via hole trapping. Using the optimized copper-doped CQWs as the gain material, excellent lasing performance with the threshold as low as $4.1 \mu\text{J}/\text{cm}^2$ in the VCSEL device comprising of two distributed Bragg reflectors has been demonstrated. Future efforts following this study lie in the physical

understanding of the copper's role on the biexcitons in CdSe host including the formation mechanism and the constituent of biexcitons.

Appendix 1: Experimental methods

1.1 Synthesis of Cu:CdSe CQWs

Cu-doped 4 ML CdSe CQWs are synthesized by our previous reported recipe with few modifications^{[50][51]}. Briefly, 340 mg of cadmium myristate, 24 mg of Se, and 30 mL of ODE were added in a 100 mL flask. We degassed and stirred the solution for 1h at 95 °C. After dissolution of cadmium myristate we shifted to argon and raised the temperature of solution to 240 °C. At 190 °C we injected the Cu precursor slowly. The addition of dopant precursor should be completed before the temperature of reaction solution reaches ~195-198 °C. This was followed by the quick introduction of 120 mg of cadmium acetate dihydrate. Thereafter, the crude solution was maintained at 235-240 °C for 10 min for the growth of CQWs. After 10 min we injected 1 mL of oleic acid and cooled down the solution to room temperature by using a water bath. During cooling 5 mL of hexane was added to this crude reaction solution below 80 °C. Then we centrifuged the solution at 6000 rpm for 5 min. To the supernatant we added ethanol and again centrifuged for 10 min at 6000 rpm and dissolved the precipitates in hexane.

For the preparation of dopant precursor in the current study, 30 mg of copper (II) acetate was mixed with 3.6mL of TOP and 0.4 mL ODE in N₂ filled glove box. The mixture was stirred at 90 °C for 8 h and stored in glove box for further use.

1.2 Linear optical characterization of Cu:CdSe colloidal quantum wells

Absorption spectra of Cu:CdSe CQWs in hexane is measured by a UV-VIS spectrophotometer (Shimadzu, UV-1800). PL spectra of Cu:CdSe CQWs in hexane are recorded using a fiber-

coupled ANDOR spectrometer (monochromator: ANDOR Shamrock 303i, CCD: ANDOR iDus 401) with a diode laser excitation (Cobolt 06-MLD, excitation wavelength: 405 nm). Quantum yield (QY) of Cu:CdSe CQWs in hexane is measured with an integrating sphere and calculated as the ratio of absolute emission and absorption photons. The accuracy of the QY measurement is verified using Rhodamine 6G, whose QY of 94.3% measured in our setup, is found in good agreement with the standard value of 95%.

1.3 Estimation the Cu atomic level

With Inductively coupled plasma mass spectrometry (ICP:MS) we estimated Cu atomic levels with respect to cadmium and selenium. Average dimensions of our 4 ML Cu:CdSe CQWs measured by TEM microscopy are $(36 \pm 1.9) \times (15.0 \pm 1.5) \times 1.2$ nm, which suggests 13500 cadmium and 10600 selenium atoms in one CQW. Therefore, using ICP:MS measurements we can estimate Cu atoms per CQW.

1.4 Time-resolved photoluminescence measurement

Time-resolved PL (TRPL) measurements are performed with a streak camera from Optronics. The 400-nm pump laser pulses for TRPL are generated from a 1000 Hz regenerative amplifier (Coherent Libra™). The beam from the regenerative amplifier has a center wavelength at 800 nm, a pulse width of around 150 fs and is seeded by a mode-locked Ti-sapphire oscillator (Coherent Vitesse, 80MHz). 400-nm pump laser was obtained by frequency doubling the 800-nm fundamental regenerative amplifier output using a BBO crystal. All measurements are performed in the solid film at room temperature in ambient air ($53 \pm 2\%$ humidity) conditions.

1.5 Transient absorption spectroscopy

TA spectroscopy is performed using a Helios™ setup (Ultrafast Systems LLC) and in transmission mode with chirp-correction. The white light continuum probe beam (in the range of 400-800 nm) is generated from a 3 mm sapphire crystal using 800 nm pulse from the

regenerative amplifier as mentioned in TRPL measurement. The pump beam spot size is ~ 0.5 mm. The probe beam passing through the sample was collected using a detector for UV–Vis (CMOS sensor). All measurements are performed at room temperature in solution (hexane).

1.6 Amplified spontaneous emission measurement

The pump laser at 355 nm used for stripe excitation in the ASE measurement is a frequency tripling of Nd:YAG laser with a pulse width of 0.5 ns and a repetition rate of 100 Hz. The laser beam is focused onto a stripe along the drop-casted film on the glass substrate using a cylindrical lens and incidenting from the Cu:CdSe CQWs. The width of the stripe, which contains $(1-1/e)$ of the power in the laser beam, is 50 μm , determined using the knife-edge method. In the experiment, the stripe length is 4 mm. An automatically rotated $\lambda/4$ waveplate (WPQ05M-532, THORLABS) and polarizer (CCM1-WPBS254, THORLABS) are used to adjust the pump fluence. Then, the emission is collected via a fiber-coupled ANDOR spectrometer (monochromator: ANDOR Shamrock 303i, CCD: ANDOR iDus 401). The collection geometry is perpendicular to the laser pump. All measurements are performed at room temperature in air.

1.7 Vertical-Cavity Surface-Emitting Laser

Two kinds of DBRs with 5.5 (top DBR) and 13.5 (bottom DBR) periods of alternating $\lambda/4$ layers of $\text{Nb}_2\text{O}_5/\text{SiO}_2$ are fabricated using ion beam sputter deposition (IBSD) leading to a stop-band width of 140 nm around the emission wavelength and $R_{\text{max}} > 99\%$. As the optical gain medium, Cu:CdSe CQW film is deposited on the surface of one DBR at a spin-rate of 2,000 rpm for 60 s using a concentrated solution (20 mg/mL in hexane). Then, a differential micrometre drive (DM22, THORLABS, the smallest incremental move: 50 nm) is used to push the second DBR close to the CQW film, also controls the cavity optical length to achieve

single-mode or multi-mode lasing. All measurements are performed in the reflection geometry at room temperature in air and using the same laser pulse as described in the amplified spontaneous emission measurement.

Appendix 2: Theoretical calculations

2.1 Calculation of the biexciton binding energy based on emission spectra

The biexciton binding energy is defined as the energy difference between biexciton states and two free excitons: $\Delta_{biex} = 2E_{ex} - E_{biex}$, where Δ_{biex} is the biexciton binding energy; E_{ex} and E_{biex} is the energy of exciton and biexciton, respectively. Considering that the radiative recombination of one biexciton will generate one exciton and emit one photon: $E_{biex} = E_{ex} + h\nu_{xx} = h\nu_x + h\nu_{xx}$ ($h\nu_x$ and $h\nu_{xx}$ is the photon energy of exciton and biexciton emission, respectively). Thus, we can calculate the biexciton binding energy (Δ_{biex}) based on the spectra shift: $\Delta_{biex} = h\nu_x - h\nu_{xx}$.

2.2 Thermal intensity distribution fitting

As explained in **Figure 2.5**, assuming the formation rate of biexciton is roughly constant with varying temperature, while the decay rate (γ_{biex}) is enhanced by the thermal energy, the temperature dependent biexciton emission intensity change can be fitted by a Boltzmann distribution function: $b/[1+a*\exp(-E/kT)]$, where b is a constant, a is the coefficient, and E is the activation energy which is corresponding to the biexciton binding energy.

2.3 Exciton/Biexciton Coupled Kinetic Model

Here, we model the emission intensity and the temporal dynamics of exciton/biexciton as a function of pump fluence in terms of coupled kinetic equations. The standard coupled rate equations proposed by Heinz et al.^[8] and Cerullo et al.^[71] are considering the following scenario (see **Figure A1**): When the density of exciton is reaching certain level, the biexciton can be formed through the exciton-exciton interaction process, in which excitons form

biexcitons. And the dissociation of biexciton will generate one exciton and emit one photon. Such process is widely reported in other colloidal semiconductor materials and mono-layer TMDs.

Figure A1 Sketch of the energetic levels and the formation/dissociation of exciton/biexciton scenario in Cu: CdSe CQWs.

Considering in our Cu: CdSe CQWs, copper dopants play a role on the band edge recombination dynamics and thermal equilibrium condition is not valid. On the other hand, there is no doubt that exciton-exciton interaction process will be enhanced with high fluence due to the increased exciton density. Here, we assume the limitation of exciton-exciton interaction rate is reaching the ASE rate. Hence, we modify the standard coupled rate equation model to predict the exciton/biexciton density and dynamics variation with pump fluence in the copper doping nanomaterials, the full set of equations are shown as following:

$$\begin{aligned}
 \frac{dn_{ex}}{dt} &= -\gamma_{ex}n_{ex} + \gamma_{biex}n_{biex} - 2k_{ex-ex}n_{ex}^2 + G_{ex} \\
 \frac{dn_{biex}}{dt} &= k_{ex-ex}n_{ex}^2 - \gamma_{biex}n_{biex} \\
 \gamma_{ex} &= \max\{\gamma_{ex}^{un-doped}, \gamma_{ex}^{un-doped} + \gamma_{hc}(1 - \frac{F}{F_0})\} \\
 k_{ex-ex} &= k_{ASE}(\frac{F}{F_{th}})^\beta
 \end{aligned} \tag{A1}$$

Where n_{ex} and n_{biex} is the density of exciton and biexciton, respectively. F is the pumping fluence. F_0 is the pump fluence at which copper sites are full filled (saturated). F_{th} is the threshold of ASE. β is a fitting parameter which is related to the non-equilibrium condition. G_{ex} is the pump-generated rate for exciton. γ_{hc} is the hole-capturing rate and k_{ASE} is the ASE rate.

Figure A2 Numerical simulation (solid lines) of exciton temporal dynamics as a function of fluence.

As shown in **Figure A2**, the temporal dynamics of exciton exhibits different trends under low and high pump fluences. When pump fluence is low, the recombination rate of exciton decreases as fluences increase due to the state filling of copper dopants. While with high pump fluence, the recombination rate of exciton becomes faster due to the enhanced exciton-exciton interaction process. These simulation results allow us to reproduce the fluence dependent exciton dynamics presented in **Figure 2.6**.

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Chapter 3: Förster resonance energy transfer to control exciton flow

3.1 Motivation and Introduction

Exciton-based solid-state devices have potentials to be essential building blocks^{[1][2]} for modern information technology to surpass the performance of conventional electronic devices since excitonics combines the ultrafast operation speed^[3] with the highly compact footprint^[4]. Because of the direct interaction with photons, excitonic devices effectively eliminate the interconnection delay between photon-based information communication and electron-based information processing. Unlike photonic devices with diffraction limit of footprint, the exciton thermal de Broglie wavelength is extremely small (around 10 nm) at room temperature. Exploiting excitonic devices requires the ability to control the excitonic properties (e.g., exciton flow, recombination rates or exciton energy) in an optically active medium^{[2][5]}. Until now, a series of excitonic schemes have been used to achieve the controllability based on exciton-photon polariton^{[6][7]}, coupled indirect excitons^{[4][5]}, DNA nanotechnology^{[8][9]} or electric-field modulation^{[1][2]}. Unfortunately, these configurations restrict their application in integrated circuits because they either sacrifice the operation speed due to applying gate voltage or are inherently complex due to the requirement of high Q-factor microcavity, engineered electron/hole wavefunction overlap or nanometer-scale precise DNA scaffold.

Targeting the above-described challenges, the scheme with an emphasis on all-optical controlling, bottom-up fabrication and self-assembly offers a more attractive solution. Förster resonance energy transfer (FRET) is a particularly promising mechanism for excitonics as dipolar coupling between a donor and an acceptor permits efficient and directed exciton flow in a simple solid mixture^[10-13]. On the other hand, stimulated emission, where exciton

recombination dynamics differs dramatically from that in spontaneous emission, is a possible controlling mechanism because FRET process significantly depends on the density of excitons in donor and acceptor populations^{[14][15]}. Colloidal quantum wells (CQWs) with high quantum efficiency, tunable energy bandgap and solution processability, have recently attracted broad research interest for optoelectronic devices^[1 * MERGEFORMAT 6-19]. In particular, CQWs have exhibited robust excitons at room temperature with a binding energy up to 150 meV^{[16][18]}, extraordinary optical gain performance^{[19][20]} and near-unity FRET efficiency^{[10][21]}, promising an ideal platform to achieve an all-optical control of exciton flow using FRET.

In the first part of chapter 3, we propose a strategy to control the exciton flow based on stimulated emission mediated FRET process in a binary nanomaterial complex consisting of 4 monolayer (ML) core-only CdSe CQWs (the donor) and 8 ML core-shell CdS/CdSe/CdS CQWs (the acceptor). Specifically, in spontaneous emission regime, nearly 50% of the exciton population in the donor outflows into the acceptor via FRET. Controlling the pumping level to achieve stimulated emission in the acceptor not the donor, we can almost shut down the excitonic emission in donor since quick depletion of excitons in the acceptors significantly promotes FRET. Upon further increasing excitation, stimulated emission in the donor totally switches off the exciton flow toward the acceptors since lasing occurs much faster than FRET. Furthermore, we develop a FRET-coupled kinetic model to identify the competing processes that are responsible for the variation of exciton flow. Our results, which demonstrate a prototype of controllable exciton flow with multiple modulation stages and exceptional contrast ratio, may inspire the design of all-optical excitonic circuits.

Förster resonance energy transfer (FRET), which describes the non-radiative energy transport via dipolar coupling from a donor to an acceptor^{[13][22]}, is a powerful tool used in various domains spanning from biophysics^[23-25], for detecting inter-/intra-molecular interactions at nanometer-scale, to energy optoelectronics^[26-28], for enhancing light-conversion or light-

harvesting via modulating FRET rate. In biophysics, the dynamics in biomolecules of interest can be quantified by monitoring the FRET rate between a labelled donor/acceptor pair^{[29][30]}. However, conventional FRET in a binary complex is a one-way process and only offers one output information. This makes the interpretation of potential dynamics incomprehensive or even inaccurate, since the rate of FRET depends on a number of factors^{[13][31][32]}, including the distance between the donor/acceptor pair, the spectral overlap between the donor emission and the acceptor absorption, the quantum efficiency of donor, and the dielectric environment. On the other hand, control of FRET is always at the forefront of energy optoelectronics. Recent years, multiple external stimuli, such as temperature^[21], electric field^[32], the local density of states (LDOS)^{[33][34]}, or the Coulomb screening^[31], have been successfully adopted to control FRET in nanomaterial complexes. Unfortunately, such conventional FRET with intrinsically unidirectional energy transfer restricts our control capability for multi-parameter systems, e.g., light-conversion among red, green and blue colours^{[35][36]}.

Colloidal quantum wells (CQWs)^{[17-19][37]}, owing to their high quantum efficiency, narrow emission spectrum and solution processability, have recently evoked considerable attention in FRET studies^{[10][38][39]}. Several unique properties have set CQWs rather than lower-dimensional nanomaterials (like 0D and 1D) as ideal FRET donors and acceptors. Specifically, the extended 2D geometry which enhances the dipole interactions^{[10][11]}, and atomic thickness control in the quantum-confined dimension which reduces the possibility of homo-FRET^[40] ensure the binary CQW complex to achieve near-unity FRET efficiency^[21] and Auger-outpaced FRET rate^[10]. Noteworthy, the significant development of transition metal ion doped CQWs (e.g., Ag, Cu or Mn) over the past few years has led to a new possibility for FRET in a binary CQW complex^{[16][41-43]}. Metal ion dopants, which introduce mid-gap energy levels and radiatively capture the conduction band electrons, can generate a new emission band with a huge Stokes-shift^[44]. An appealing conjecture in the binary complex consisted of doped and

undoped CQWs is that if the metal ions can also behave as donors, FRET back and forth between doped and undoped CQWs can offer extended capability for FRET-based applications.

In the second part of chapter 3, encouraged by the new FRET possibility induced by dopants and high FRET efficiency in CQWs, we have explored energy transfer between copper-doped 3 ML CQWs (d-CQWs) and undoped 4 ML CQWs (u-CQWs). For the first time in a binary inorganic colloidal nanomaterial complex, mutual FRET is unambiguously observed by the steady state emission intensity, time-resolved PL (trPL) and photoluminescence excitation (PLE) spectroscopies. Since the d electrons in Cu^+ can be directly excited into the conduction band of CQW host, the d-CQWs and u-CQWs play the role of donor and acceptor simultaneously in the complex. The experimental results show that the exciton energy in 3 ML d-CQWs is effectively transferred to the 4 ML u-CQWs with an efficiency up to ~50%. Meanwhile, the exciton energy in 4 ML u-CQWs is harvested backwards by the copper dopants in 3 ML d-CQWs with a lower efficiency (< 10%) due to the small absorption cross-section of dopant transition^{29,30}. Moreover, three emission bands from the CQW complex are matching the three primary colours (red, green and blue) for the human visual perception, which further enhances the favourability for practical applications. Our binary CQW complex, which presents mutual FRET beyond the unidirectional limitation in conventional systems and exhibit superior emission abilities, may provide a new design strategy for quantifying the biophysical phenomena and constructing controllable lighting schemes.

3.2 Controllable exciton flow

Excitonics, an alternative to electronics, becomes more promising to process information since the semiconductor electronics is rapidly approaching the end of Moore's law. Currently, the development of excitonic devices, where exciton flow is controlled, is mainly focused on

electric-field modulation or exciton-polaritons in high-Q cavities. Here, we show an all-optical strategy to manipulate the exciton flow in a binary colloidal quantum well (CQW) complex through stimulated emission mediated Förster resonance energy transfer (FRET). In the spontaneous emission regime, FRET occurs naturally between a donor and an acceptor. In contrast, upon stronger excitation, the ultrafast consumption of excited species by stimulated emission effectively engineers excitonic flow from the donor to the acceptor. The acceptor's stimulated emission accelerates the exciton flow while the donor's stimulated emission shuts this exciton flow down. On this basis, a FRET-coupled rate equation model is derived to understand the controllable exciton flow by density of the donor's excitons and the unexcited (ground stated) acceptor. The results may provide a useful enlightenment for the future design of all-optical excitonic devices.

3.2.1 Dual colour lasing in the complex

The donor/acceptor pair used in this study are core-only CdSe and core-shell CdS/CdSe/CdS CQWs, composed of 4 ML and 2/4/2 ML in the vertical quantum-confinement direction, respectively. Both materials are synthesized according to previously published literature^{[17][20]}. Two basic requirements for FRET to occur are spatial and energetical overlap^{[10][11][13][21]}. The former implies the distance between a donor-acceptor pair should be smaller than the Förster radius; and the latter means spectral overlap between the donor emission and the acceptor absorption should be non-zero. The spatial overlap is easily satisfied in the CQW complex due to their extended plate geometry and large absorption cross-section ($> 10^{-14} \text{ cm}^2$), as detailed previously^{[10][38]}. In fact, the Förster radius for the CQW donor-acceptor pair^[38] has been measured to be as large as 10 nm. For the energetical overlap, as shown in **Figure 3.1a and 3.1b**, the photoluminescent (PL) emission band of core only CQWs fully overlaps with the absorption features of core-shell CQWs; therefore, FRET can be expected in the binary complex.

Meanwhile, CQWs are also extraordinary optical gain materials benefitting from i) a suppressed Auger recombination^{[16][17]} because momentum conservation is harder to be satisfied compared to that in colloidal quantum dots, and ii) a giant modal gain coefficient^{[20][45]} because increased exciton center-of-mass extension results in enhanced extinction coefficients. Before investigating the FRET mediated by simulated emission in the binary complex, the lasing action of each individual component is checked as a reference.

Figure 3.1 Optical characterizations of the pure donor and the pure acceptor. (a-b) Absorption (solid line) and emission spectra (dashed line) of 4 ML core only CdSe CQWs which serve as the donor (a) and 2/4/2 ML CdS/CdSe/CdS core/shell CQWs which play the role of acceptor (b) dissolved in hexane. Inset: a TEM image of the CQWs, scale bar: 100 nm. (c-d) PL spectra of the donor (c) and the acceptor (d) coated inside a hollow capillary tube with an inner diameter of $\sim 102 \mu\text{m}$ under different pump fluences (laser pulse: 355 nm, 500 ps). Left insets: Optical images (with the pumping laser light filtered out) showing emission below, near and above the threshold. Right inset: Integrated intensity of the stimulated emission indicating a clear threshold behaviour (integrating only the stimulated emission intensity).

Here, we use a hollow quartz capillary tube to serve as a whisper-gallery-mode (WGM) resonator considering the ease of sample preparation (see **Appendix 1.1**). The PL spectra of the CQWs filled in the tube with a diameter of $\sim 102 \mu\text{m}$ are presented in **Figure 3.1c and 3.1d**. It is seen that for both core-only and core-shell CQWs, lasing is easily achieved, and the lasing peaks can be well-assigned to the multiple WGM modes (see **Figure 3.2**). It is worth noting that core-shell CQWs exhibit lower threshold than core only CQWs ($11 \mu\text{J}/\text{cm}^2$ versus $74 \mu\text{J}/\text{cm}^2$ respectively in the right inset of **Figure 3.1c and 3.1d**). This can be easily understood because the CdS shell significantly increases the absorption cross-section and passivates the structure defects^[46], reflecting in their quantum yield difference: $\sim 45\%$ and $\sim 80\%$ for core-only and core-shell CQWs, respectively. Here, to extract the threshold, Voigt fitting is used to separate the spontaneous and stimulated emission from the cavity spectra^{[29][47-51]}, see **Figure 3.3 and Figure 3.4** for details.

Figure 3.2 Lasing modes of both core-only (a) and core-shell (b) CQWs are well assigned according to the first radial order WGM model ($q = 1$), supporting WGM lasing mechanism. The resonant condition is given by:

$m\lambda_m = \pi Dn$. Where m is the mode number, D is the inner diameter of our tube ($\sim 102 \mu\text{m}$), n is the effective refractive index of gain material.

Figure 3.3 Separation the spontaneous emission and stimulated emission in core-only CQWs. Voight fitting is adopted to reproduce the spontaneous emission profile^[48]. The spectra's intensity is cut the maximum of the spontaneous emission. Black dashed line is the fitting result for spontaneous emission only.

Figure 3.4 Separation the spontaneous emission and stimulated emission in core-shell CQWs. Voight fitting is adopted to reproduce the spontaneous emission profile^[48]. The spectra's intensity is cut the maximum of the spontaneous emission. Black dashed line is the fitting result for spontaneous emission only.

Figure 3.5 Optical characterizations of the mixed donor/acceptor. **(a)** The normalized absorption and PL spectra of the mixture in the solution and in the film, respectively (top panel). Bottom panel: PLE spectra of the mixed film with detection at the PL peak of core-shell CQWs (~628 nm). **(b)** The normalized contour map of emission spectra when the mixture is coated in the same hollow capillary tube described in **Figure 3.1**. Emission intensity is plotted in log scale. White dashed lines indicate the thresholds of red lasing and green lasing. Top inset: optical images corresponding to spontaneous emission, red lasing and dual lasing, respectively. **(c)** Integrated intensity of the stimulated emission as a function of the pump fluence for the donors (green dots/line) and the acceptors (red dots/line). Similar to **Figure 3.1**, Voigt fitting is used to separate the spontaneous/stimulated emission from the cavity spectra and only the separated stimulated emission intensity is integrated. Three emission regimes are shaded in grey, light red and light green, respectively. **(d)** Abnormal spontaneous emission behaviour of the donor when pump fluence is around the threshold of red lasing. Inset: zoom in the donor's spontaneous emission.

The stimulated emission mediated FRET process between the core-only and core-shell CQWs can now be investigated. We first present the photoluminescence (PL) and photoluminescence excitation (PLE) spectra in **Figure 3.5a** to verify the FRET process between the donors (core-only CQWs) and the acceptors (core-shell CQWs). Due to the large separation in the solution (i.e. low loading fraction of CQWs), FRET is negligible between the donors and the acceptors^{[10][12]}.

Figure 3.6 Time-resolved PL measurement. **(a)** The PL decay of the donor at different mixture ratio. When the acceptor ratio increases, the exciton lifetime of the donor becomes faster. **(b)** The PL decay of the acceptor at different mixture ratio. When the acceptor ratio decreases, their exciton lifetime becomes significantly extended. **(c)** The calculated FRET efficiency based on the acceleration of the donor's lifetime^[13]. For our designed ratio (0.25), the calculated efficiency of $\sim 51.7\%$ is used to normalize the emission intensity in the mixed film, as discussed in **Figure 3.5**. **(d)** The calculated FRET rate based on the acceleration of the donor's exciton lifetime^[13].

As the quantum yield and extinction coefficient of the two CQWs are different, the molar concentration ratio is intentionally adjusted to make sure that the emission intensity from each

component in the solution is relatively equal (core-only : core-shell = 4 : 1), which can be used as a reference to indicate the occurrence of exciton flow in the mixed film. The accelerated emission of donors and the delayed emission of acceptors observed in the time-resolved PL measurement can be the first evidence for the FRET process in the mixed film, as shown in **Figure 3.6**. Using the equation^[13]: $\eta = 1 - \tau_{donor}^{mix} / \tau_{donor}^{pure}$ (where τ_{donor}^{mix} and τ_{donor}^{pure} are the lifetime of donor in mixed and pure film, respectively), we have extracted the efficiency at the designed ratio to be ~51.7%. By assuming the emission intensity change of the donor is solely attributed to the FRET process, we can use this efficiency to normalize the emission intensity in the mixed film using^{[52][53]}: $\eta = 1 - I_{donor}^{with FRET} / I_{donor}^{without FRET}$ (where I is the integrated emission intensity), the result (orange dots) is shown in **Figure 3.5a**. Furthermore, the PLE results of the mixed film with detection at the PL peak of core-shell CQWs (~ 628 nm) show two tips corresponding to the absorption peaks of core-only CQWs. These three experimental results (time-resolved PL, steady-state PL and PLE) unambiguously indicates that the excitons in core-only CQWs are outflowing into the core-shell CQWs via the FRET process.

The mixed solution with the designed molar concentration ratio (donor : acceptor = 4 : 1) is loaded and then dried in the same hollow capillary tube as described in **Figure 3.1** and excited by the same sub-nanosecond laser pulses.

The emission spectra from the WGM cavity (see **Figure 3.5b**, the spectra with different pump fluences are shown in **Figure 3.7**) exhibit three different regimes according to the increasing pump fluence: I) with low pump fluence, only two spontaneous emission bands are presented; II) as pump fluence increases, the red lasing from the acceptor is observed at a lower threshold of ~ 5.3 $\mu\text{J}/\text{cm}^2$ due to the indirect pumping from the donor via FRET (see **Figure 3.5c**); III) the onset of green lasing is observed at very high pump fluence (~ 369 $\mu\text{J}/\text{cm}^2$ as in shown **Figure 3.5c**), which is almost five times increase from the threshold of the pure core-only

CQWs since population inversion in the donors is largely hindered by the energy transfer. More significantly, the abnormal behaviour of the spontaneous emission in the donors when the cavity emission is crossing from regime I into regime II causes our great attention. As shown in **Figure 3.5d**, when pump fluence is $4 \mu\text{J}/\text{cm}^2$ (below the threshold of red lasing) and $10 \mu\text{J}/\text{cm}^2$ (above the threshold of red lasing), we can barely observe the intensity increase of the spontaneous emission in the donors, which is contradicting with the common sense that: in the spontaneous emission regime, the intensity is linearly increasing with the pump fluence.

Figure 3.7 Emission spectra of the binary CQW complex in the WGM cavity with different pump fluences. (a) The emission spectra plot together. (b) The individual spectra under different pump fluence, the maximum intensity is limited to exhibit spontaneous emission. Voigt fitting (the black dashed line) is adopted to extract the lasing threshold for donors and acceptors.

3.2.2 Controllable exciton flow

To investigate the abnormal emission spectra of the binary complex in greater depth, we will mainly focus on the donors' spontaneous emission rather than the acceptors' emission. The reason for this is that the change of donors' spontaneous emission intensity can be directly used to characterize the exciton flow process while the change of acceptors' spontaneous emission is a convolution of the self-radiative recombination and the energy transfer process. In addition, for the majority of our pump fluence, donors' PL is pure spontaneous emission, which ensures that exciton flow is the only process responsible for the intensity change. As shown in **Figure 3.8a**, we have presented the integrated intensity of donors' emission (green circles) and a linear fitting to the first four integrated points are also presented as a reference (the green dashed line). We can observe that in regime I (the emission of both donors and acceptors is pure spontaneous, shaded in grey), the donors' emission increases almost linearly with the pump fluence, suggesting that FRET efficiency (i.e., the exciton outflow efficiency) is nearly a constant and matches the previous observations that FRET process is independent of the low pump fluence in the spontaneous emission regime^{[13][54]}. Once the red lasing occurs (regime II, shaded in light pink), the spontaneous emission intensity of the donors drops dramatically, which indicates a significant enhancement of the exciton outflow efficiency. With a further increase of pump fluence (regime III, shaded in light green), the integrated intensity of donors' emission soars up due to the onset of lasing action.

We can now calculate the outflowing efficiency of the donors' excitons in the regime I and II, where the donors exhibit pure spontaneous emission, by using the same equation as discussed in **Figure 3.5**: $\eta = 1 - I_{donor}^{with\ FRET} / I_{donor}^{without\ FRET}$. We still rely on the fact that FRET process is the only reason for the spontaneous emission intensity change in donors. For absolute calibration of FRET efficiency in the full range of pump fluences, we use the FRET efficiency of ~51.7%

when pump fluence is $0.5 \mu\text{J}/\text{cm}^2$ as the reference point (measured in **Figure 3.5a** and **Figure 3.6**).

Figure 3.8 Controllable exciton flow between the donor-acceptor pair. (a) The normalized integrated intensity of donors' spontaneous emission in the mixture coated in the hollow capillary tube. Green circle: the experimentally integrated intensity which is normalized by the maximum value; Green dashed line: the linearly fitting to the integrated intensity in regime I. (b) The calculated exciton outflowing efficiency in the donor. Three emission regimes are shaded in grey, light red and light green, respectively. In regime I and II (squares), the outflowing efficiency is calculated based on the measured spontaneous emission intensity of donors. In regime III (circles), the outflowing efficiency is estimated from the lasing and FRET rate. (c) Illustration of controlling exciton flow by stimulated emission. N_1^D and N_0^A denote density of the excited donors and the unexcited (ground state) acceptor, respectively.

As we can see, in the grey shaded regime (i.e., the acceptors' emission is pure spontaneous), the FRET occurs naturally between the donors and the acceptors with an efficiency of $\sim 50\%$.

Interestingly, with the onset of red lasing, the exciton population in the donors almost fully outflows into the acceptors with the efficiency of above 90%. In the regime III, when stimulated emission in donors occurs, we cannot use the same method to extract the exciton outflowing efficiency since FRET is not the only process that changes the emission intensity.

To address this issue, the ultrafast lasing dynamics in donors is resolved by the streak camera and a lasing rate constant (γ_{lasing}^{donors}) is evaluated to be $\sim(16 \text{ ps})^{-1}$ (see **Figure 3.9** for details), which is more than 50 times greater than the FRET rate (γ^{FRET}) of $(\sim 1.2 \text{ ns})^{-1}$ at our design donor/acceptor ratio. By considering the consumption rate of excitons (N_{donor}^{mix}) in donors:

$dN_{donor}^{mix} / dt = -(\gamma_{donor}^{pure} + \gamma^{FRET} + \gamma_{lasing}^{donor})N_{donor}^{mix}$, we can roughly estimate that the exciton outflow efficiency via FRET will be less than 2% due to the huge contrast between the FRET rate and lasing rate.

The efficiency variation in the binary CQW complex with respect to the occurrence of stimulated emission unambiguously implies the modulation of the exciton flow in the donor/acceptor pair. The qualitative explanation of the modulation mechanism is illustrated in **Figure 3.8d**. The FRET-based exciton flow efficiency ($\eta^{exciton \text{ flow}}$) depends on not only the FRET rate ($k_{FRET}^{D \rightarrow A}$), but also the density of the donor's excitons (N_1^D) and the unexcited (ground stated) acceptors (N_0^A) as: $\eta^{exciton \text{ flow}} \propto k_{FRET}^{D \rightarrow A} N_1^D N_0^A$. When lasing occurs in the acceptor (regime II), the ultrafast consumption ($< 1 \text{ ps}$) of the excited states in the acceptor leads to an increase in N_0^A , and enhanced $\eta^{exciton \text{ flow}}$, which is depicted in the middle panel of **Figure 3.8d**, the red boy (red lasing) is pulling very hard to accelerate the exciton flow. While lasing occurs in the donor (regime III), the ultrafast consumption of the excitons in the donor (suppression of N_1^D quickly to approach zero) leads to a negligible $\eta^{exciton \text{ flow}}$. In other words,

the FRET rate (in our case, 0.78 ns^{-1}) is not fast enough to compete with the stimulated emission³³, and as a result, the exciton flow is switched off in this regime.

Figure 3.9. Lasing rate constant in core-only CdSe CQWs (donors). (a) The streak camera images when the fluence is beyond lasing threshold. (b) When lasing occurs, a fast recombination with the lifetime of $\sim 16 \text{ ps}$ is observed.

Indeed, using a FRET-coupled kinetic equation model for the controllable energy transfer process mediated by stimulated emission^{[15][55]}, we can reproduce the observed modulation of the exciton flow. For simplicity, we assume that the stimulated emission system in our CQWs is a three-level system. We model the stimulated emission process in the donors and the acceptors by introducing the ultrafast recombination rate, k_{lasing} , when pumping fluence is

higher than the corresponding threshold. The full set of rate equations and related explanations are provided in **Appendix 2.1** for details.

Figure 3.10 A kinetic model to explain the controllable exciton flow. The calculated product $k_{FRET}^{D \rightarrow A} N_1^D N_0^A$ exhibits three different regimes, which agree with the experimental observations. Top inset: density of the donor's excitons and unexcited (or ground stated) acceptor in three different regimes. A_{th} : the lasing threshold of the acceptor. D_{th} : the lasing threshold of the donor.

To numerically evaluate our FRET-coupled model, we plug in the parameters extracted from the measurements (e.g., FRET rate, decay rate of the donor and the acceptor), while for the remaining parameters (i.e., multiple-exciton states decay rate), we adopt the values from previous reports^{[14][55][56]}. The numerical result is shown in **Figure 3.10**, exhibiting a superior agreement with the up and down behaviour of the exciton outflow efficiency presented in **Figure 3.6b**. Specifically, stimulated emission can effectively modify the density of the excited donors and unexcited acceptors, leading to a considerable modulation of the exciton flow. It is worth to mention that the exact exciton outflow efficiency predicted by this model

differs from the experiment due to our simplification. In particular, we have ignored the role of multiple-exciton states to the stimulated emission and the transition of recombination rate from spontaneous emission to stimulated emission during the pumping pulse width, which is considerably longer than many excitonic processes here. Nevertheless, our model can qualitatively reproduce the exciton flow from the donors to the acceptors as demonstrated in our experiments.

3.3 Mutual energy transfer

Förster resonance energy transfer (FRET) is a fundamental process that is key to optical biosensing, photosynthetic light harvesting and down-converted light emission. However, all in all, conventional FRET in a donor-acceptor pair is essentially unidirectional, which impedes practical application of FRET-based technologies. Here, we propose a mutual FRET scheme that is uniquely bi-directional in a binary colloidal quantum well (CQW) complex enabled by utilizing the d orbital electrons in a dopant-host CQW system. Steady state emission intensity, time-resolved and photoluminescence excitation spectroscopies have demonstrated that two distinct CQWs play the role of donor and acceptor simultaneously in this complex consisted of 3 mono-layer (ML) copper-doped CQWs and 4 ML undoped CQWs. Band-edge excitons in 3 ML CQWs effectively transfer the excitation to excitons in 4 ML CQWs, whose energy is also harvested backwards by the dopants in 3 ML CQWs. This binary CQW complex, which offers unique mutual energy transfer mechanism, may unlock revolutionary FRET-based technologies.

3.3.1 Steady-state characterization

In this work, copper-doped CdSe CQWs with 3 ML vertical thickness and undoped CdSe CQWs with 4 ML vertical thickness are selected as the donor-acceptor pair. Both the d-CQWs

and u-CQWs are synthesized using modified recipes from our previous works^{[16][20]} and the materials characterization is detailed in our previous works^{[16][33]}.

Figure 3.11 Static characterizations of 3 ML d-CQWs and 4 ML u-CQWs for FRET. (a) Absorption (black solid line) and emission spectra of 3 ML copper-doped CQWs dissolved in hexane. The band edge emission (BE) is shaded in blue and copper-related emission (CE) is shaded in red. Inset: a TEM image of 3 ML d-CQWs, scale bar: 20 nm, the lateral size of 3 ML d-CQWs is $\sim (45 \text{ nm} \times 41 \text{ nm})$. (b) Absorption (black solid line) and emission spectra of 4 ML undoped CQWs dissolved in hexane. The band edge emission (BE) is shaded in green. Inset: a TEM image of 4 ML u-CQWs, scale bar: 20 nm, the lateral size of 4 ML u-CQWs is $\sim (41 \text{ nm} \times 16 \text{ nm})$. (c) Normalized 2D emission map of 3 ML d-CQWs dissolved in hexane under excitation with progressively lower photon energy. The excitation light (brown colour, maximum intensity is cut at 1 due to the much higher intensity) is also included for reference. (d) Comparison of the steady state PL between CQW complex and pure component. The molar concentration ratio between u-CQWs and d-CQWs is 1:10. All samples are in solid film. Top panel: excitation light peaks at 435 nm, corresponding to the light-hole electron transition in 3 ML d-CQWs. Bottom panel: excitation light peaks at 480 nm, corresponding to the light-hole electron transition in 4 ML u-CQWs. (e) Schematic illustration of the potential mutual energy transfer in the CQW complex. CB: conduction band. VB: valence band. The values of energy edges of CB are: -3.20 eV (3 ML) and -3.41 eV (4 ML); and the values of energy edges of VB are: -5.87 eV (3 ML) and -5.82 eV (4 ML). The energy level of copper dopants distributes in a wide range, here, for clarity, we only present the highest density states. R, G and B denote the three primary colours, respectively. They correspond to three radiative transitions: CE of d-CQWs, BE of u-CQWs, and BE of d-CQWs.

Two basic requirements for FRET to occur are spatial and energetical overlap^{[10][13]}. The former implies the distance between a donor-acceptor pair should be smaller than the Förster radius; and the latter means spectral overlap between the donor emission and the acceptor absorption should be non-zero. The spatial overlap is easily satisfied in the CQW complex due to the extended plate geometry and large absorption cross-section ($> 10^{-14} \text{ cm}^2$) as detailed previously^{[20][40]}. In fact, the Förster radius for the CQW donor-acceptor pair^{[10][38]} has been measured to be larger than 10 nm. Here, we will mainly focus on the energetical overlap to explore the possible FRET in this two-component CQW complex.

Figure 3.12 Optical absorption and PL spectra of copper-doped and undoped 3 ML CdSe CQWs under 365 nm UV lamp excitation. Result shows that the doping does not change the essential excitonic transitions (light-hole/electron and heavy-hole/electron) in CdSe host. Along with the narrow BE emission, these undoped 3 ML CQWs also exhibit weak trap emission bands (extremely broad), which was reported in our previous work^[41].

The absorbance and PL spectra of d-CQWs (**Figure 3.11a**) show that the electron/heavy-hole transition of the CdSe host peaked at ~461 nm is resonant with a narrow band-edge emission

(BE, shaded in blue) at ~465 nm (FWHM of ~14 nm). The absorption and emission spectra of undoped 3 ML CdSe CQWs presented in **Figure 3.12** demonstrate that the exciton energy in CQW host is not affected by the copper dopants^{[41][42]}.

Considering that the u-CQWs absorb significantly at the BE range of d-CQWs (**Figure 3.11b**), this suggests that FRET between BE in d-CQWs (donor) and u-CQWs (acceptor) is possible. Furthermore, it is worth noticing that, in the absorbance spectrum of d-CQWs, there exists a broad absorption tail on the red side of the electron/heavy-hole excitonic feature. This broad absorption tail, which is nearly resonant with the broad copper-related emission (CE) in **Figure 3.11a** (shade in red), can only be assigned to the promotion of the *d* orbital electrons in Cu^+ to the conduction band of CdSe host, this is expressed as: $[\text{Ar}]3d^{10} + h\nu \rightarrow [\text{Ar}]3d^9 + e$, where $h\nu$ is the energy of Cu-related absorption and e denotes an electron in CB^[43]. Thus, another possible FRET between u-CQWs (donors) and CE in d-CQWs (acceptors) will occur if the CE can be directly excited by the green emission in u-CQWs. To confirm this possibility, we progressively tuned the excitation photon energy below the bandgap of host CdSe from 500 down to 590 nm. As shown in **Figure 3.11c**, CE is still observed, indicating that Cu^+ is photoexcited directly to Cu^{2+} without the hole-trapping process. Comparing the steady state PL properties between mixed and pure CQW films is a straight-forward way to explore the possible FRET between d-CQWs and u-CQWs (optically clear and uniform films for various mixture ratios are critical, see the details of film preparation in **Appendix 1.2**)^{[10][12]}. When the excitation energy matches the electron/light-hole transition of d-CQWs (~435 nm, top panel of **Figure 3.11d**), emission from the mixed film reveals an increase in the intensity of BE in u-CQWs while accompanied by a decrease in the intensity of BE in d-CQWs. Similarly, when we excite at the electron/light-hole transition of u-CQWs (~480 nm, bottom panel of **Figure 3.11d**), quenching of the BE in u-CQWs and enhancement of the CE in d-CQWs are observed in the mixed film. Together, these are the first evidences that mutual FRET (**Figure 3.11e**)

occurs in this CQW complex, where the excitation energy transfers from d-CQWs' excitons to u-CQWs' excitons and then back to the copper dopants in d-CQWs.

3.3.2 Dynamic characterization

Figure 3.13 Dynamic characterizations of the CQW complex for FRET. Laser pulse: 100 ps, 100 nJ/cm² and 355 nm. (a) Time-resolved PL decay of the CQW complex collected in the blue emission range (from 450 to 480 nm). Dots and solid lines are the results of experiments and numerical fittings, respectively. PL decay of pure 3 ML d-CQWs is also presented as a reference (black dots and line). (b) Time-resolved PL decay of the CQW complex collected in the green emission range (from 500 to 535 nm). Dots and solid lines are the results of experiments and numerical fittings, respectively. PL decay of pure 4 ML u-CQWs is also presented as a reference (black dots and line). (c) Averaged lifetime of R, G, B emission as a function of the molar concentration ratio between 4 ML u-CQWs and 3 ML d-CQWs. (d) Calculated FRET (the blue-to-green) efficiency as a function of the molar concentration ratio between 4 ML u-CQWs and 3 ML d-CQWs. Inset: the corresponding FRET rate. The dash-dot lines are for guiding the eyes.

To further confirm the proposed mutual FRET and determine the rate/efficiency, time-resolved PL is conducted. We have prepared twelve mixed film samples on the quartz substrates with different molar ratios between u-CQWs and d-CQWs (denoted as 4ML:3ML hereafter), in addition to the reference samples of pure u-CQWs and pure d-CQWs.

As shown in **Figure 3.13a**, trPL of BE in d-CQWs becomes shorter-lived with larger 4ML:3ML, indicating that a newly built-up relaxation channel in blue emission is enhanced with increasing u-CQWs concentration in the mixed film. In the case of decay kinetics for u-CQWs (**Figure 3.13b**), the lifetime is observed to be more prolonged with smaller 4ML:3ML, suggesting that green exciton feeding becomes more significant with increasing d-CQWs concentration in the mixed film. The faster PL dynamics in BE of d-CQWs (donor) corroborating with the slower PL kinetics in u-CQWs (acceptor) is the characteristic signature of FRET^{[12][32]}, and this ascertains the outflow of energy from the blue to the green.

Due to the multiple recombination channels in ensemble CQWs, the PL dynamics exhibits a multiple-exponential behaviour^{[13][21][38][39]}, an amplitude-weighted average lifetime (τ_{av}) is adopted to quantify the observed differences in the decay kinetics (see all the fitting parameters for lifetime with different molar ratios in **Table 3.1, 3.2 and 3.3**). As shown in **Figure 3.13c**, τ_{av} of blue emission does not change noticeably when 4ML:3ML is above 1.5, indicating a saturation of FRET between the donor/acceptor pair.

Subsequently, using the fitted τ_B^{mix} for the mixed film and τ_B^{pure} for the pure d-CQW film, the efficiency ($\eta_{FRET}^{B \rightarrow G}$) and rate ($k_{FRET}^{B \rightarrow G}$) of the blue-to-green FRET for all molar ratios can be calculated as follows:

$$k_{FRET}^{B \rightarrow G} = k_B^{mix} - k_B^{pure} = \frac{1}{\tau_B^{mix}} - \frac{1}{\tau_B^{pure}}$$

$$\eta_{FRET}^{B \rightarrow G} = 1 - \frac{\tau_B^{mix}}{\tau_B^{pure}} = 1 - \frac{k_B^{pure}}{k_{FRET}^{B \rightarrow G} + k_B^{pure}} \quad (1)$$

where k_B^{mix} and k_B^{pure} are the blue emission rates in mixed and pure film, respectively.

Table 3.1 Fitting components (three-exponential) for trPL decay curves of the mixed CQW films measured at the blue. The results for twelve different molar ratios and a pure film are presented.

Blue emission (BE in d-CQWs)							
4ML:3ML ratio	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1	A_2	A_3	τ_{avg} (ns)
pure	0.24	1.93	7.69	0.578	0.384	0.038	1.17
0.01	0.23	1.9	7.67	0.598	0.367	0.035	1.095
0.05	0.22	1.87	7.25	0.638	0.332	0.030	0.979
0.1	0.23	1.82	6.84	0.658	0.316	0.026	0.905
0.2	0.2	1.77	6.32	0.658	0.317	0.025	0.848
0.4	0.18	1.71	6.05	0.663	0.314	0.023	0.796
0.6	0.18	1.6	6.14	0.654	0.330	0.016	0.744
0.8	0.16	1.52	5.77	0.635	0.352	0.013	0.713
1	0.14	1.44	5.26	0.620	0.369	0.011	0.676
1.25	0.15	1.38	5.13	0.617	0.374	0.009	0.654
1.5	0.15	1.36	4.78	0.619	0.372	0.009	0.641
1.75	0.14	1.31	4.62	0.603	0.389	0.008	0.63
2	0.15	1.38	4.63	0.628	0.362	0.010	0.639

Table 3.2. Fitting components (three-exponential) for trPL decay curves of the mixed CQW films measured at the green. The results for twelve different molar ratios and a pure film are presented.

Green emission (BE in u-CQWs)							
4ML:3ML ratio	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1	A_2	A_3	τ_{avg} (ns)
pure	0.41	2.72	11.58	0.714	0.248	0.038	1.41
0.01	0.73	3.24	15.71	0.622	0.271	0.107	3.014
0.05	0.61	3.12	14.66	0.601	0.309	0.090	2.653
0.1	0.58	2.99	14.23	0.553	0.363	0.084	2.599
0.2	0.59	2.91	14.11	0.541	0.383	0.076	2.507
0.4	0.58	2.95	13.79	0.535	0.395	0.070	2.446
0.6	0.58	2.93	13.64	0.531	0.400	0.069	2.416
0.8	0.57	2.91	13.22	0.529	0.401	0.070	2.392
1	0.55	2.87	12.93	0.521	0.408	0.071	2.374
1.25	0.54	2.84	12.67	0.511	0.419	0.070	2.356
1.5	0.52	2.8	12.31	0.501	0.426	0.073	2.35
1.75	0.51	2.78	12.04	0.487	0.436	0.077	2.383
2	0.49	2.76	11.88	0.465	0.456	0.079	2.422

From **Figure 3.13d**, it can be seen that the efficiency of the blue-to-green FRET raises with increasing molar ratios of u-CQWs and then reaches a saturated level of ~48%. Compared to the theoretical prediction of FRET efficiency in CQWs is greater than 95%, the limited efficiency in our experiments is mainly because it is not possible to have all CQWs inter-mixed (that is, co-facial donor-acceptor pairs: DAD or ADA), but instead there are self-mixed CQWs (that is, only donor or acceptor assemblies, DDD or AAA)^{[10][38]}.

Table 3.3 Fitting components (three-exponential) for trPL decay curves of the mixed CQW films measured at the red. The results for twelve different molar ratios and a pure film are presented.

Red emission (CE in d-CQWs)							
4ML:3ML ratio	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	A_1	A_2	A_3	τ_{avg} (ns)
pure	68.5	242.3	768.5	0.177	0.723	0.100	252.1
0.01	72.3	241.4	764.7	0.166	0.729	0.105	255.9
0.05	74.7	249.1	763.2	0.162	0.743	0.095	257.4
0.1	75.8	245.3	771.5	0.164	0.745	0.091	253.1
0.2	75.4	244.6	765.3	0.158	0.738	0.104	259.8
0.4	75.9	250.5	772.4	0.158	0.755	0.087	256.7
0.6	76.1	249.4	770.3	0.161	0.759	0.080	251.3
0.8	76.7	247.1	765.2	0.155	0.758	0.087	253.8
1	77.1	248.4	761.1	0.163	0.730	0.107	262.7
1.25	76.4	249.2	765.4	0.158	0.754	0.088	254.9
1.5	77.5	254.8	766.2	0.157	0.759	0.084	257.3
1.75	78.4	247.7	773.3	0.161	0.748	0.091	255.5
2	82.3	250.3	768.9	0.156	0.755	0.089	256.9

3.3.3 Resonant PLE spectroscopy

The characterizations of one-way FRET process (from the blue-to-green) in the CQW complex are obvious as presented above, however, it is hard for us to identify the FRET process from the u-CQWs to copper dopants in d-CQWs with the trPL measurements. There are two major reasons for this: **i)** The PL decay of green emission is a convolution of the delayed acceptor kinetics (FRET from the blue-to-green) and accelerated donor dynamics (FRET from the green-to-red). In **Figure 3.13c**, we can observe that when 4ML:3ML is larger

than 1.5 (when the blue-to-green FRET is saturated), the lifetime of green emission slows down again. This behaviour implies that green-emission excitons play multiple roles in the FRET process since when amounts of donors (u-CQWs) increases, the acceleration of green emission decay will be typically suppressed^[12]; **ii)** The PL kinetics of red emission (**Figure 3.13c**) does not exhibit the delayed dynamics as expected for acceptors since CE in d-CQWs originates from the radiative recombination of CB electrons in CdSe host to the localized intragap states of copper and offers a long lifetime of ~ 250 ns. As a result, FRET process with a fast rate may not be able to make a noticeable change to the CE dynamics (see the measured PL decay of CE with different 4ML:3ML ratios in **Figure 3.14**).

Figure 3.14 Normalized time-resolved PL decay curves of CE in copper-doped 3 ML CdSe CQWs (collected range: 580-680 nm) with different molar concentration ratios (4ML: 3ML). The solid lines show the exponential fitting results. The detailed explanation of the CE lifetime can be found in our previous reports^[41].

To characterize the second FRET process (from the green-to-red), photoluminescence excitation (PLE) spectroscopy across exciton absorption resonances is conducted. The

different PLE intensity of the CQW complex compared to that of pure CQW film is widely used to extract the FRET information^{[52][53][57]}.

Figure 3.15 PLE spectroscopy of the CQW complex probed at the blue emission (~ 465 nm). (a) Normalized 2D PLE intensity. The light-hole/electron transition (~ 435 nm) of d-CQWs can be observed. (b) 2D PLE enhancement factor. The quenching of the blue emission indicates the energy is outflowing. (c) The calculated FRET efficiency (from blue-to-green) based on the PLE enhancement factor using equation 3 in the main text. The trend and the values (maximum: $\sim 47.3\%$) of this FRET efficiency extracted using PLE exhibit good agreement with the results from the trPL measurement (**Figure 3.13**). (d) The calculated FRET rate (blue to green) based on the PLE enhancement factor using equation 3 in the main text. It also exhibits consistency with the results from the trPL measurement (**Figure 3.13**).

Here, assuming the change of PLE intensity is solely attributed to FRET process, a model of single exciton dynamics (due to low excitation intensity in PLE measurement) is used to estimate the FRET efficiency (η_{FRET}) and rate (k_{FRET}) from the enhancement factors of PLE

spectra (defining as the PLE intensity ratio between the mixed film and the pure film with the same amount of CQWs of interest), shown as follows:

$$k_{FRET} = \left(\frac{I^{pure}}{I^{mix}} - 1 \right) \times k^{pure} \quad (2)$$

$$\eta_{FRET} = 1 - \frac{k^{pure}}{k^{pure} + k_{FRET}} = 1 - \frac{I^{mix}}{I^{pure}}$$

where I^{pure} and I^{mix} are, respectively, the PL intensity of donor excited at a wavelength of choice (typically, exciton features are selected); k^{pure} is the recombination rate of pure donors. Details of the derivation of FRET rate and efficiency are described in **Appendix 2.2**. This model is also used to calculate the blue-to-green FRET (see **Figure 3.15**) and compared to the results presented in **Figure 3.13**, the good agreement of these two results using PLE and trPL spectroscopy validates our model.

More importantly, the complex can be excited at a preferred wavelength to enable only the green-to-red FRET process. As shown in **Figure 3.16a**, the CQW complex is resonantly excited at the energy of light-hole/electron exciton of u-CQWs (~480 nm, which is below the bandgap of d-CQWs) and as a result, the blue-to-green FRET will not be triggered and pure green-to-red FRET can be characterized. **Figure 3.16b** shows the colour plot of PLE enhancement with different molar ratios probed at the energy of green excitons (~ 514 nm). The individual PLE enhancement spectra are shown in **Figure 3.17**. In contrast to the PLE of pure u-CQWs, enhanced emission intensity (red colour, enhancement factor: >1) is observed at the wavelength corresponding to the electron/heavy-hole (~ 461 nm) and electron/light-hole (~ 435 nm) transitions in d-CQWs, signifying the blue-to-green FRET. More attractive observation for us is the quenched PL intensity (blue colour, enhancement factor: <1) located at the wavelength around the electron/heavy-hole transition of u-CQWs (~ 480 nm). Furthermore, as shown in **Figure 3.16c**, the PLE enhancement map probed at the red emission

wavelength (~ 638 nm, the individual PLE enhancement spectra is shown in **Figure 3.18**) exhibits two clear enhancement regions exactly located at the electron/heavy-hole (~ 480 nm) and electron/light-hole (~ 512 nm) transitions in u-CQWs.

Figure 3.16 PLE spectroscopy of the CQW complex. (a) Schematic illustration of the working principle to characterize the FRET from excitons in 4 ML u-CQWs to dopants in 3 ML d-CQWs. hh: heavy hole, lh: light hole. (b) 2D PLE enhancement map for the green emission (probed at ~ 514 nm). The three dashed lines indicate the absorption transition features. Red colour is coded for the region with an enhancement factor larger than 1; blue colour is coded for the region with an enhancement factor smaller than 1; white colour is coded for the region with an enhancement factor of 1. (c) 2D PLE enhancement map for the red emission (probed at ~ 628 nm). The two dashed lines indicate the absorption transition features in 4 ML u-CQWs. The same colour coding for the map as illustrated in Figure 3b. (d) Calculated FRET (from the green-to-red) efficiency as a function of the molar concentration ratio between 4 ML u-CQWs and 3 ML d-CQWs. Inset: the corresponding FRET rate. The dash-dot lines are for guiding the eyes.

Figure 3.17 Individual PLE (probed at the green wavelength of ~ 514 nm) enhancement factor of the mixed CQW films with different molar concentration ratios (4ML:3ML). The 2D map in **Figure 3.16b** is using the data presented here with interpolation.

Figure 3.18 Individual PLE (probed at the red wavelength of ~ 638 nm) enhancement factor of the mixed CQW films with different molar concentration ratios (4ML:3ML). The 2D map in **Figure 3.16c** is using the data presented here with interpolation.

These two observations unambiguously indicate that the exciton energy in u-CQWs is outflowing into the copper-dopants in d-CQWs (the green-to-red FRET). Therefore, in **Figure 3.16b**, we can characterize the FRET through the emission intensity change excited at the electron/heavy-hole transition of u-CQWs (~ 480 nm) using the established model. The calculated efficiency and rate of green to red FRET are presented in **Figure 3.16d**. The efficiency of the green-to-red FRET is below 10% due to the small absorption cross-section of directly dopant transition (excite d electrons of Cu^+ to the conduction band of CdSe host), as reported by Gamelin and co-workers^{[42][43]}.

3.4 Summary

In the first part of this chapter, controllable exciton flow from the donors to the acceptors in a binary CQW complex has been realized by mediating FRET with the stimulated emission. Ultrafast modulating the density of excited donors and the unexcited acceptors by stimulated emission plays the key role in controlling exciton flow. Three distinct exciton flow regimes with an efficiency of $\sim 50\%$, $\sim 90\%$ and $\sim 2\%$ are triggered by the continuous transition from spontaneous emission to the acceptors' stimulated emissions then to dual stimulated emission (both the donors and the acceptors). Our study not only offers a deeper insight into the understanding of FRET process but also proposes that combining FRET with stimulated emission is a way to control exciton flow and possibly realizes all-optical excitonic circuits.

In the second part of this chapter, we have demonstrated the first example of how doped CQWs can be used to achieve a mutual FRET in a binary CQW complex. In the complex composed of 3 ML d-CQWs and 4 ML u-CQWs, distinct two-way energy transfer routes in which the d-CQWs and u-CQWs serve both as donors and acceptors simultaneously have been presented in detail through analysing the steady state emission intensity, time-resolved PL and PLE spectroscopies. These findings provide a promising approach beyond the

unidirectional limitation for applications in the various fields such as biophysics, by offering a cross-check configuration to precisely probe the dynamics in biomolecules, and energy optoelectronics, through enabling more external control parameters. Future efforts in this study lie in the improvement of mutual FRET efficiency that can enhance the signal-to-noise ratio for FRET-based fluorescence probing and expand the tunability for an external stimulus.

Appendix 1: Experimental methods

1.1 Loading the mixture into the capillary tube

The donor-acceptor mixture is infiltrated into the tube by capillary effect. To make sure the solution forms uniform film inside the tube, the tube is placed on a flat plate until the solvent is evaporated. After that, the two ends are sealed with wax to avoid contamination.

1.2 Preparation of the solid CQW films

3 ML d-CQWs and 4 ML u-CQWs dissolved in hexane are prepared to have the same molar concentration (10^{-4} mol/L). Solutions having different 4ML: 3ML molar ratios are mixed using ultrasonication for 5 minutes. The quartz substrates of 1.5 by 1.5 cm in size are cleaned using detergent, DI-water, acetone and ethanol. After drying the substrates in an oven at 80 °C for 30 min, spin coating (at 1,500 rpm for 2 min) is adopted to ensure optically clear (minimum scattering) and uniform solid films. The same solution concentration and spin-coating recipe are important to have the same film thickness and morphology for different 4ML: 3ML molar ratios.

lifetime data from the time-resolved PL measurements (**Figure 3.6**), we can generate the dynamics of each states, and therefore, predict the FRET-mediated exciton flow.

2.2 Estimation of FRET rate from PLE spectroscopy

To evaluate the FRET process in the PLE spectroscopy, we introduce rate equations of single exciton dynamics. Because the excitation is weak in PLE measurement, multiexciton recombination is not significant.

We assume that the recombination dynamics changes of excited species in the CQW complex is solely attributed to the FRET process. We can build the rate equations^{[52][53]}:

$$\begin{aligned}\frac{dN^{pure}}{dt} &= P - k^{pure} N^{pure} \\ \frac{dN^{mix}}{dt} &= P - k^{mix} N^{mix} = P - (k^{pure} + k_{FRET}) N^{mix}\end{aligned}\tag{A2}$$

Where P is the generation factor for excited species in the donors and N is the population of corresponding excited species in the donors.

The population of excited species in the donor can be derived from the steady-state solutions and expressed as:

$$N^{pure} = \frac{P}{k^{pure}}; N^{mix} = \frac{P}{k^{pure} + k_{FRET}}\tag{A3}$$

The emission intensity is proportional to the radiative decay rate as follows:

$$I^{pure} = \frac{P k^{pure,rad}}{k^{pure}}; I^{mix} = \frac{P k^{pure,rad}}{k^{pure} + k_{FRET}}\tag{A4}$$

Where k^{rad} is the radiative recombination rate of excited species in the donors.

Thus, we can calculate the rate of FRET using the following:

$$k_{FRET} = \left(\frac{I^{pure}}{I^{mix}} - 1 \right) \times k^{pure} \quad (A5)$$

Similarly, the efficiency of FRET can be determined as:

$$\eta_{FRET} = 1 - \frac{k^{pure}}{k^{pure} + k_{FRET}} = 1 - \frac{I^{mix}}{I^{pure}} \quad (A6)$$

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Chapter 4: Strong Wannier Mott Exciton-plasmon polariton

4.1 Motivation and Introduction

Interaction between excitons and localized surface plasmons (LSPs) sustained in metallic nanostructures is at the heart of future nanodevice research in view of deep subwavelength confinement of the electromagnetic fields^[1-4], which allows size scalability and open cavity configuration^[5-10] ensuring easy access to probe/manipulate light-matter coupling. If the coherent energy exchange rate between excitons and LSPs is faster than any other dissipative dynamics, the most intriguing regime, the so-called strong interaction, is achieved^[11-13]. In this regime, there is a change from the irreversible spontaneous emission (Purcell effect)^[14] to a reversible energy exchange (Rabi splitting) between excitons and LSPs^{[5][9][11-13]}. This regime can benefit not only fundamental studies in cavity quantum electrodynamics (QED)^[11], but also advanced nanophotonic devices, such as ultrafast optical switches^{[1][3]}, single-atom lasers^{[2][14]} and quantum information storage^{[1][3]}. From the plasmonic application perspective, Rabi splitting energy is a key figure of merit^{[9][15-17]}. Systems with large Rabi splitting have enabled several promising properties, including strong coupling strength, enhanced optical nonlinearity and ultrafast coherent energy exchange^{[1][12][18]}.

To overcome the fast dissipation of a plasmonic mode in metallic nanostructures, organic molecules that exhibit giant oscillator strength and large absorption cross-section are commonly reported emitters to attain the strong coupling regime^[19-29]. Recent studies have demonstrated strong exciton-plasmon interaction involving both multiple molecules and a single molecule. To date, Shegai *et al.*^[25] observed a Rabi splitting of ~400 meV using multiple J-aggregate molecules and a silver nanoprism. Wang *et al.*^[29] achieved strong

interaction between a single J-aggregate molecule and a gold nanorod with a Rabi splitting of ~ 42 meV. However, organic molecules are suffering from limited photostability, large inhomogeneous broadening and are prone to emission bleaching^[30]. These issues have severely hindered the practical applications of organic-plasmonic systems.

Inorganic colloidal nanomaterials, which not only retain the strength of organic molecules (e.g., solution processability and scalability) but also possess a number of advantages over organic molecules (e.g., optical stability, suppressed emission broadening and endurance of high photon density)^[31-33], have emerged as another promising class of materials for strong exciton-plasmon interaction. Quasi-two-dimensional CdSe colloidal quantum wells (CQWs)^[34], as colloidal counterparts of epitaxial quantum wells, offer superior properties which can benefit exciton-plasmon interaction. Compared to other 0D (quantum dots) and 1D (nanowires, nanorods) colloidal nanomaterials, CQWs exhibit extremely narrow emission linewidth (< 40 meV) due to vertical thickness control at the mono-atomic level^{[34][35]} and significantly enhanced absorption coefficients ($\sim 3 \times 10^7$ cm⁻¹ in CQWs versus $\sim 2 \times 10^4$ cm⁻¹ in quantum dots) resulting from increased exciton center-of-mass extension^{[34][36]}. Just six months ago, for the first time, Norris *et al.*^[15] demonstrated strong exciton-plasmon interaction using CdSe CQWs and a metallic photonic crystal. However, due to the relatively low exciton binding energy, non-perfectly matched exciton dipole orientation with respect to electric field distribution and fast non-radiative dissipative dynamics (i.e., Förster resonant nonradiative energy transfer, FRET) in a dense film, the Rabi splitting energy observed in CQW-metal system is only 110 meV, even smaller than the value reported in colloidal quantum dots (up to 160 meV)^{[17][37]}.

Generally, Rabi splitting energy ($\hbar\Omega$) is in accordance with $\hbar\Omega = 2g \propto \sqrt{fN/V}$ ^{[12][13]}, where g is the coupling strength, f is the oscillation strength of the exciton, V is the optical mode volume and N is the saturated concentration of excitons involved in strong coupling. Here, to achieve

ultra-strong exciton-plasmon interaction, we utilize the high aspect ratio colloidal quantum wells (HARCQWs) with one lateral size tailored down to ~ 6 nm (the exciton Bohr radius in CdSe: ~ 5.7 nm)^[38] as the exciton source. The greatly enhanced exciton binding energy resulting from an additional quantum confinement dimension and inefficient FRET due to non-stacking properties^[39-41] in HARCQW assembly are beneficial to improve the oscillator strength. Furthermore, we achieved face-down HARCQW assembly due to weak Van der Waals interactions^[39-42] between HARCQWs to ensure the maximum overlap (effective N) between exciton dipole orientation and electric field in LSP. For the plasmon part, instead of using top-down metallic nanostructures fabricated by lithography, we adopt solution-processable colloidal silver nanocubes with different sizes to tune the resonance energy^[43]. The anti-crossing behaviour of two polaritonic states in dark-field scattering measurement shows a giant Rabi splitting energy exceeding 400 meV (corresponds to 0.1 fs^{-1} energy transfer rate). To the best of our knowledge, this is the largest Rabi splitting observed in any Wannier Mott exciton and plasmon systems. Moreover, photoluminescence spectra of the hybrid system arising from the low polariton branch further demonstrate ultrafast coherent energy exchange between excitons and plasmons. These results provide a way toward exploring practical applications of bottom-up and small footprint exciton-plasmon polariton nanodevices.

4.2 Ultrastrong plasmon-exciton interaction

The strong interaction between excitons and plasmons, manifested as Rabi splitting of the eigen energies, is of fundamental interest for manipulating and guiding photons in nanoscale devices. Recently, inorganic quantum emitters have attracted tremendous attention for plasmon-exciton studies thanks to their enhanced photostability and minimal inhomogeneous broadening compared to organic molecules. However, a relatively small Rabi splitting (~ 100

meV) with inorganic materials severely stymies the active plasmonic operation considering its weak optical nonlinearity and slow energy exchange between excitons and localized surface plasmons (LSP). Here, we circumvent this problem in a hybrid system consisting of high aspect ratio colloidal quantum wells (HARCQWs) and an individual plasmonic silver nanocube. By taking advantages of highly in-plane oriented exciton, enhanced exciton binding energy and non-stacking properties in HARCQWs, we demonstrate unprecedented giant Rabi splitting energy up to 400 meV under ambient conditions, which is observed not only in scattering, but also in photoluminescent spectra. These findings make a key step towards achieving inorganic plasmonic devices such as SPASER, all-optical plasmonic switching and single-photon transistors.

4.2.1 The ultra-strong plasmon-exciton interaction

The hybrid plasmon-exciton systems are produced experimentally as illustrated in **Figure 4.1a**. The transverse magnetic (TM) polarized light excites both LSPs in the silver nanocube and Wannier Mott excitons in HARCQWs. Here, we only consider longitudinal LSP mode since the near-field electric field enhancement of transverse LSP mode is one-two orders of magnitude weaker^{[6][43][44]}. When the LSP resonance is crossing the excitonic transition (spectral overlap) and the excitons are close enough to experience the enhanced near-field in-plane plasmonic mode (spatial overlap), strong plasmon-exciton interaction (mode splitting) can be most likely achieved^{[2][13]}.

The exciton components of the hybrid system are shown in **Figure 4.1b**. Four mono-layer (4 ML) CdSe CQWs are synthesized with the previous recipes^{[34][35]}, which we optimize to obtain desirable aspect ratio here (see details in **Appendix 1.1**). Transmission electron microscopy (TEM) characterization of the CQWs (the inset in **Figure 4.1b**) reveals that they

are approximately rectangular shape with an aspect ratio as large as ten to one (lateral size: ~50 nm by 5-8 nm, see the lateral size deviation of CQWs in **Figure 4.2**).

Figure 4.1 The hybrid exciton-plasmon system. (a) A schematic showing the hybrid system consisting of an individual silver nanocube coupled to the densely packed HARCQW film. The excitons and LSPs are excited by the TM-polarized white light. TM polarization is defined by the electric field along x-direction. (b) Normalized photoluminescence (blue) and absorbance (red) spectra of HARCQWs dispersed in hexane. Inset: TEM image of CQWs indicating the high aspect ratio; scale bar: 25 nm. (c) Scattering spectra measured for silver nanocubes with varying sizes. As the size of the nanocube increases, the LSP peak (black circles) shifts to lower energies as highlighted by dashed line. Top inset: SEM image of an individual silver nanocube with the size of 75 nm, scale bar: 50 nm. Bottom inset: Dark-field scattering image of silver nanocubes over the SiO_2/Si substrate illuminated by TM-polarized light, scale bar: 1 μm . (d) Near-field electric-field intensity distribution of an individual silver nanocube over the densely packed HARCQW film. The contours are normalized by the incident electric field and correspond to the LSP peak (2.41 eV) of a silver nanocube with the size of 75 nm. Upper: electric field distribution in the silver nanocube, top view (xy-plane); Middle: electric field distribution in the HARCQW film, top view (xy-plane); Lower: electric field distribution in the HARCQW film, side view (xz-plane). White dashed lines indicate the outline of the silver nanocube, scale bar: 50 nm.

Also, the quantum yield (QY) is around 55% suggesting negligible cracking or strain in these HARCQWs. It is important to note that the absorption peaks (heavy-hole transition: 2.417 eV, light-hole transition: 2.578 eV), emission peak (2.413 eV) and linewidths (~ 40 meV) of HARCQWs are consistent with the values previously reported for those low aspect ratio CdSe CQWs^{[34][36][39-41]}.

Figure 4.2 Lateral size distribution of high aspect ratio 4 ML CdSe CQWs. (a) TEM images, the scale bar is 20 nm. (b) Size histograms of the short side. Red line is the Gaussian fitting curves, indicating the short side length is in the range of 5-8 nm (Bohr radius of CdSe: ~ 5.7 nm).

Considering an additional confinement along the lateral direction in HARCQWs, the independent relationship between the excitonic transitions and aspect ratios means that a larger exciton binding energy can be expected in HARCQWs, which will be later discussed further in the later section. Typically, there is a square-root dependence of the Rabi energy on the number of dipoles coupled to the LSP mode ($\hbar\Omega \propto \sqrt{N}$)^{[15][29]}. For this reason, densely packed HARCQW film is preferred to achieve large mode splitting. However, the Rabi energy cannot be endlessly enhanced via increasing the film thickness due to the exponentially decaying intensity of the LSP mode (in the z-direction, the penetration length of the electric field of the LSP mode is ~ 100 nm in the green spectral range)^{[3][15]}. Thus, beyond the

saturation condition (i.e. thickness > 100 nm), increasing the film thickness should not further enhance the Rabi energy because the excitons no longer experience the LSP mode^[15]. Here, we drop-cast HARCQWs dissolved in hexane onto Si substrate with a 100 nm thermally grown SiO₂ film. The thickness of the HARCQW film is controlled by varying the concentration in hexane while fixing the drop-cast area. The thickness of HARCQW film experimentally investigated extends up to 400 nm, which is already beyond the penetration depth of LSP mode.

Figure 4.3 Features over the Si/SiO₂ substrate as an indicator of the nanocube location. (a) Dark-field scattering image, the scale bar is 5 μm . (b) Bright-field microscopy image, the scale bar is 5 μm . (c) SEM image, the scale bar is 10 μm .

Another component of the hybrid system is the metallic nanocavity. In this study, we choose silver nanocube considering that gold is limited to operate with photon energies below the

heavy-hole exciton transition (2.4 eV)^[45]. These silver nanocubes composed of a PVP layer (2-3 nm) to avoid oxidation are purchased from Nanocomposix^[46].

Figure 4.4 Silver nanocubes. (a) The size distribution of silver nanocubes. Cited from <https://tools.nanocomposix.com:48/cdn/coa/Silver/Nanocubes/>. The mean value is ~78 nm and the deviation is ~6.5%. (b) The SEM images of nanocubes on Si/SiO₂ substrate (using 65, 75, 85 and 95 nm as examples). The size is marked using SMILEVIEW software. (c) The scattering peak versus nanocube size. As the size of silver nanocube increases, the scattering peak red-shifts in the contribution of retardation effect^[43]. (d) The linewidths change of scattering spectra. As the size of silver nanocube increases, the spectra become broader as the diluted surface charge density distribution in larger silver nanocube^[44].

To ensure only individual nanocube is characterized and mapped, very diluted nanocubes dispersed in ethanol (1,000 times of the commercial concentration) are sparsely deposited onto the SiO₂/Si substrate or the densely packed HARCQW film via spin-casting. Multiple individual silver nanocubes in a square area of 100 $\mu\text{m} \times 100 \mu\text{m}$ are characterized by dark-

field scattering spectroscopy (see the details in **Appendix 1.2**) and their locations are optically imaged/labelled according to the large surface features over the SiO₂/Si substrate (see **Figure 4.3**).

Then, each specific nanocube is imaged using scanning electron microscopy (SEM) to extract size information and exclude clusters or distorted nanocubes. The scattering spectra of an individual nanocube over SiO₂/Si substrate (in the absence of HARCQWs) with varied sizes are presented in **Figure 4.1c**, confirming the spectral overlap of each nanocube with the HARCQW heavy-hole exciton peak (2.42 eV). In particular, the scattering spectrum shifts from 2.49 to 2.24 eV as the size of the nanocubes increases from 65 to 95 nm due to the retardation effect^[43], accompanied with a broader spectral profile (see the SEM images of nanocubes with varied size and linewidths change of scattering spectra in **Figure 4.4**). A scattering image of an example area is shown in the bottom inset of **Figure 4.1c**, nanocubes are isolated and appear cyanish under TM illumination.

To fully understand the plasmon-exciton interaction in such a hybrid system, we compute the near-field electric field intensity distribution using the finite-difference time-domain modelling (see **Appendix 2.1**). The separation between the nanocubes and HARCQWs is estimated to be ~4-6 nm according to the organic ligand length of HARCQWs (2-3 nm)^{[34][42]} and the thickness of PVP protective layer covering the nanocubes. The computed electric field map corresponding to the photon energy of 2.41 eV is shown in **Figure 4.1d**. As can be seen, electric field sustained by the silver nanocube is highly confined around the sharp edges, significantly reducing the optical mode volume of the nanocubes. We also observe that the electric field intensities effectively localize in the HARCQW layer (spatial overlap) both on the top and side views. Thus, the hybrid system with a small optical mode volume together with the large overlap between the plasmonic fields and the excitons should be an excellent breeding ground for strong exciton-plasmon interaction.

Figure 4.5 Ultrastrong coupling in silver nanocube-HARCQW hybrid system. (a) Normalized dark-field scattering spectra for -183, -74, 4 and 63 meV detuning. The dashed green line locates at the energy of the heavy-hole exciton transitions in HARCQW. Insets are the corresponding dark-field microscopy images, which display different colour based on the intensity ratio between UPB and LPB. (b) Normalized 2D scattering spectra map with different levels of detuning between the heavy-hole exciton energy and the plasmon resonance. The dashed white line indicates the heavy-hole exciton transition energy. (c) Dispersions of the exciton-plasmon polariton states as a function of the detuning. The blue squares (peak energy of the upper polariton branch, UPB) and the red circles (peak energy of the lower polariton branch, LPB) are experimental data. The blue (UPB) and red (LPB) solid lines are the computational results using the coupled harmonic oscillator model. The dashed black line indicates the heavy-hole exciton transition energy and the dashed green line indicates the uncoupled LSP energy. (d) Coupling strength (red circles), g , extracted from the experimental results with varied nanocube sizes (different detuning). The dash-dot black line is a model fitting (L : nanocube size; $n = 1.23 \pm 0.28$), which is in good agreement with theoretical expectation. Blue squares depict the strictest criterion of strong coupling. (e) The comparison of Rabi energy and cooperativity in different exciton-plasmon hybrid systems. The hollow stars represent organic materials and the solid stars denote the inorganic materials.

Here, we experimentally demonstrate that the silver nanocube-HARCQWs hybrid system enters the strong coupling regime by measuring its dark-field scattering spectra. As previously

discussed in Fig. 1c, silver nanocubes with sizes ranging from 65 to 95 nm allow us to detune the plasmon resonance energy between +63 and -183 meV crossing the heavy-hole exciton transition at 2.42 eV. Four representative scattering spectra for the hybrid systems with different detuning energies ($\delta = E_{plasmon} - E_{ex}$) are presented in **Figure 4.5a**, in which the transparency dip (highlighted by dashed green line) covering the heavy-hole exciton transition clearly indicates two prominent hybrid modes (upper polariton branch: UPB, and lower polariton branch: LPB).

Specifically, as the detuning energy changes from positive to negative value, the LPB overwhelms UPB and the scattering spectra shifts to the red region. This trend can also be observed in the dark-field scattering microscopy images; as plasmon energy decreases, the colour of silver nanocube changes from bluish to reddish. In particular, as the detuning energy is close to zero, the intensities of the UPB and the LPB are comparable with each other and the dark-field scattering image looks whitish.

The anti-crossing behavior can be seen more clearly on the contour map of normalized scattering spectra (**Figure 4.5b**). First, the dispersionless dip is exactly located at the energy of ~ 2.41 eV (white dashed line), which corresponds to the electron-heavy hole transition in HARCQWs. In addition, two peaks associated with the LPB and the UPB are expectedly dispersive following the detuning change. Furthermore, these experimental data can be corroborated with numerical simulations to verify the exciton-plasmon interaction in the hybrid system. As shown in **Figure 4.5c**, we utilize the coupled harmonic oscillator mode^{[16][18][47][48]} (see Appendix 2.2 for details) to reproduce the dispersions of the peak energies of the hybrid states and thus, extract the coupling strength and the Rabi energy. From both the experimental contour map of the scattering spectra (**Figure 4.5b**) and the phenomenological model (**Figure 4.5c**), we can unambiguously conclude that as the plasmon resonance energy varies across the heavy-hole exciton transition, the scattering spectrum splits

into two polariton bands, exhibiting a distinct anti-crossing behavior with a giant Rabi splitting of ~ 402 meV. Our achieved Rabi energy present the highest value ever reported for Wannier Mott excitons, which indicates an ultrafast energy transfer cycle^[47-49] with a corresponding rate of ~ 0.1 fs⁻¹.

More insight into the nature of light-matter interaction of our hybrid system can be obtained by investigating the coupling strength (g). Here, we adopt the strictest criterion, $(2g)^2 > \gamma_{LSP}^2 + \gamma_{hl-ex}^2$, to indicate that the strong coupling regime has been reached, in comparison to $2g > (\gamma_{LSP} + \gamma_{hl-ex})/2$ or $2g > \gamma_{LSP}$ used in previous reports^{[5-8][10][11][29]}, where γ_{LSP} and γ_{hl-ex} are the linewidths of plasmon resonance and heavy-hole exciton transition, respectively. Therefore, fulfilment of our criterion guarantees the strong-coupling condition between exciton and plasmon in our hybrid system. In **Figure 4.5d**, we plot g as a function of the nanocube size (i.e. different detuning values) and observe that g is always larger than all of the corresponding critical values. This finding suggests that spectral splitting in our system is caused by Rabi energy exchange rather than Fano resonance or absorbance dip enhancement. We also notice that g varies with the nanocube size (smaller nanocube exhibits larger g). This trend can be fitted by a scaling of $g \propto 1/L^n$ ($n = 1.23 \pm 0.28$), which is roughly consistent with the expected scaling^{[27][29]}: $g \propto 1/\sqrt{V} \propto 1/L$. However, the correlation is not very strong, which is possibly due to the roughness of the HARCQW film, the variance in the number of excitons per nanocube, and also the diversity of the distance between nanocubes and HARCQW film.

For active operation of plasmonic devices, besides the Rabi energy, another benchmarking parameter is cooperativity (C), defined as $(\hbar\Omega)^2 / (\gamma_{LSP}\gamma_{hl-ex})$, which quantifies the probability that an optical emitter radiates into a distinct light mode^{[15][49][50]}. **Figure 4.5e** compares the Rabi energy and the corresponding cooperativity in different plasmon-exciton systems. Typically, inorganic materials (e.g., TMDs and CdSe quantum dots) only exhibit small Rabi

energy (< 200 meV) and C value (less than 4) due to the weak oscillator strength of Wannier Mott excitons^{[5-11][15-17]}. On the other hand, C value in organic materials can be as large as 9 benefitting from the intrinsic properties of Frenkel exciton^[19-29]. Very recently, Norris *et al.*^[15] achieved C value up to 10.5 in CdSe CQWs-plasmon system by taking advantage of the sharp LSP resonance (linewidth: 32 meV) in electron-beam-lithographically fabricated metallic photonic crystals, although the Rabi energy in their system is only 110 meV. Here, in our simple and solution-processable system, we achieve cooperativity exceeding 11 in spite of the broad plasmon profile (linewidth: ~ 340 meV).

4.2.2 Microscopic origin of the ultra-strong interaction

Let's revisit this relationship: Rabi energy or coupling strength is proportional to $\sqrt{fN/V}$, to figure out the possible mechanisms that are responsible for the giant Rabi splitting observed in our silver nanocube-HARCQW system (we also analyze the coupling using low aspect ratio CQWs, which presents a Rabi energy of ~ 160 meV, matching the values in previous reports^{[15][17][37]}, see **Figure 4.6** in details).

The first term coming into the picture is exciton binding energy (E_{bx}) considering that larger exciton binding energy greatly suppresses the thermal ionization or other dissociation processes, thus allowing for the stable and strong energy exchange between excitons and plasmons^{[3][5]}. In low aspect ratio CQWs (LARCQWs), such as square shape, quantum confinement is only strong along the vertical direction because the lateral sizes are much larger than the exciton Bohr radius (~ 5.7 nm)^[38]. In contrast to LARCQWs, excitons in HARCQWs are additionally confined along one lateral direction since the lateral size is significantly tailored down (see **Figure 4.7a**). As shown in the inset of **Figure 4.7b**, additional dimension in quantum confinement is expected to increase the band gap. However, the shift of excitonic transition is negligible (see the comparison of absorbance in **Figure 4.8**) with

respected to the aspect ratio of CQWs. This implies a significant increase of the exciton binding energy in these HARCQWs (inset of **Figure 4.7b**).

Figure 4.6 The Rabi splitting in the same hybrid system using low aspect ratio CQWs. (a) The dark-field scattering spectra. (b) Anti-crossing behaviour, the calculated Rabi energy is ~ 162 meV. (c) The coupling strength as a function of nanocube size. The dashed black curve is a fitting ($g \propto 1/L^n$, $n: \sim 1.17$).

To further confirm our interpretation, we compute the exciton binding energy in 4 ML CdSe CQWs with varying lateral sizes (the energy of free electron-hole pair are calculated by means of 8-band $k \cdot p$ model; then, using the measured first excitonic absorption features, the exciton binding energy can be extracted, see details in **Appendix 2.3**)^[51]. **Figure 4.7b** exhibits the exciton binding energy holds a negative correlation with the lateral size of CQWs,

agreeable to our previous explanation. Notably, when the lateral size is close to or beyond the Bohr radius (vertical dashed line in **Figure 4.7c**), E_{bx} is enhanced by more than 50% compared to the value in square-shaped CQWs^{[38][51]}.

Figure 4.7 Material properties responsible for a giant Rabi energy. (a) Morphology of the HARCQWs. Top panel: schematic of the HARCQWs. Bottom panel: self-assembly of HARCQWs. The TEM image shows the random oriented, non-stacking and face-down assembly. The inset of bottom panel: TEM image of individual HARCQW, the lateral size is about ~ 50 nm by 5-8 nm. (b) The exciton binding energy as a function of the lateral size in 4 ML CdSe CQWs. The solid line is guide to the eye. Dashed black line indicates the exciton Bohr radius (~ 5.7 nm) in bulk CdSe. Inset: impact of the aspect ratio on exciton binding energy. High aspect ratio is expected to enhance the exciton binding energy, indicated by the horizontal dashed line. The vertical dashed line exhibits the negligible shift of the absorbance feature with respect to aspect ratio. (c) Time-resolved PL decay curves of the HARCQWs (squares: in film; circles: in hexane) and LARCQWs (squares: in film; circles: in hexane). Black dashed lines are the multiexponential fits. (d) Experimental and simulated k -space image of HARCQW film. Left part: calculated results for pure in-plane dipole orientation. Right part: experimental data of our HARCQW film. (e) Comparison between the experimental (red circles) and simulated (black line) results cutting along the line in which $k_x = 0$ (p polarization) to extract the fraction of in-plane dipole in our HARCQW film.

Figure 4.8 The normalized absorbance spectra of 4 ML CdSe CQWs with varying lateral size (high: $\sim 50 \times \sim 8$ nm, medium: $\sim 24 \times \sim 14$ nm; low: $\sim 14 \times \sim 12$ nm). The right-top corner is the zoom-in of electron-heavy hole transition, which suggests that the energy shift of the first excitonic transition in CQWs with varying lateral size is negligible.

Figure 4.9 TEM image of stacked LARCQWs (lateral size: $\sim 24 \times \sim 14$ nm). We can clearly see the column-like chain is formed in the LARCQW ensemble.

Fast exciton consumption is another challenge in hybrid systems since energy exchange needs to be faster than any dissipative processes in excitons to achieve strong interaction^[1]. Self-assembling (or stacking) in CQW solid film has been problematic for exciton reservation^[39-42]. Our group has reported that, owing to large absorption cross-section of CQWs and their close-packed collinear orientation in a stacked CQW film, homo-FRET (Förster resonance energy transfer among the same material) is extremely fast (< 100 ps) and ultra-efficient (efficiency can reach more than 60% at room temperature), which can even dominate the multiexciton Auger recombination^[39]. Thus, the exciton transfer and trapping are rapidly boosted.

Table 4.1 Fitting components of trPL decay for HARCQWs (in film and in hexane) and LARCQWs (in film and in hexane). The measurement is probed at the band-edge emission wavelength (electron-heavy hole transition: ~514 nm).

	τ_1 (ns)	τ_1 (ns)	τ_1 (ns)	A_1 (%)	A_1 (%)	A_1 (%)	τ_{avg} (ns)
HARCQWs							
(in solution)	0.91	4.15	16.8	60.7	30.9	8.4	3.25
HARCQWs							
(film)	0.88	3.47	15.3	60.2	34.5	5.3	2.54
LARCQWs							
(in solution)	0.87	4.05	16.3	55.3	36.9	7.8	1.41
LARCQWs							
(film)	0.41	2.72	11.6	71.4	24.8	3.8	3.26

The main reason for stacking^[42] is the Van der Waals attraction tends to align the lateral faces of CQWs parallel to each other in long needle-like chains^{[40][41]} (see the TEM image of

stacked LARCQWs in **Figure 4.9**). If we approximate the CQW as an ideal flat plate, we can express the attraction energy for stacking as follows^[42]: $E_{\text{attraction}} = \frac{HA_{\text{eff}}}{12\pi D^2}$, where H is Hamaker constant, D is the distance between the CQWs and A_{eff} is the effective interaction area. If the attraction energy is larger than kT (the thermal energy), the CQW film will prefer to be stacked. Thus, the unstacking criterion can be given by $D > \sqrt{\frac{HA_{\text{eff}}}{12\pi kT}}$, which implies that the distance should be larger than a certain value to avoid stacking.

By using the Hamaker constant from ref. 42, the minimum distance for LARCQWs with a square shape (18×18 nm) is ~ 7.1 nm by assuming the whole surface area is effective. This distance is larger than the length of two oleic acid ligands ($4\sim 6$ nm)^{[34][42]} and explain why LARCQWs are easy to stack. However, for HARCQWs, A_{eff} can be quite small considering any small tilting or offset will significantly change the effective interaction area. If the minimum distance is reduced to be smaller than the length of two oleic acid ligands, the CQW film will not be stacked anymore. There is no doubt that HARCQWs satisfy this criterion, as shown in **Figure 4.7a**, random oriented CQWs are flat-lying on the TEM grid and there is no indication of stacking. To further support our argument, we have checked the time-resolved photoluminescence (trPL) of CQWs in solution dispersion and a solid film (see **Figure 4.7c**). Both low and high aspect ratio CQWs in solution display a similar decay behavior with an average lifetime of ~ 3.2 ns (see **Table 4.1** for the tri-exponential lifetime fitting). On the other hand, in solid film, for LARCQWs, the average lifetime accelerates to ~ 1.4 ns, indicating a strong exciton trapping via the homo-FRET process caused by stacking^[39]. However, the homo-FRET process is greatly suppressed in a HARCQW film with a prolonged average lifetime of ~ 2.5 ns, suggesting the induced non-radiative channel is weakened.

Beyond the intrinsic properties of HARCQWs, one more point needed to be considered in our hybrid system is the effective dipole numbers^[19], N_{eff} . As discussed in **Figure 4.1**, the total

number of dipoles (N) is enough in the solid film to ensure that they can cover the whole penetration depth of LSP. Indeed, the coupling strength (g) depends on the orientation of transition dipoles with respect to electric field of the LSP mode. For a single dipole: $g_i \propto \sqrt{\cos^2(\theta_i) \times f/V}$, where θ_i denotes the angle between the dipole momentum and the electric field^{[12][13][19]}. Thus, Rabi energy is proportional to the square root of effective dipole numbers ($N_{eff} = \sum_{i=1}^N \cos^2(\theta_i)$) rather than the total dipole number (N). In our system, the electric field of plasmon mode sustained in a silver nanocube is mainly confined in the xy-plane (in-plane) and oscillating along the nanocube edge^[7] as seen in **Figure 4.1d**. Therefore, in-plane dipoles can maximize $\cos^2(\theta)$ and achieve a larger Rabi energy while the vertically stacked CQWs would suppress N_{eff} to the minimum. Dipole orientation in CdSe CQWs has been symmetrically studied by Gao *et al.*^[52] and Scott *et al.*^[53], demonstrating that the fraction of in-plane dipole is close to unit ($> 95\%$) if the CQWs in film are laid face-down. Instead of using non-polar solvent to change the interfacial energy and lay down the LARCQWs as in their works, here, HARCQWs are naturally face-down in film (see the bottom panel of **Figure 4.7a**) benefitting from the non-stacking properties. This is understandable as the formation of edge-up assembly (as opposed to face-down) is because the stacking allows enough supporting area to make the CQWs standing up (the edge thickness of CQWs is only 1.2 nm). To double-check the face-down assembly in our HARCQW film, we follow Gao and Scott's works to use back focal plane (BFP) images to determine the dipole orientation (see the details of the BFP image set-up and simulation in **Appendix 2.4**). **Figure 4.7d** shows the calculated intensity pattern for the pure in-plane dipole orientation and an experimental BFP images for our HARCQW film, which shows the mirror relationship between the simulation and the experiment, suggesting a high fraction of in-plane dipoles in the HARCQW film. To extract the fraction of in-plane dipoles, we compare the experimental and simulated curves along $k_x =$

0 (p-polarization). The two dips ($k_y = \pm k_0$) of experimental data are found to considerably approach 0, and we can calculate the fraction of in-plane dipoles is ~95%.

4.2.3 The emissive polaritons

In view of the ultra-strong interaction between exciton and plasmon in our hybrid system, it is natural to expect the observation of splitting in PL as previous reports exciton-photon strong coupling system^{[54][55]}. The PL signal from our hybrid system at room temperature is shown in **Figure 4.10** (see the optical measurement in **Appendix 1.3**). The corresponding dark-field scattering spectrum (detuning: ~4 meV) and PL of uncoupled HARCQW film are also presented. We can clearly observe the complex PL spectrum consisting of the broad emission originating from LPB and the narrow emission resulting from uncoupled band-edge excitons (located at 2.42 eV). This uncoupled emission is expected because the silver nanocube distribution is sparse and laser focus spot is much larger than the nanocube size^{[15][54][56]}. Notably, the LPB emission spectrum (peaking at ~2.27 eV) is blue-shifted with respected to the corresponding LPB scattering spectrum (~ 2.21 eV). The reason for the higher energy LPB peak in the PL compared to the scattering is not totally understood. Our speculation for this observation is related to ‘polariton bottleneck’ and the contribution of dark polariton states. The former implies that the PL emission originates from not fully relaxed lower polariton states. When the pump fluence is high, the strong scattering among polariton states in LPB will accelerate the decoupling process (photons will be emitted before polariton states can relax to the bottom of LPB), which is similar to the ‘polariton bottleneck’ observed in exciton-photon polariton systems^[55]. The latter associates with N excitons coupled to the plasmon to generate two bright hybrid states (LPB and UPB) and $(N-1)$ dark polariton states. Although these dark polariton states absorb weakly, they may contribute to the high energy part of the LPB emission when exciton density is high, as theoretically predicted in Ref. 57 and 58.

Figure 4.10 PL spectra (top panel) at room temperature of the coupled hybrid system. The narrow emission located at the high energy side is attributed to the uncoupled band-edge exciton emission. The vertical green dashed line indicates the heavy-hole exciton transition at 2.42 eV. The broad emission peaking at the low energy side is originating from the lower polariton states. Comparing with the dark-field scattering spectra, the low polariton states in PL exhibits a blue-shifted behaviour.

4.3 Summary

In this chapter, we have demonstrated ultra-strong interactions between excitons in CdSe HARCQWs and localized plasmon resonance in silver nanocubes. The observed value of collective Rabi splitting is up to 402 meV, which is the highest value ever achieved for Wannier excitons, also corresponds to the largest cooperativity (> 11) ever reported in an open cavity exciton-polariton system. Importantly, the ultra-strong exciton-plasmon coupling is observed in both dark-field scattering and photoluminescence measurement, unambiguously suggesting the strong intermixing of excitons with plasmons to create polaritons. The main mechanisms responsible for these observations are the enhanced oscillation strength and improved in-plane exciton dipole orientation in HARCQWs. These exciton-plasmon hybrid

system, based on fully solution-processable quantum emitters and metal nanostructures, may provide a feasible recipe for active all-optical nano-circuits and devices.

Appendix 1: Experimental methods

1.1 Synthesis of high aspect ratio CdSe CQWs

CdSe CQWs are synthesized by following the earlier reported recipe with few modifications^{[35][59]}. Briefly, we start with 340 mg of cadmium myristate, 24 mg of Selenium, and 30 mL of 1-octadecene in a 100 mL flask. While degassing the temperature of solution is slowly increased up to 95 °C and thereafter keeps at this temperature for 30 min in order to evaporate extra solvents and dissolve myristate completely. Hereafter we raise the temperature to 245 °C and switch the solution under argon at 100 °C. At approximately 195 °C when the colour of solution becomes bright yellow, we introduce the 120 mg of cadmium acetate having different amounts of hydrate in the crude reaction solution. This variation in hydrate content results in a different aspect ratio for CQWs. The variation of the hydrate content in cadmium acetate is obtained by using different ratios of cadmium acetate anhydrous/cadmium acetate dihydrate ($\text{Cd}(\text{OAc})_2/\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$)^[59]. Thereafter, we keep the solution at 240 °C for 8-10 min. The reaction is completed by the addition of 1 mL of oleic acid in the solution followed by cooling the crude reaction solution to room temperature using a water bath. Using size selective precipitation, the pure 4 ML CdSe CQW populations are separated from the crude reaction solution. The cleaning procedure is exactly followed as earlier reported^[59]. Finally, the precipitated sample is dissolved in hexane and is used for different characterizations and applications.

1.2 Dark-field scattering spectroscopy

Dark-field scattering experiment is conducting based on a 100x objective lens (NA = 0.95) and the Xenon light source (Thorlabs). Scattered photons are collected by the same objective

lens and directed into a hyperspectral system (Cytoviva) for spectral analysis. A background spectrum taken from a nearby area is subtracted from each measured silver nanocube spectrum.

1.3 PL measurement of the hybrid system

All measurements are conducted using a frequency tripling of Nd:YAG laser (355 nm) with a pulse width of 0.5 ns at a repetition rate of 100 Hz. The sample is mounted on a three-dimensional moving stage. The laser beam is focused onto the hybrid system using a long working distance objective lens (ZEISS, NA: 0.65, 63x). The emission signal is collected using the same objective lens with a long pass filter (>450 nm).

Appendix 2: Theoretical calculations

2.1 Simulation of the electric field distribution in hybrid system

Three-dimensional finite difference time domain (FDTD) simulations were performed to calculate the optical modes in plasmonic cavities. A silver nanocube is directly placed on top of CdSe CQW film. The silver nanocube is assumed to be 75 nm edge length, edge rounding of 3 nm and corner rounding of 5 nm. The silver nanocube is also coated with 3 nm polyvinylpyrrolidone (PVP) to increase the stability in the air. The silver nanocube are modelled as a dispersive Drude metal with parameters obtained by fitting tabulated data from Palik in the experimental wavelength range (from 400 nm to 600 nm). And the PVP layer is modelled as a dispersionless dielectric with a refractive index of 1.53.

The dielectric properties of CdSe CQW film is measured using an ellipsometer (VASE, J.A. Woollam, spectral range from 193 nm to 3200 nm) and the results are shown in **Figure A1**:

Figure A1. Permittivity of CdSe CQW film.

Moreover, a dielectric layer on top of CdSe CQW film with the thickness of 3 nm is inserted to consider the oleic acid ligands. The ligand layer is also modelled as a dispersionless dielectric with a refractive index of 1.45.

The construct is illuminated with a plane wave (Total field scattered field source, X polarization) at the angle of 0° to couple with in-plane plasmon cavity modes. The incident wavelength is swept from 400 nm to 650 nm using inbuilt sweep parameter. Three DFT-Monitors (Frequency domain power monitor) are used to obtain the electric field distributions at x-y, x-z views in **Figure 4.1d**.

2.2 Coupled harmonic oscillator model

The exciton-photon hybrid states can be described by the coupled harmonic oscillator model:

$$\begin{pmatrix} E_{LSP} - i\frac{\gamma_{LSP}}{2} & g \\ g & E_{hl} - i\frac{\gamma_{hl}}{2} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E_p \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (A1)$$

Where E_{LSP} and E_{hl} are the energy of plasmon mode and heavy-hole exciton, respectively. g is the coupling strength. γ_{LSP} and γ_{hl} are the linewidth of plasmon mode and heavy-hole exciton,

respectively. α and β are Hopfield coefficients. Diagonalize this Hamiltonian and do approximation to find the two eigenvalues:

$$E_p = \frac{(\delta + 2E_{hl}) \pm \sqrt{4g^2 + \delta^2}}{2} \quad (\text{A2})$$

Where δ is the detuning energy and defined as: $\delta = E_{LSP} - E_{hl}$. At zero detuning, the energy difference between lower and high polariton states is the Rabi energy.

The calculated dispersion of LPB and UPB is shown in **Figure A2**, which exhibits great agreement with experimental data. In addition, the extracted Hopfield coefficients of LPB and UPB are shown below:

Figure A2. Hopfield coefficients for LPB (a) and UPB (b), calculated using the coupled harmonic oscillator model.

It can be seen that as the plasmon energy increases (larger detuning), the fraction of exciton constituent in LPB will be enhanced, while in UPB, the fraction of exciton constituent will be suppressed. Specifically, the polariton modes becomes half plasmon half exciton when the plasmon energy is matching the energy of excitonic transition in HARCQWs.

2.3 8-band $k \bullet p$ model

The 8-band $k \bullet p$ is used to study the energy levels of free electron-hole pair in colloidal quantum wells (CQWs). Then using the measured first excitonic absorption features, we can

calculate the exciton binding energy. The Hamiltonian is represented in the Bloch function basis $|S, \uparrow\rangle, |S, \downarrow\rangle, |11, \uparrow\rangle, |10, \uparrow\rangle, |1-1, \uparrow\rangle, |11, \downarrow\rangle, |10, \downarrow\rangle, |1-1, \downarrow\rangle$ as:

$$H_8 = H_0 + V \quad (\text{A3})$$

Where H_0 describes the material and the V denotes the confinement of the CQWs. As we use the basis $|10\rangle, |1-1\rangle, |11\rangle$ for the p-like states instead of $|HH\rangle, |LH\rangle, |SO\rangle$, the form of Hamiltonian is different from the traditional JJ_z representation model and can be transformed into it under an unitary transformation. The details of the elements in H_0 is given as follows:

$$H_0 = \begin{pmatrix} E^C & 0 & iP_-^* / \sqrt{2} & iP_z & iP_+^* / \sqrt{2} & 0 & 0 & 0 \\ 0 & E^C & 0 & 0 & 0 & iP_-^* / \sqrt{2} & iP_z & iP_+^* / \sqrt{2} \\ -iP_- / \sqrt{2} & 0 & HH & S & R & 0 & 0 & 0 \\ -iP_z & 0 & S^* & Q - 2\lambda & S & -\sqrt{2}\lambda & 0 & 0 \\ -iP_+ / \sqrt{2} & 0 & R^* & S^* & HH - \lambda & 0 & \sqrt{2}\lambda & 0 \\ 0 & -iP_- / \sqrt{2} & 0 & -\sqrt{2}\lambda & 0 & HH - \lambda & S & R \\ 0 & -iP_z & 0 & 0 & \sqrt{2}\lambda & S^* & Q - 2\lambda & S \\ 0 & -iP_+ / \sqrt{2} & 0 & 0 & 0 & R^* & S^* & HH \end{pmatrix} \quad (\text{A4})$$

where

$$\begin{aligned} E^C &= E_g + \frac{\hbar^2}{2m_0} \gamma_c (k_x^2 + k_y^2 + k_z^2) + \delta E_{strain}^{CB}; HH = -\frac{\hbar^2}{2m_0} \left[\frac{L' + M'}{2} (k_x^2 + k_y^2) + M' k_z^2 \right] + \delta E_{strain}^{HH} \\ Q &= -\frac{\hbar^2}{2m_0} [M' (k_x^2 + k_y^2) + L' k_z^2] + \delta E_{strain}^Q; S = -\frac{\hbar^2}{2m_0} \left[\frac{1}{\sqrt{2}} N' (k_x + ik_y) k_z \right] + \delta E_{strain}^S \\ R &= -\frac{\hbar^2}{2m_0} \left[\frac{L' - M'}{2} (k_x^2 - k_y^2) + iN' k_x k_y \right] + \delta E_{strain}^R; \\ P_- &= p_0 (k_x' - ik_y'); P_+ = p_0 (k_x' + ik_y'); P_z = p_0 k_z'; p_0 = \hbar \sqrt{E_p / 2m_0} \\ L' &= L - \frac{E_p}{E_g}; N' = N - \frac{E_p}{E_g}; M' = M; \lambda = \Delta_{so} / 3; \gamma_c = \frac{m_0}{m_c} - \frac{E_p}{3} \left(\frac{2}{E_g} + \frac{1}{E_g + 3\lambda} \right) \end{aligned} \quad (\text{A5})$$

As in our CdSe CQWs, the strain is taken to be zeros. The confinement potential V is described by the function:

$$V = \begin{cases} 0, & \text{in} \\ V_0, & \text{out} \end{cases} \quad (\text{A6})$$

Table A1 All parameters used for calculation^[51].

Physical parameter		Value
E_g (eV)	Bandgap energy	1.732
E_p (eV)	kane matrix element	16.5
Δ_{so} (eV)	Spin-orbital splitting energy	0.42
γ_1	Luttinger parameters	3.265
γ_2	Luttinger parameters	1.162
γ_3	Luttinger parameters	1.443
m_c	Electron effective mass	0.12

We assume that the QDs are periodically arranged in three dimensions and with the period L_x, L_y, L_z . We have used the plane waves to expand the basis as follows:

$$\Phi_m = \{\Phi_m^j\} (j=1, 2, \dots, 8) \quad (\text{A7})$$

With $\Phi_m^j = \frac{1}{\sqrt{V}} \sum_{n_x, n_y, n_z} \alpha_{m, n_x, n_y, n_z}^j \exp[i(k_{nx}x + k_{ny}y + k_{nz}z)]$. Where $V = L_x L_y L_z$, $k_{nx} = \frac{2\pi n_x}{L_x}$,

$k_{ny} = \frac{2\pi n_y}{L_y}$, $k_{nz} = \frac{2\pi n_z}{L_z}$ and n_x, n_y, n_z are the integer of plane wave numbers. Here we set the

range of these plane wave numbers from -3 to 3. The j is the index of basis. All parameters used in calculation are listed in **Table A1**.

2.4 Back focal plane image

We follow the work of Gao *et al.*^[52] and Scott *et al.*^[53] to simulate the back focal image of nanoparticles' emission. About the details of the Formula Derivation, we recommend readers refer to the original publication. Here, we reproduce their final version of formulas to fit our experimental results and extract the fraction of in-plane (IP) and out-plane (OP) dipoles.

Figure A3 The geometry of three-layer structure.

The geometry (three-layer structure) used for back focal plane imaging simulation is shown in **Figure A3**. Using the Fresnel equations, we can calculate the reflection and transmission coefficients of S/P polarization in the interface between two adjacent layers:

$$\begin{aligned} r_{ij}^p &= \frac{n_j^2 k_{zi} - n_i^2 k_{zj}}{n_j^2 k_{zi} + n_i^2 k_{zj}}; t_{ij}^p = \frac{2n_i n_j k_{zi}}{n_j^2 k_{zi} + n_i^2 k_{zj}}; \\ r_{ij}^s &= \frac{2k_{zi}}{k_{zi} + k_{zj}}; t_{ij}^s = \frac{k_{zi} - k_{zj}}{k_{zi} + k_{zj}}; \end{aligned} \quad (\text{A8})$$

Where k_z is the wave-vector along z direction and derived based on the wave-vector conservation along X/Y direction, n_i is the refractive index of i_{th} layer.

$$\begin{aligned}
\rho_{IP}^s &= \frac{1}{8\pi k_0 k_{z3}} \left| \frac{t_{32}^s e^{\frac{ik_{z2}L}{2}} (1 + r_{21}^s e^{ik_{z2}L})}{1 - r_{21}^s r_{23}^s e^{2ik_{z2}L}} \frac{k_y}{\sqrt{k_x^2 + k_y^2}} \right|^2; \\
\rho_{IP}^p &= \frac{1}{8\pi k_0 k_{z3}} \left| \frac{t_{32}^p e^{\frac{ik_{z2}L}{2}} \frac{k_{z2}}{n_2 k_0} (1 - r_{21}^p e^{ik_{z2}L})}{1 - r_{21}^p r_{23}^p e^{2ik_{z2}L}} \frac{k_x}{\sqrt{k_x^2 + k_y^2}} \right|^2; \\
\rho_{OP}^p &= \frac{1}{8\pi k_0 k_{z3}} \left| \frac{t_{32}^p e^{\frac{ik_{z2}L}{2}} \frac{k_x}{n_2 k_0} (1 + r_{21}^p e^{ik_{z2}L})}{1 - r_{21}^p r_{23}^p e^{2ik_{z2}L}} \right|^2;
\end{aligned} \tag{A9}$$

Based on these coefficients, we can calculate the local density of optical states (LDOS) for IP dipole and OP dipole using the above equations (here, OP dipole can only show P polarization), where k_0 is the wavevector in air, L is the thickness of nanoparticle layer and other symbols are denoted as mentioned before.

Thus, we can calculate the emission intensity of s- or p-polarization projected on the back focal plane with certain wave-vector (k_x, k_y) based on the population fraction (f) and LDOS (ρ) of IP or OP dipoles (C is an experimental determined constant):

$$\begin{aligned}
I^s &= C \rho_{IP}^s f_{IP} |\mu_{IP}|^2 \\
I^p &= C (\rho_{IP}^p f_{IP} |\mu_{IP}|^2 + \rho_{OP}^p f_{OP} |\mu_{OP}|^2)
\end{aligned} \tag{A10}$$

The simulated BFP image densities for pure IP and OP transition dipoles are shown below:

Figure A4 Simulated BFP image of IP (a) and OP (b) dipole transitions.

Figure A5 Ray tracing of the set-up to measure BFP image.

For the experimental part, the set-up used to measure the BFP image is shown in **Figure A5** (excitation laser, polarizer and CCD camera are not presented). To confirm the validation of the set-up, we have utilized the strip silver grating to compare the real-space image and Fourier-space image, the result is shown in **Figure A6**, we can observe that in Fourier space, the horizontal stripes in real-space have been converted into vertically distributed dots.

Figure A6 Validation of our set-up.

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Chapter 5: Charged excitons to control lasing

5.1 Motivation and Introduction

Since CQDs were first demonstrated as an optical gain medium for lasing applications, the search for CQDs with low gain threshold has been hindered by non-unity degeneracy of the band-edge states^{[1-5][7]}, which means multiple-exciton gain is needed to achieve light amplification^[6]. This condition requires that the average number of excitons per CQD is greater than one ($\langle N \rangle > 1$), signifying that considerable percentage of CQDs should contain at least biexciton. This results in the accelerated non-radiative Auger process^[8-12], whereby electron-hole recombination energy is non-radiatively transferred to a third carrier. Auger recombination is almost two orders of magnitude faster than the radiative process in typical CQDs^{[4][14-16]}, which has been the main obstacle to achieve sustainable and low-threshold CQD lasing.

Multiple strategies have been proposed to overcome this challenge and achieve low-threshold CQD lasers. Much work has pursued the idea of suppressing Auger recombination. This non-radiative Auger rate (inverse of Auger lifetime) can be reduced by engineering the wavefunction confinement of electrons and holes in CQDs including type II CQDs[17], alloyed core-shell interface CQDs[18], and ‘giant’ or tailored CQDs[19]. Another effort to reduce the optical gain threshold is to inject electrons into the conduction band, i.e., negatively charged CQDs. Such extra electrons contribute to the carrier population in the excited state of the CQDs, significantly reducing the reabsorption (optical loss) or even creating optical transparency at the emission wavelength^[20]. Therefore, the population inversion or stimulated emission can be obtained at much lower pumping levels^[7].

Very recently, Klimov's group has demonstrated population inversion with optical pumping threshold at $\langle N \rangle = 0.02$ in charged CQDs via photochemical reduction^[7]. Also Guyot-Sionnest's group had investigated the lowering amplified spontaneous emission (ASE) threshold in CQDs by electrochemical charging at low temperature^[12]. However, photochemical doping requires CQDs in oxygen-free environment; otherwise, all these changes are reversed completely^[20]. And electrochemical method demands solution (electrolyte) environment to charge CQDs. Given the final goal of achieving a practical CQD laser, a method to charge CQDs reliably in an optoelectronic device is preferred^[16]. Employing electric field to modulate the spontaneous emission properties of nanoparticles in a capacitor had been explored by Delehanty's group^[11] and Woggon's group^[21] as a "device ready" approach. To date, the investigation remaining in the spontaneous regime might be utilized for sensing applications. Here, for the first time, we demonstrate the control of CQDs' ASE in the device structure via electric field induced charging. By adjusting the voltage bias on the device, we are able to regulate the average charging level in the CQD film; and lower ASE threshold is achieved with optimum charging level where the advantages of low population inversion threshold dominate the adverse effect of Auger recombination.

5.2 Controllable optical gain

Colloidal quantum dots (CQDs) are highly promising materials for light amplification and lasing thanks to their efficient photoluminescence, tune-able emission wavelength and low-cost synthesis. Unfortunately, as an optical gain medium, CQDs are suffering from band-edge state degeneracy which demands multiple excitons to achieve population inversion. As a result, non-radiative Auger recombination increases the lasing threshold and limits the gain lifetime. Here, we demonstrate that the amplified spontaneous emission (ASE) threshold is controllable in a device where CdSe/CdS/ZnS core-shell-shell CQD film is exposed to external electric

field. This effect is attributed to electric field induced negative charge in CQDs. We utilize singly-charged CQDs to build up population inversion due to the pre-existing electron in the conduction band. However, strongly enhanced Auger recombination in doubly charged CQDs stymies the ASE, though the population inversion is ready at any pumping level. Experimental results and kinetic equation model show that ASE threshold reduces 10% even if our device only charges ~17% of CQD population. Our results open new possibilities for controlling exciton recombination dynamics, populating the conducting band and achieving nearly zero-threshold CQD lasing, and electrically pumped CQD lasers.

5.2.1 Spontaneous emission of CQDs in the device

We investigated CdSe/CdS/ZnS core-shell-shell CQDs, which were produced using a slightly modified synthesis recipe (1) reported by Bawendi's group (detail in **Appendix 1.1**). This quasi-type II structure, shown as an inset in **Figure 5.1a**, has advantages of suppressed Auger rate, high quantum yield and enhanced absorption cross-section, which are beneficial for laser applications. The high bandgap ZnS shell with thickness of ~1.5 nm passivates the potential surface traps and still maintains the quasi-type II structure. The absorbance and photoluminescence (PL) spectra of the diluted CQDs dispersed in toluene (1 mg/mL) at room temperature are presented in **Figure 5.1a**. The PL spectrum (FWHM of ~34 nm) is broader than that of typical CdSe/CdS CQDs, which is attributed to the ZnS outermost shell as widely discussed in literatures for this core/shell/shell structure^{[5][8]}. Both two well-resolved excitonic transitions and clean emission spectrum with more than 70% quantum yield suggest the high quality of CdSe/CdS/ZnS CQDs. High concentration CQDs (> 100 mg/mL) in toluene were prepared for subsequent spin-cast compact CQD films.

We utilized a capacitor structure to apply electric field on our CQD film. To avoid CQDs being directly adjacent to electrodes, which would quench the photon emission, CQD film was

sandwiched between two dielectric layers (SiO_2 and poly(4-vinylphenol) (PVP), see device fabrication in **Appendix 1.2**).

Figure 5.1 Optical properties of CQD materials under increasing electric field in a capacitor device. **(a)** Normalized PL and absorbance spectra of diluted CQDs in toluene. Left inset: schematics of the core-shell-shell CQDs. Right inset: TEM image of the CQDs indicating the shape distribution and the crystalline structure; scale bar: 10 nm. **(b)** Schematics of the sandwich-like device structure. A sinusoidal-function bias (128 Hz) is applied to induce the electric field and the device is optically pumped at a wavelength of 532 nm using a sub-nanosecond pulsed laser (500 ps/100 Hz). **(c)** Scanning electron microscopic image of a device's cross-section, scale bar: 100 nm. **(d)** Electric field dependent PL spectra of CdSe/CdS/ZnS CQDs with the pump fluence of $272 \mu\text{J}/\text{cm}^2$. These emission spectra exhibit intensity decrease, red shift and broadening with increasing electric field. **(e)** The decrease of integrated PL intensity as a function of electric field, which was normalized by the zero-field integrated PL intensity. The solid line is guide to the eye. It shows ~18% intensity drop in the maximum electric field of 264 kV/cm. **(f)** Electric field dependent peak wavelength shift and PL spectrum broadening. The solid lines are guides to the eye. Only slight changes are observed here (~1.5 nm red shift and ~2 nm broadening under the maximum electric field).

Meanwhile, this multiple-layer capacitor structure limits the electrical current (see measured current in **Figure 5.2**) through the CQD film to a maximum extent. This is important as

electric current through a photoconductive device can lead to heavily charging and result in totally quenched emission of CQDs^[22].

Figure 5.2 Measured current flowing through the circuit. The current flowing through the circuit was recorded by the multi-meter as a function of V_{FG} . The current is stable in the order of 100 nanoampere for entire range of electric field, indicating good insulating layers between two electrodes. The effect of applied electric field on CQDs is dominant in our device. It is worth to note that **Figure 5.2** shows the stable AC current while the DC current behaved very unstable. The DC current started in the nanoampere range as AC current then increased gradually to few tens of microampere in the time frame of seconds to minutes. The slow behavior of DC current suggests chemical changes in CQD film during the DC current. The process can be repeated again if the device is rested after a run. This indicated the reversible process was happening in the CQD film under DC bias. The AC bias (few hundred Hz) was chosen to achieve very stable current and consistent optical properties of CQD film.

Figure 5.1b illustrates the schematic of the device's layer structure and the excitation geometry for optical characterization. Accordingly, the spectroscopic modulation observed in our device is attributed to the applied electric field. A sinusoidal AC bias is applied to introduce the external electric field through two electrodes (ITO and aluminium) attaching to the top and bottom dielectric layers. The AC bias was chosen to avoid slow chemical

processes happening reversibly with DC bias. The thickness of each layer is determined by cross-sectional imaging of the capacitor structure by scanning electron microscopy, as shown in **Figure 5.1c**, which is in good agreement with the measurement by a surface profiler (see thickness results in **Figure 5.3**). Given the three layers between two electrodes, the device is equivalent to three capacitors in series, a reference capacitor is adopted to measure the voltage drop across the CQD film (the detail of calculation is presented in **Appendix 2.1**). Together with the measured thickness of the CQD film, the electric field can be obtained more accurately for the CQD layer.

Figure 5.3 Thickness measurement conducted by surface profiler (Dektak XT surface profiler). (a) CQD layer. It shows good consistence with the SEM result (b) PVP layer. The slight difference between SEM result and surface profiler measurement is caused by spin-casting films on different substrates: the PVP layer is on top of CQD layer in SEM measurement, while in surface profiler measurement, the PVP layer is spin-casted on a glass substrate.

The emission properties of the CQD film under external electric field were investigated by employing a sub-nanosecond pulse laser with a stripe-excitation geometry (**Figure 5.1b**). Firstly, we checked the spontaneous emission behaviour with increasing electric field. When pumping with a fluence of $\sim 272 \mu\text{J}/\text{cm}^2$, CQD film exhibited a decrease in the emission intensity (**Figure 5.1d and 5.1e**), accompanied with red-shifted emission peak and broadening of the emission profile (**Figure 5.1d and 5.1f**) with increasing electric field. Basically, these

three observations match the expectation of quantum confined stark effect (QCSE), which relies on the pulling effect in different directions on electron and hole wave functions in a spatially confined structure induced by external electric field^{[23][24]}. Because of the wave function adjustment, QCSE leads to a decrease of radiative recombination rate (PL quenching)^{[21][25]}, a band gap reduction (PL red shifting)^[26] and enhanced phonon-exciton interaction (PL broadening)^{[23][24][26]}.

Due to the promising applications in nano-optoelectronics, intensive research had been focused on QCSE in nanoparticles. Bawendi's group^[23] demonstrated over 40 meV red shift and more than 3-fold spectral broadening in a single quantum dot at 10 K in an electric field of 350 kV/cm. In 2012, Weiss's group^[24] reported about a 36% loss in PL intensity, 41 meV red shift and more than 30% spectrum broadening in a single, permittivity-engineered type II tailored-nanoparticle at room temperature in an electric field of 400 kV/cm. Here, in our case, a PL decrease of ~18% in the maximum electric field of 264 kV/cm is roughly consistent with the previous results. In contrast to PL quenching, emission spectra do not exhibit any significant diffusion with increasing electric field: the red-shift and broadening of PL spectrum are less than 2 nm (~ 6 meV) at the maximum electric field of 264 kV/cm. We should note that at room temperature, the local traps and excitons are much easier to be filled and charged, causing confined potential fluctuation and resulting in weaker QCSE^[24]. Besides the weak QCSE, the charging effect of CQDs in our device could be another factor for the observed phenomena: the enhanced non-radiative Auger recombination rates in charged CQDs causes a remarkable PL quenching; the electrostatic interaction among multiple charges (negative trion) leads to a slight PL red-shift; the inhomogeneous charging of CQDs contributes to small PL broadening. The PL broadening effect might also be attributed to sinusoidal sweeping of the applied electric field across the CQD layer.

5.2.2 Electric field dependent amplified spontaneous emission

Figure 5.4 Edge emission as a function of pump fluence without electric field under 500 ps laser pulse excitation (532 nm). (a) Emission spectra. (b) The 2d spectra map normalized by the peak ASE intensity at the maximum pump fluence to show the intensity increase of ASE peak. (c) The 2d spectra map normalized by the peak intensity at each pump fluence to show the narrowing effect of ASE peak. (d) Integrated emission intensity

(log-log plotting) and the FWHM of emission profile (semi-log plotting) as a function of pump fluence. (e) The peak wavelength of ASE as a function of pump fluence. The emission spectra were measured at different pump fluences (from $270 \mu\text{J}/\text{cm}^2$ to $1605 \mu\text{J}/\text{cm}^2$). In the device, with the two dielectric layers as spacers from two electrodes, our CQD film's emission was not quenched and its optical gain is excellent. If pump fluences are beyond threshold, we can see a shoulder appearing at $\sim 640 \text{ nm}$, which indicates the start of ASE. As presented in **Figure 5.4b** and **5.4c**, the large reduction in the FWHM and sudden increase in the peak intensity of the edge emission also provide a strong evidence of transition from spontaneous emission to ASE. The signature of biexciton gain is observed with red-shift of ASE peak from spontaneous emission peak (**Figure 5.4e**). The threshold extracted from the log-log fitting of the light input-light output curve is $\sim 891 \mu\text{J}/\text{cm}^2$, which is higher than the value in previous reports²⁷ (threshold of CdSe/CdS/ZnS CQDs is $\sim 600 \mu\text{J}/\text{cm}^2$, corresponding $\langle N \rangle$ is ~ 1.9 , pump by femtosecond pulse laser, 480 nm). To get more insights, we also pumped our CQDs with 100 fs laser pulse excitation (400 nm), the extracted threshold is $\sim 53 \mu\text{J}/\text{cm}^2$, corresponding $\langle N \rangle$ is 1.29 , suggesting the good performance of our CQDs in terms of optical gain.

With increasing optical pump fluence across our device under zero electric field, a remarkable reduction in the FWHM and sudden increase in the integrated intensity of the edge emission show a clear transition from spontaneous emission to ASE (see **Figure 5.4**). The ASE peak has a red shift of $\sim 3.4 \text{ nm}$ compared to spontaneous emission peak when the pump fluence increases from 270 to $1605 \mu\text{J}/\text{cm}^2$ as expected from biexcitonic gain in our CQDs.

The ASE threshold is around $890 \mu\text{J}/\text{cm}^2$, which is higher than the previously reported threshold (27) for CdSe/CdS/ZnS CQDs ($\sim 600 \mu\text{J}/\text{cm}^2$, when pumped by a femtosecond pulse laser). Three effects here are possibly responsible for the increased ASE threshold: (i) The multiple layers can cause the pump fluence reduction because of the reflection and scattering at each layer and their interfaces. (ii) Compared with the femtosecond laser, our 0.5 ns pulsed laser pump has to compete with very fast non-radiative Auger recombination to build up the population inversion. (iii) The significant reduction of CQD absorption at our pumping wavelength (532 nm) when compared to that at the femtosecond pump wavelength (480 nm), as seen in **Figure 5.5a**.

Figure 5.5 Electric field dependent ASE characteristics. (a) Emission spectra as a function of electric field with the pump fluence of $1605 \mu\text{J}/\text{cm}^2$, indicating the ‘increases first and decreases later’ trend of the emission intensity. (b) The 2D spectra map normalized by the maximum peak ASE intensity, the maximum peak intensity is occurred in an electric field of ~ 20 kV/cm. (c) The peak wavelength of ASE as a function of electric field, the stimulated emission peaks exhibit a blue shift of ~ 1.2 nm under the maximum electric field of 264 kV/cm. The solid line is guide to the eye. (d) Integrated emission intensity (log-log plotting) and the FWHM of emission profile (semi-log plotting) as a function of electric field. Turning point of the integrated emission intensity and the FWHM implies different dominant recombination process as electric field increases. (e) The 2D spectra map normalized by the peak ASE intensity at each electric field, showing spectrum width reduces first and increases afterwards. (f) Light input-light output curves with increasing electric field. The straight lines are guides to the eyes. It shows clear evidence of controlling and tuning the ASE by electric field.

Here, we explore electric field dependent ASE at a pump fluence of $1605 \mu\text{J}/\text{cm}^2$, which can show the dominant stimulated emission and will not cause thermal degradation of the device.

The stimulated emission spectra as a function of the electric field is presented in **Figure 5.5a**. The increasing electric field leads to a continuous enhancement in the stimulated emission intensity (**Figure 5.5b**), which is predicted for charged CQDs (see the charge injection mechanism in **Appendix 2.2**) as it is easier for them to achieve population inversion.

Meanwhile, the ASE peaks exhibit a blue shift of ~ 1.2 nm (see **Figure 5.5c**) when the electric field increases from 0 to 264 kV/cm. The blue shift in the spectrum, together with the intensity enhancement of ASE, indicates contradicting behaviours associated with the QCSE, implying the dominant charging effect in our CQD device. The blue shift in ASE implies lower reabsorption along the stripe waveguide due to the occupied state in the conduction band by extra electrons. However, the increase of ASE intensity is only true when the electric field is low. As the applied electric field exceeds a certain value, the behaviour of stimulated emission goes to an opposite direction.

It is clearly shown in **Figure 5.5d**, at the turning point of ~ 20.13 kV/cm, we observe a reversed knee behaviour in the integrated ASE intensity versus the applied electric field. It is akin to the ASE's pumping threshold extracted from the light input–light output curve^[28], here we name it as the 'E-field threshold'. Below the E-field threshold, the FWHM of the stimulated emission is narrower and the intensity of the stimulated emission is enhanced as the electric field increases (shown in **Figure 5.5b** and **5.5e**). Beyond the E-field threshold, the ASE intensity decreases exponentially as the electric field increases, as shown by the fit to the experimental data in **Figure 5.5d**. At the electric field of 264 kV/cm, the FWHM increases to ~ 33.3 nm, which is close to that of spontaneous emission (~ 35 nm) of the CQD films.

As shown in **Figure 5.5d**, we have achieved $\sim 10\%$ reduction in the ASE threshold by applying electric field, which is far from the theoretical calculation: $\sim 40\%$ threshold reduction is expected for singly charged CQDs and the zero threshold is predicted for doubly charged

CQDs^[7]. However, it should be noted that the theoretical calculation for the threshold is only for population inversion or the optical transparency of the materials while the ASE threshold can be only achieved with the net gain where the optical gain dominates all the optical loss. One can probe the optical transparency of the material with transient absorption experiment, might not achieve ASE due to low gain coefficient and large optical loss^[29]. Nevertheless, this behaviour of first increasing and then decreasing threshold in our device with respect to electric field implies multiple competing mechanisms. This leads us to delve into the electric field induced spectroscopy in greater depth and figure out the dominant recombination processes with respect to different electric field.

5.2.3 Competing mechanism in CQDs under varied electric field

Quantifying the bleaching of the absorbance features can shed light on the occupied states in the conduction band of CQDs and give us more information about the on-going transition processes. Here, we calculate the absorbance spectra from measuring electric field dependent reflectance spectra of our device under different electric fields (see related equations, measurement setup and data in **Appendix 2.3**). As illustrated in **Figure 5.6a**, the increase of the applied electric field results in progressively reducing in the amplitude of the first and second excitonic absorbance peaks. We also notice that the absorbance at the pumping wavelength (532 nm) is enhanced slightly as electric field increases due to the reduced energy required for trion formation. However, at ~21 kV/cm, this enhancement (<0.3%) is negligible compared to the achieved threshold modulation (>10%), more detail is presented in **Appendix 2.4**. To be quantitative about the degree of charging (the average excess electrons per CQD, $\langle n_e \rangle$), the absorbance spectra are fitted to the sum of four Gaussians (see **Figure 5.6b**, details of the fitting is presented in **Appendix 2.4**)^{[20][30][31]}. According to the two lowest allowed interband transitions in CdSe/CdS/ZnS CQDs (inset of **Figure 5.6b**)^[31], we can assign the 1st

Gaussian peak (A1) to $1S(e)$ - $1S_{3/2}(h)$ transition and the 2nd Gaussian peak (A2) to $1S(e)$ - $2S_{3/2}(h)$ transition.

Figure 5.6 Quantifying of the charging level in CQDs. (a) Visible absorbance spectra of CQDs under different electric fields. Inset: absorbance spectra difference of the first excitonic features which is defined as the CQD absorbance under electric field subtracted by the CQD absorbance under no electric field. (b) An example of deconvolution of the absorbance spectrum into the sum of four Gaussians. Inset: the lowest three allowed interband transitions of CQDs. (c) Normalized integrated area of A1 and A2 as a function of electric field, suggesting the electron occupation of the $1S(e)$ state of the conduction band. Inset: Relationship between the relative bleach of the 1st and the 2nd transition, the solid line with the slope of ~ 1.05 is the linear fitting of the data ($A1^0$, $A2^0$ denote A1 and A2 under no electric field, respectively). (d) Average electron number per CQD, $\langle n_e \rangle$, with respect to electric field. The red circles are $\langle n_e \rangle$ extracted from the absorbance bleach of the $1S(e)$ - $1S_{3/2}(h)$ transition via Gaussian deconvolution. The blue squares are $\langle n_e \rangle$ calculated from the integrated absorbance difference which is normalized by the maximum $\langle n_e \rangle$ obtained by Gaussian deconvolution. The solid line shows the linear fitting to the data, the turning point (21.22 kV/cm) is consistent with the e -field threshold (20.13 kV/cm) defined in **Figure 5.5**.

Thus $\langle n_e \rangle$ can be estimated from the reduction of the integrated area of each Gaussian fitting providing that a 100% bleaching corresponds to two excess electrons occupied 1S(e) state in the conduction band^{[20][32]}. A plot of the integrated area of A1 and A2 as a function of the applied electric field (**Figure 5.6c**) indicates that bleaching of the 1S(e)-1S_{3/2}(h) and 1S(e)-2S_{3/2}(h) almost changes at the same pace with the increase of electric field.

Specifically, the decrease of the integrated area of A2 ($-\Delta A2/A2^0$) versus the decrease of the integrated area of A1 ($-\Delta A1/A1^0$) can be well fitted by the line with a slope of ~ 1.05 (inset of **Figure 5.6c**). The result suggests that 1S(e)-1S_{3/2}(h) and 1S(e)-2S_{3/2}(h) transitions have the same absorption strength^[30] and show the same degree of bleaching in the absorption spectra when applying electric field because the single state 1S(e) involves in both transitions. However, when the E-field is high (> 200 kV/cm), the $-\Delta A2/A2^0$ increases slower than $-\Delta A1/A1^0$, implying more absorption strength reduction for 1S(e)-1S_{3/2}(h) than 1S(e)-2S_{3/2}(h). Meanwhile, the integrated areas of other two Gaussian curves, A3 and A4 (**Figure 5.7**) remain virtually unchanged with respect to the applied electric field, implying that no excess electrons can be induced in the states beyond 1S(e) with electric field up to 264 kV/cm.

Figure 5.7 The integrated area of A3 as a function of electric field.

We adopt two ways to calculate $\langle n_e \rangle$. One method is based on extracting $\langle n_e \rangle$ from the first Gaussian fitting of the absorbance spectra. Another way is to calculate $\langle n_e \rangle$ by integrating the absorbance difference (inset of **Figure 5.6a**). As shown in **Figure 5.6d**, they are consistent with each other. Up to the electric field of 264 kV/cm, we find a maximum $\langle n_e \rangle$ of ~ 0.35 . According to the previous reports about photochemical charging^[20], there is a linear correlation between $\langle n_e \rangle$ and the amount of hole quenchers, while it is also true for electrochemical charging where $\langle n_e \rangle$ varies linearly with the charges flowing into the CQDs^[32]. Here, linear relationship between $\langle n_e \rangle$ and applied electric field is still valid in our case. However, $\langle n_e \rangle$ increases at different rates in the low and high regimes of electric field. A reasonable explanation for this observation is the different charging levels for a portion of CQDs in the thick film. Though $\langle n_e \rangle$ is only 0.35, the charges are likely distributed to the CQDs at the interfaces with other dielectric materials (SiO₂ and PVP) while the measured absorbance bleaching is the average effect of the ensemble CQDs. Hence, the turning point in the electric field of ~ 21 kV/cm is the indication that singly negative charged CQDs are starting to become doubly negative charged CQDs. Due to the Coulomb repulsion effect, it is more difficult for the electric field to induce one more electron to singly charged CQDs compared with the neutral ones. The electric field value of ~ 21 kV/cm matches the E-field threshold that we discussed in **Figure 5.5**, signifying that singly charged and doubly charged CQDs should be responsible for the E-field threshold behavior of ‘first increasing and then decreasing’ ASE intensity.

To further verify the validity of the electric field induced charging process in CQDs, we analyze the effect of the applied electric field on photoluminescence dynamics. Different processes associated with different physical properties of CQDs can be distinguished via the time-resolved PL (trPL) analysis if their decay rates are different.

Figure 5.8 Evolution of decay lifetime in CQDs with respect to the applied electric field. **(a)** Time-resolved PL decays with increasing electric fields. Dots are the experimental results and solid lines are the fitting curves. The dark yellow decay curve is the result of bare CQD film on glass without electric field while the black one is the decay of CQD film in the device structure without electric field. **(b)** Lifetimes as a function of the electric field extracted from the fitting of the decay curves with three exponential components. X , X^{1-} , and X^{2-} denote the neutral CQDs, singly charged CQDs, and doubly charged CQDs, respectively. Inset: Normalized population of X , X^{1-} and X^{2-} as a function of the electric field. **(c)** Compare average charge per CQD, $\langle n_e \rangle$, extracted from absorption spectra and PL decays. The consistence here supports our previous explanations in **Figure 5.5** and **Figure 5.6**. **(d)** The Auger and radiative lifetimes of different electron-hole states. XX denotes biexciton of neutral CQDs. The biexciton lifetime used here is cited from Ref 33 for a similar CQD structure. In our device structure, Auger lifetime of biexciton is quite close to Auger lifetime of doubly charged trion (0.75 ns compared with 0.79 ns).

More importantly, the radiative lifetime value inferred from the trPL measurement can elucidate the question in **Figure 5.1** about the dominant factor causing the reduction of spontaneous emission intensity: whether QCSE or charging effect dominates in CQDs. The two factors affect the spontaneous emission in different ways: QCSE weakens the radiative recombination^[23] whereas trions, on one hand, enhance radiative process compared with neutral exciton^[13] and, on the other hand, introduce non-radiative Auger recombination.

Figure 5.8a shows the PL decay of CQD film measured under different electric fields. All the data are measured with the same collection time and then normalized by the maximum intensity of CQD film without electric field. Hence, the results allow us to extract not only the decay rates but also the relative intensity among different electric fields at any decay time. Without electric field, the single-exponential decay process for CQD film (lifetime: ~20.1 ns) in the device structure is slightly faster than that for a bare CQD film on glass (lifetime: ~25 ns) due to the different dielectric environments^[7,13]. We notice that the PL signal at early time increases relative to that in neutral CQDs. This phenomenon results from the enhanced radiative process in charged CQDs and supports the argument that charging effect instead of QCSE is responsible for the spectroscopy changes. However, time-integrated PL still shows the intensity reduction with the increasing electric field due to the Auger process caused by extra electron. As electric field increases, both enhanced radiative recombination and Auger process are responsible for trPL to become continuously faster.

To develop more insight, we fit each decay curve to extract the dynamics with different electric fields (solid lines in **Figure 5.8a**). With increasing electric fields, two new fast decay components appear. As illustrated in **Figure 5.8b**, these two fast decay components (4.1 ns and 0.75 ns) are well correlated with the singly charged exciton lifetime (5 ns) and doubly charged exciton lifetime (2 ns) measured in single quasi type II CQD for blinking study^[33]. Slightly faster decay in our sample compared to ref.33 is understandable as a single CQD

normally has a longer lifetime than CQD ensemble and our CQD film experiences different dielectric environments. To eliminate other possibilities (Auger process or carrier trapping), we have conducted fluence dependent trPL to justify the lifetime assignment:

To eliminate the possibility that the fast decay is arising from other possibilities (i.e., Auger process or carrier trapping), we have performed fluence dependent lifetime measurement to check the Auger recombination process in our CQDs. Here, we utilized the femtosecond laser as the pump source (100 fs, 400 nm, the picosecond laser does not have enough power to achieve multiple excitons) and streak camera to check the carrier dynamics of the device. We calculate the $\langle N \rangle$ for each pump fluence.

Figure 5.9 Fluence dependent lifetime probe at peak wavelength. (a) The decay traces. (b) Fitting result.

As it can be seen in **Figure 5.9a**, when the fluence is low (exciton per quantum dot: $\langle N \rangle$ is smaller than 0.1), the PL decay can be fitted by a mono-exponential decay function with a lifetime of ~ 20 ns. As the fluence is furtherly increased, we start to observe the build-up of a faster decay component, which is attributed to the decay of the multiexciton where the non-radiative Auger recombination can be resolved^[27]. Specifically, when the fluence is 50 uJ/cm^2 ($\langle N \rangle \sim 1.21$), 34% of the CQDs have multiple-excitons corresponding to the Poisson distribution, the lifetime of the fast decay component is 600 ± 1 ps. This fast decay is quite different from the fast decay component (~ 750 ps) observed in our device when electric field

is applied. This could be the evidence that the fast decay in our device with electric field is not caused by Auger process. It is worth to note that we cannot increase the fluence further since the ASE threshold is $\sim 53 \mu\text{J}/\text{cm}^2$, after which the decay process is dominated by ASE. Then, we can calculate the Auger lifetime using the following equation^{7,43}:

$$\tau_{AR}^{-1} = \tau_{XX}^{-1} - 4\tau_X^{-1}$$

Where $4\tau_X^{-1}$ is the radiative recombination rate of the biexciton, and the factor 4 indicates the number of recombination channel of the biexciton. The extracted Auger lifetime of biexciton in our CQDs is 730 ± 47 ps, which is agreeable with the biexciton Auger lifetime (~ 750 ps) of CdSe/CdS/ZnS CQDs in ref. 35 and slightly faster than the Auger lifetime (~ 1.25 ns) of CdSe/CdS reported in ref. 43. Furthermore, the slower lifetime component, corresponding to the radiative decay, is also slightly accelerated (~ 18.9 ns) compared to the case at low pump fluence due to the multiple exciton radiative enhancement^[31].

Another possibility which can change the decay trace is the trapping process, as claimed in a blinking study^[34]. This process can also be ignored in our QDs because the trPL data can be fitted by a mono-exponential decay when the pump fluence is low. This means the active trap states are not observed^[31]. Moreover, the recombination of trapped carriers is a rather slow process which will give us a delay emission (> 100 ns), as reported in ref. 44, however, our lifetime decay did not show this slow component. The negligible active trap density is also consistent with the high quantum yield in CQDs.

Now, turning back to our electric field dependent trPL measurement data presented in **Figure 5.8**. The first thing we can conclude is that the lifetime changing is caused by only the applied electric field. Then, we should notice that, with increasing electric field, other two discrete fast components appear (4.1 ns and 0.75 ns), these three decay channels are quite different from one other. Moreover, the electric field changes only the amplitude ratio among these three

components. This suggests that the long-time decay originates from radiative recombination of neutral QDs, the other two faster components of the trPL are from new generated groups. The electric field only changes the population distribution not the decay process.

The two fast components (4.1 ns and 0.75 ns) in our device with E-field and low fluence ($N < 0.1$) are also distinguished from the fast decay component (biexciton decay: ~ 600 ps) when pumping at high fluence ($N > 1.2$) and without E-field. With fixed low excitation level when we conducted the measurement for our device with E-field, Auger process is negligible. Therefore, we can safely conclude that the new fast decay components are arising from the charged quantum dots. A similar discussion can also be found in ref. [1,7,21,25].

Hence, we can safely assign the lifetimes of 20.1 ns, 4.1 ns and 0.75 ns to neutral exciton, singly charged exciton and doubly charged exciton, respectively. It is important to note that these three lifetimes remain almost constant with increasing electric field, implying that electric field changes only the population of X^0 , X^{1-} and X^{2-} and furtherly confirming that a change of the integrated wavefunction overlap caused by the electric field (QCSE) is very small in our case.

From the fitting parameters of trPL, we can derive populations of X^0 , X^{1-} and X^{2-} (inset of **Figure 5.8b**) with different electric field. With low electric field, only neutral state and singly charged exciton contribute to the PL intensity dynamics. However, as electric field goes beyond a certain level (~ 21 kV/cm), the amount of X^{2-} soars up while the population of neutral CQDs remains unchanged. This trend largely agrees with the conclusion drawn from the steady-state absorbance analysis: electric field can only charge a portion ($\sim 19\%$) of the CQD populations. At the optimal electric field (~ 21 kV/cm), our device charge 17% of CQD population to lower the threshold by $\sim 10\%$.

We can perform a simple calculation to extract $\langle n_e \rangle$ ($\langle n_e \rangle = 0 \cdot X^0 + 1 \cdot X^{1-} + 2 \cdot X^{2-}$) based on the derived populations. As shown in **Figure 5.8c**, $\langle n_e \rangle$ extracted from the PL decay exhibits a good agreement with that obtained from the optical bleaching. The maximum deviation of less than 0.04 electron per CQD is acceptable considering the Gaussian deconvolution and exponential fitting process. From the standpoint of optical gain applications, we concern more about the radiative recombination and the Auger process under different conditions. We assume that neutral exciton lifetime (20.1 ns) is purely radiative based on the fact that PL of CQDs without electric field is a single exponential decay (almost a straight line in our semi-log plotting). Hence, we can deduce the radiative lifetime of X^{1-} , X^{2-} , and neutral biexciton, XX , using the relationship $\tau_{\text{radiative}} = 20.1/\alpha$ (α : the radiative enhancement factor). Statistically, α is 4 for biexciton while α is 2 for singly and doubly charged exciton. However, recent reports^[33] show that electron repulsion effect occurred in charged CQDs will result in a factor less than 2. Here we use $\alpha = 1.5$ according to the fitting results of PL dynamics using a Poisson distribution model, details are shown below^[7]:

When a CQD is charging, the extra electrons occupy the conduction band, the radiative recombination will be enhanced. We can deduce the radiative lifetime of singly charged CQDs and doubly charged CQDs using this relationship:

$$t_{\text{radiative}} = \frac{20.1}{\alpha}$$

Where 20.1 ns is the radiative lifetime of neutral exciton and α is the radiative enhancement factor. Statistically, α is 2 for singly and doubly charged exciton. However, recent reports^[7,34] show that electron repulsion effect occurred in charged CQDs results in a factor less than 2. To determine α in charged CQDs, we rescale the intensity of PL decay curves so that they all match to each other at the long-time tail (20 ns ~ 60 ns) which is the decay feature of the

neutral CQDs only. The difference between decay curve of CQDs in electric field and that of CQDs in no electric field is associated to charged CQDs.

Figure 5.10 Fitting results of the subtraction of PL dynamics at different electric field. The red solid line is the PL dynamics of neutral CQD layer. The blue solid line is the PL dynamics of CQD layer at different electric field. The curves are scaled by a ratio to match the PL decay curve of neutral CQD layer in long time range (20 ns ~ 60 ns). The black dot is the normalized subtraction of the blue line and red line. The green solid line is the fitting results using the described model.

We fit the PL dynamics using the model proposed in ref. 7. The subtracted PL dynamics can be expressed as below with consideration of a Poisson distribution for the number of neutral exciton, singly charged exciton and doubly charged exciton.

$$PL_decay_{subtracted} = \frac{\sum_{k=1}^{\infty} P(k) \times \alpha \times e^{-\frac{t}{\tau_k}}}{A_{\langle n_e \rangle} \times P(0)}$$

$$P(k) = \frac{\langle n_e \rangle^k \times e^{-\langle n_e \rangle}}{k!}$$

Where $A_{\langle n_e \rangle}$ is the scaled constant for PL decay of CQD layer when the average electron per dot is n_e , $P(k)$ is the Poisson probability when the electron number in the CQD is k , τ_k is the recombination lifetime and α is the radiative enhancement factor, respectively. Given that $\langle n_e \rangle$ in our case is less than 1 (maximum is about 0.4), we can ignore the contributions of those $k \geq 3$ components. And then plug in our measured $\langle n_e \rangle$, lifetime and we got the radiative enhancement factor $\alpha = 1.517$, to show very good fitting results of the subtracted PL decays, as shown in **Figure 5.10**.

Thus, we can calculate the Auger lifetime using following equation: $1/\tau_{total} = 1/\tau_{radiative} + 1/\tau_{Auger}$. As shown in **Figure 5.8d**, the Auger lifetime of X^{1-} is about 5.9 ns, which is much lower than the Auger process ($\sim 730 \pm 47$ ps, see **Figure 5.9**) in biexciton^[35]. However, the Auger lifetime of doubly charged exciton (~ 790 ps) is quite close to the value in neutral biexciton. Importantly, the stimulated emission rate of X^{2-} is two-fold less than the stimulated emission rate in biexciton.

5.2.4 Modelling the electric field dependent threshold

We have now quantified the lifetimes of X, XX, X^{1-} and X^{2-} by fitting the PL dynamics. Meanwhile, we know the population of each state as a function of the applied electric field

obtained by analysis the trPL and absorbance bleaching data. Therefore, we can apply the rate equations to evaluate the ASE threshold with different electric fields. The model we use here is based on the recent calculations for optical gain, which considers both the Auger process and optical cavity losses^[36-38].

Figure 5.11 Modelling of the ASE threshold using the kinetic equations and experimental parameter inputs. (a) Schematics of the ASE process in neutral and charged CQDs. Blue hollow circles represent holes in the valence band. Black solid circles represent photo-generated electrons while red solid circles denote excess electrons induced by the electric field. XX, X¹⁻ and X²⁻ are the same denotations as previously described in **Figure 5.8**. (b-c) The emission intensity decay map normalized by the peak value of the photon density under each electric field at the pump fluence of 800 μJ/cm² and 1000 μJ/cm², respectively. At 800 μJ/cm², the abrupt acceleration of emission (ASE) only occurs under the e-field threshold (20.13 kV/cm). The white dash line locates at the e-field threshold. At 1000 μJ/cm², the ASE can be observed under the electric field smaller than 149.2 kV/cm (white dash line). (d) Integrated photon density (log scale) map as a function of both the applied electric field (linear scale) and the pump fluence (log scale), the white dash line indicates the e-field threshold and the blue dash line indicates the threshold behavior under different electric fields. (e) Simulated and experimental ASE threshold behavior as a function of the applied electric field.

We adopt the rate equations for neutral and singly/doubly charged CQDs and plug in the electric field dependent population distribution and all the recombination rates to complete our model. See the detailed parameters, transition processes, rate equations and simulated dynamics are presented in detail in **Appendix 2.5**.

Figure 511a shows a cartoon of the stimulated emission process in neutral, singly and doubly charged CQDs, respectively. In neutral CQDs, biexciton is required for population inversion, which is harder to achieve but provides better gain coefficient. Singly charged CQDs lower the requirement for population inversion due to the pre-existing electron in the conduction band. For X^{2-} , the doubly charged CQDs are transparent and achieve population inversion with any excitation level. However, the enhanced Auger recombination (compared with singly charged CQDs) and less efficient radiative recombination (compared with biexciton) deplete the exciton very fast. This affects the optical gain in two ways: fewer emission photons to trigger stimulated emission and fewer excitons to contribute to stimulated emission. One can experimentally show negative absorption (population inversion) in transient absorption measurement at very low pumping level but the demonstration of ASE where the gain has to overcome various losses is very challenging^[29]. In addition, obtaining the net gain out of the doubly charged CQDs is more difficult with our sub-nanosecond pumping source due to very short gain lifetime, governed by dominant non-radiative Auger recombination.

Here we simulate the dynamics of emitted photon density as a function of the applied electric field under different pump fluence. As presented in **Appendix 2.5**, we only consider the photons coupling to the waveguide and participating in ASE process. Non-coupling photons (~95.5%, see the COMSOL simulation in **Appendix 2.5**) are spontaneously emitted out of the CQD film. At the pump fluence of $800 \mu\text{J}/\text{cm}^2$ (**Figure 5.11b** and **Figure 5.12a**), the abrupt acceleration of photon emission, which is the evidence of the onset of ASE, can only be achieved with the electric field around 21 kV/cm. When the electric field is too low or too

high, there is only spontaneous emission. It is consistent with the E-field threshold of ~ 20 kV/cm extracted from the electric field dependent ASE characterization (**Figure 5.5**), implying that singly charged CQDs help building up the net gain in our device. In the case of high pump fluence, $1000 \mu\text{J}/\text{cm}^2$ (**Figure 5.11c** and **Figure 5.12b**), the ASE can happen with the electric field up to ~ 149 kV/cm. This behaviour illustrates the stimulated emission process presented in **Figure 5.11a**: optimum electric field creates enough single charged CQDs and enables ASE at lower threshold while higher electric field increases the population of doubly charged CQDs and results in higher threshold for optical net gain (ASE). Our model also suggests that if a device can charge the entire CQD population with single electron, we would be able to lower the ASE threshold down to $\sim 35\%$ compared to neutral CQDs, which is slightly less than the theoretical improvement ($\sim 40\%$) for population inversion threshold^[7] due to finite loss in ASE.

Figure 5.12. The 2d emitted photon decay map under each electric field at the pump fluence of $800 \mu\text{J}/\text{cm}^2$ (a) and $1000 \mu\text{J}/\text{cm}^2$ (b). At $800 \mu\text{J}/\text{cm}^2$, the white dash line locates at the e-field threshold. At $1000 \mu\text{J}/\text{cm}^2$, the ASE can be observed under the electric field smaller than $149.2 \text{ kV}/\text{cm}$ (white dash line).

The time-integration of the emitted photon density (log scale) as a function of the applied electric field (linear scale) and pump fluence (log scale) is shown in **Figure 5.11d**. The threshold with different electric field (the dash blue line in **Figure 5.11d** and the separated

light-in-light-out curve in **Figure 5.13**) is extracted as the transition point from spontaneous emission to stimulated emission. In **Figure 5.11e**, we compare the simulated ASE threshold trend with the experimental results. With low electric field, the simulated result is in very good agreement with the ‘up and down’ threshold behaviour (**Figure 5.5**) up to electric field of ~ 200 kV/cm. At higher electric field, the simulation shows lower threshold than the experiment data. This is, in fact, understandable as our model considered only up to doubly charged CQDs, which would be only valid at low electric field. Auger recombination rate will increase faster with more extra electrons in CQDs, and therefore achieving the optical net gain is harder in the experiment.

Figure 5.13 Photon emission density as a function of pumping intensity.

5.3 Summary

In this chapter, we have demonstrated controllable and tune-able ASE in a colloidal semiconductor device, for the first time, via electric field induced charging. The contribution

of neutral, singly and doubly charged CQDs to the ASE are quantitatively determined by analyzing the competing mechanisms happening in the CQD population. Neutral CQDs need high optical pump to create biexciton, compete with fast non-radiative Auger recombination and achieve high optical gain. Singly charged CQDs can lower the optical gain threshold because of partially filled conduction band and low Auger recombination rate. Doubly charged CQDs can in principle achieve population inversion with any pumping level but achieving the net gain still requires significantly high pumping level due to enhanced non-radiative Auger recombination and low gain coefficient. Our kinetics model to simulate the ASE behavior shows very good consistence with the experimental results, highlighting the dominant role of singly charged CQDs to achieve low ASE threshold. Our conducted work demonstrates the feasibility of controlling not only exciton recombination dynamics, but also CQD charging level to lower the threshold of CQD lasing in a device structure. Our results suggest that a good control of charging process for entire CQD film will significantly improve the CQD lasers, lower the threshold to possibly enable continuous wave (CW) or electrically driven devices. Future thinking about this work will be: since our device allows us to control charge for 17% of CQD population and result in reducing the ASE threshold by 10%, a better device that allows control charge delivery to 100% CQD population could allow us to reduce ASE to theoretical value of 40%.

Appendix 1: Experimental methods

1.1 Synthesis of CdSe/CdS/ZnS CQDs

Here the recipe is a slightly modified facile one-pot method^{[1][27][34]}. An amount of 1 mmol Cadmium oxide (CdO, >99.99%), 18.85 mmol Oleic acid (OA, 90%) and 2 mmol zinc acetate (Zn(AC)₂, 99.99%) are mixed with 25 mL 1-octadecene (1-ODE, 90%) in a three-neck flask. The mixture is evacuated for 15 min and heated to 300 °C under nitrogen condition. After that,

selenium precursor made by dissolving 0.2 mmol selenium powder (Se, >99.99%) in 0.2 mmol trioctylphosphine (TOP, 90%) is quickly added into the reaction flask at 300 °C. Three minutes later, 0.3 mL dodecanethiol (DT, >98%) is injected slowly into the mixture. The reaction lasts for 20 min to get CdSe/CdS QDs. Subsequently, sulfur precursor made by dissolving 2 mmol sulfur powder (S, >99.5%) in 1 mmol TOP is added to react with the excess Cd ions and passivate the surface with ZnS shell. CdSe–CdS–ZnS (core–shell–shell) CQDs are purified with ethanol for several times and dispersed in toluene for film fabrication.

1.2 Device fabrication

Firstly, the glass substrate with ITO is patterned to yield three devices per substrate, the top two devices are with CQD film which provides redundancy in the fabrication process for testing reproducibility, while the bottom one is exactly same structure but without CQDs film which is used as for reference for steady-state absorption measurement (see details in supplementary part 3). After that, glass substrates are carefully cleaned and ultra-sonicated. Then, a SiO₂ layer with the thickness of ~160 nm is deposited via sputtering (UNIVEX 350, RF: 150 W). The CQD film is deposited by the spin-casting technique (spin duration: 3 mins, spin velocity: 500 rpm/s). Another dielectric layer is a PVP film deposited on top of the CQD film also by spin-casting (PVP dissolved in ethanol, 20 mg/mL, spin duration: 45 s, spin velocity: 2000 rpm/s). All the spin-casting processes are made inside the glove box and each spin-casting step is followed by baking the device at 60 °C in a nitrogen environment for 20 mins. Finally, the sample is loaded into a thermal evaporator to deposit the aluminium layer as the top electrode.

Appendix 2: Theoretical calculations

2.1 Determine the electric field applied on CQDs

Here, the two electrodes and the wire we used have negligible resistance compared to that of the layered device. Our capacitor device with 3 dielectric layers is equivalent to 3 capacitors in series. Using a reference capacitor^[11], we can calculate the voltage cross the CQD layer (see **Figure A1**).

Figure A1 Schematics of the circuit. Function generator model: FG500A, WAVETEK.

Here, we have a circuit with four capacitors in series:

$$\begin{aligned}
 V_{FG} &= V_{ref} + V_{SiO_2} + V_{CQD} + V_{PVP} \\
 Q_{ref} &= Q_{SiO_2} = Q_{CQD} = Q_{PVP} = V_{ref} \times C_{ref}
 \end{aligned}
 \tag{A1}$$

Then, we can derive that:

$$V_{SiO_2} = \frac{V_{ref} \times C_{ref}}{C_{SiO_2}}; V_{PVP} = \frac{V_{ref} \times C_{ref}}{C_{PVP}} \quad (A2)$$

Just plug into the voltage formula:

$$V_{CQD} = V_{FG} - V_{ref} - \frac{V_{ref} \times C_{ref}}{C_{SiO_2}} - \frac{V_{ref} \times C_{ref}}{C_{PVP}} \quad (A3)$$

Now we only need the capacitance of SiO₂ and PVP layer to calculate the voltage drop across the CQD layer. As described in method, we can calculate the capacitance using the following:

$$C = \frac{A \times \epsilon_0 \times \epsilon_r}{d} \quad (A4)$$

Where A is the area of the capacitor (8 mm * 2 mm), d is the thickness of each layer determined by the SEM measurement and supported by the surface profiler measurement (**Figure 5.1 and 5.3**) and ϵ_0 is the permittivity of vacuum and ϵ_r is the relative permittivity of each dielectric film.

Figure A3 Permittivity measurement result. (a) Fitting result of SiO₂ film. (b) n and k of SiO₂ film. (c) Fitting result of PVP film. (d) n and k of PVP film.

Relative permittivity is measured using an ellipsometer (VASE, J.A. Woollam, spectral range from 193 nm to 3200 nm) and the results are shown in **Figure A2**. We can see that the refractive index does not change too much in the visible wavelength range. Here we adopt the average refractive index (SiO₂: 1.48, PVP: 1.53) at the visible spectrum to approximate the materials' permittivity at very low frequency. Finally, we can calculate the electric field applied on the CQD film in the device from the voltage and the thickness of this layer.

Considering we utilized the average refractive index to evaluate the capacitance of the insulator layers, combining with the measurement error, it is essential to calibrate the voltage drop across the CQD layer. Here, we have fabricated the capacitor without CQD layer (the SEM picture of the structure is shown in **Figure A4a**, the thickness of these two insulator layers are the same compared to the device used in the **Figure 5.1c**). Firstly, we will use the calculated capacitance of SiO₂ layer to extract the voltage drop across the PVP layer. Then, we will use the calculated capacitance of PVP layer to extract the voltage drop across the SiO₂ layer. Since the equality of the charge of each capacitor is always true in a serial capacitor circuit, if the charge stored in SiO₂ layer ($Q = C \cdot V$, C is calculated via the thickness and permittivity of SiO₂, V is extracted using the capacitance of PVP) is equal to (in an acceptable way) the charged is stored in PVP layer ($Q = C \cdot V$, C is calculated via the thickness and permittivity of PVP, V is extracted using the capacitance of SiO₂), then we can conclude that our method should be reliable. The result is shown in **Figure A4b**, we can see that the deviation between the charges stored in these two layers is acceptable.

$$\begin{aligned}
 V_{applied} &= V_{ref} + V_{SiO_2} + V_{PVP} \\
 V_{SiO_2} &= V_{applied} - V_{ref} - V_{ref} \times \frac{C_{ref}}{C_{PVP}} \\
 V_{PVP} &= V_{applied} - V_{ref} - V_{ref} \times \frac{C_{ref}}{C_{SiO_2}} \\
 V_{PVP} \times C_{PVP} &\stackrel{?}{=} V_{SiO_2} \times C_{SiO_2}
 \end{aligned} \tag{A5}$$

Figure A4 Mutual corroboration to calibrate the voltage drop. (a) The SEM image of the device without CQD layer. (b) The Charge stored in SiO₂ and PVP layer. The slope of the black line is 1. The slope of the blue line is 1.1. The slope of the green line is 0.95.

2.2 The mechanism of electron injection

The energy level schematic of the device is shown in **Figure A5**. As it can be seen, compared to the LED device, the electrons and holes can't be directly injected into the QDs due to the two high energy barriers (SiO₂ and PVP layer). The main reason for us to choose the capacitor structure is that these two insulator layers can avoid CQDs being directly adjacent to electrodes (causing emission quench) and limits the electrical current to allow us to charge the CQDs controllably. Worth to mention that, we did not choose the CQDs sandwiched by two SiO₂ layers, as did in ref. 11, because the sputtering process can greatly degrade the optical gain performance of CQDs. For spontaneous emission, the emission degradation is less important, thus this will not be an issue for the authors of ref. 11. Here, we spin-casted the PVP polymer as another insulator layer.

Figure A5 The energy schematic of the device. The energy level values for CdSe/CdS/ZnS QDs are obtained from ref. 27. The energy level values for ITO and Al are taken from ref. 39. The energy level value for SiO₂ is taken from ref. 11. The energy level value for PVP is obtained from ref. 40.

In the device (a Sawyer–Tower circuit), capacitors in series share the charge that moved between them^[11]. When electric field was applied, the electrons/holes were accumulated at the interface of insulator/CQDs. There's a probability for them to tunnel into the CQDs. However, in quasi-type II CQDs, the energy barrier for electrons and holes are quite different (the hole wave function is well-confined in the core, while the electron wave function is delocalized over the whole core/shell/shell structure). Meanwhile, the effective mass of electron ($m_e^* = 0.13m_0$) in CdSe is much smaller than the effective mass of hole ($m_h^* = 0.3m_0$)^[42]. We can use the following equation^[41] to roughly estimate the tunnelling efficiency of electrons and holes:

$$T = \left\{ 1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16 \frac{E}{V} (1 - \frac{E}{V})} \right\}^{-1} \quad (\text{A6})$$

$$\kappa = \sqrt{\frac{2m^*}{\hbar^2} (V - E)}$$

Where E is electron or hole energy, V is the height of the energy barrier, L is the width of the barrier. For electrons, the wave function is spreading through the core and shells so the barrier width is very small (smaller than ZnS shell thickness of ~ 1.3 nm due to the delocalization). While the hole wave function is confined in the core only, the barrier width is much thicker ($\sim$ CdS/ZnS shell/shell thickness of ~ 2.5 nm). Thus, the possibility for hole tunnelling is negligible compared to that for electrons.

2.3 Steady-state absorption measurement

a. Measurement set-up

The measurement setup is shown in **Figure A6**. The white light generated by the light source (ELS-250, Asahi Spectra) was filtered by a monochromator (71SWS, spectral selection range: 330~1000 nm) and then focused onto the device from the ITO glass substrate at the angle of 45° . A silicon photodetector (Newport 2031, 400~1070 nm) was used to collect the reflection light off the device. The signal from the silicon photodetector was analysed by a lock-in amplifier (SR830, Stanford Research System). To calculate the electric field-modulated absorbance of the CQD layer only, we need to measure both the absolute reflection of the device (without electric field) and the modulated reflection when applying electric field. Here, we used an optical chopper (MC1000, THORLABS) to modulate the illumination light when no electric field was applied.

By chopping the light, we can measure light intensity precisely with lock-in technique, therefore reflectivity can be calculated correctly as many commercial instruments do. After that, the lock-in technique (locked to bias modulation frequency) does not measure the reflection anymore, it measures the amplitude of reflectivity change directly when electric field is applied.

Figure A6 The measurement set-up for electric field dependent absorbance. **(a)** The set-up for measurement of steady state absorbance. The chopper synced signal was used as the lock-in reference. **(b)** The set-up for measurement of absorption modulation under AC electric field. The synced signal from function generator was used as the lock-in reference.

b. Optical bleaching calculation

Figure A7 Measuring the transmittance of CQD layer. (a) Lock-in voltages with the light modulated by the optical chopper. (b) The calculated transmittance (blue dots) and fitting result (red solid line). (c) The spectrum of light source. The inset is the zoom-in of low energy tail. (d) The intensity fluctuation which is divided by the averaged value.

The first step is to figure out the absorbance (or transmittance) of CQD film in the device structure without electric field. As we mention in the device fabrication process (methods), we had two different sets of samples (device) on the same substrate. One was with the CQD layer, another one was without the CQD layer. Basically, we used an optical chopper to modulate the illumination light and measured the lock-in voltage for two different structures without electric field (**Figure A7a**).

Then we can calculate the absorbance of CQD layer using the following:

$$\begin{aligned} V_{without_CQDs}^{chop} &= K_1 \times I(\lambda) \times R(\lambda)_{without_CQDs}^0 \\ V_{with_CQDs}^{chop} &= K_2 \times I(\lambda) \times R(\lambda)_{with_CQDs}^0 \end{aligned} \quad (A7)$$

Where, $I(\lambda)$ is the wavelength dependent light intensity of the white light source. K_1 and K_2 is the experimental coefficient which takes care all the correction for experimental setup and equipment response such as the optical alignment or detector gain setting. $R(\lambda)^0$ is the reflectance for each case.

Considering the only difference between two cases is the CQD layer, then we can have this relationship:

$$R(\lambda)_{with_CQDs}^0 = T(\lambda)_{CQDs}^0 \times R(\lambda)_{without_CQDs}^0 \quad (A8)$$

Where, $T(\lambda)_{CQD}^0$ is the transmittance of CQD layer without electric field. The light is passing through the CQD layer twice when it reflects off the Al electrode. Here, in the reflection measurement, $T(\lambda)_{CQD}^0$ represents the equivalent transmittance of the CQD layer in the reflection measurement. Then, we can have this relationship via combining these two equations:

$$T(\lambda)_{CQDs}^0 = \frac{R(\lambda)_{with_CQDs}^0}{R(\lambda)_{without_CQDs}^0} = \frac{K_2}{K_1} \times \frac{V_{with_CQDs}^{chop}}{V_{without_CQDs}^{chop}} \quad (A9)$$

Now our task becomes finding out the value of K_2/K_1 . It is always true that our CQD layer does not absorb light beyond 660 nm, so we just need to find the ratio that makes the two lock-in voltage overlapping to the maximum extent beyond 660 nm. Here the ratio in our case is 1.437, as shown in **Figure A7a**. Then, we conduct the fitting (**Figure A7b**) and convert transmittance to absorbance.

We notice that, in **Figure A7b**, variations in the 670-700 nm range is large. We measure the spectra of the light source for 5 times shown in **Figure A7c**, as it can be seen, there are two low intensity spikes (around 420 nm and 452 nm) and one low intensity tail (beyond 660 nm). When the light intensity is low, the signal to noise ratio (SNR) is low as we can see the larger measured intensity fluctuation at long wavelength ($> 5\%$, as shown in **Figure A7d**). This variation will have a negligible effect on our interpretation. The reasons are as following: (1) When the wavelength is longer than 660 nm, the absorbance of CdSe/CdS/ZnS QDs is infinitely close to zero; (2) For the interested wavelength range (460~650 nm), the intensity variation is acceptable ($< 2\%$), and we can well-fit the transmission by choosing a proper ratio and the two absorption feature ($1S(e)-1S_{3/2}(h)$ and $1S(e)-2S_{3/2}(h)$ transitions) can be well-resolved.

After we get the absorbance of CQD layer without electric field, we need to measure how the photodetector signal is modulated by the applied AC electric field. Using the measurement set-up shown in Fig. S8b, we plot the lock-in voltage as a function of wavelength under different electric fields without CQD layer and with CQD layer in **Figure A8a and A8b**, respectively. We can connect the lock-in voltage with reflectance using following:

$$\begin{aligned} V_{without_CQDs}^E &= K_1 \times I(\lambda) \times \Delta R(\lambda)_{without_CQDs} \\ V_{with_CQDs}^E &= K_2 \times I(\lambda) \times \Delta R(\lambda)_{with_CQDs} \end{aligned} \quad (A10)$$

Here $I(\lambda)$, K_1 and K_2 are the same values as we described previously.

We observe that the device without CQD layer is also sensitive to the applied electric field (**Figure A8a**), the reason is the permittivity change of any layers in our device or control sample when electric field is applied can make this sensitivity. This is the reason why we need to have the control sample, which is identical to the real device except the CQD layer, to extract the differential transmittance of only CQD layer.

Figure A8 Steady-state absorbance measurement. (a) Lock-in voltages of the device without CQD layer versus electric field. (b) Lock-in voltages of the device with CQD layer versus electric field. (c) The calculated transmittance change at different electric field. (d) Normalized Absorbance converting from the transmittance change at different electric field and the transmittance without electric field.

Then, we still use this equation:

$$R(\lambda)_{with_CQDs}^E = T(\lambda)_{CQDs}^E \times R(\lambda)_{without_CQDs}^E \quad (A11)$$

Where, $R(\lambda)^E$ means the reflectance with electric field. Rewriting this equation, we get the following:

$$R(\lambda)_{with_CQDs}^0 + \Delta R(\lambda)_{with_CQDs} = [T(\lambda)_{CQDs}^0 + \Delta T(\lambda)_{CQDs}] \times [R(\lambda)_{without_CQDs}^0 + \Delta R(\lambda)_{without_CQDs}] \quad (A12)$$

Expanding this equation and discard the high order term ($\Delta T(\lambda)_{CQDs} * \Delta R(\lambda)_{without_CQDs}$), we get:

$$\begin{aligned}
\Delta T(\lambda)_{CQD} &= \frac{\Delta R(\lambda)_{with_CQDs} - T(\lambda)_{CQDs}^0 \times \Delta R(\lambda)_{without_CQDs}}{R(\lambda)_{without_CQDs}^0} \\
&= T(\lambda)_{CQDs}^0 \times \left(\frac{V_{with_CQDs}^E}{V_{with_CQDs}^{chop}} - \frac{V_{without_CQDs}^E}{V_{without_CQDs}^{chop}} \right)
\end{aligned} \tag{A13}$$

Note that, a square function modulation is provided by the optical chopper for the first measurement while the AC bias is a sinusoidal function for the second experiment. The lock-in technique measures the sine component at the reference frequency of the signal. According to the Fourier series of the square wave, we just modify the equation with $\pi/4$ and calculate the transmittance change (**Figure A8c**):

$$\Delta T(\lambda)_{CQDs} = T(\lambda)_{CQDs}^0 \times \frac{4}{\pi} \times \left(\frac{V_{with_CQDs}^E}{V_{with_CQDs}^{chop}} - \frac{V_{without_CQDs}^E}{V_{without_CQDs}^{chop}} \right) \tag{A14}$$

Finally, we can convert the transmittance to absorbance as shown in **Figure A8d** (**Figure 5.6a** is the zoom in plot of **Figure A8d**):

$$A(\lambda)_{CQD}^E = -\log_{10}[\Delta T(\lambda)_{CQDs} + T(\lambda)_{CQDs}^0] \tag{A15}$$

2.4 Gaussian deconvolution of absorbance data

Each absorbance spectrum is fitted by a sum of four Gaussian curves^[20]. As shown in **Figure A9**, the Gaussian curve for the shortest wavelength (A4, green solid line) is fixed for all absorbance spectra in terms of the magnitude, position and width. We only allow a small floating for the positions of two lowest energy Gaussian curves (A1, navy solid line and A2, blue solid line). The floating range of positions for A1 is from 621.5 nm to 622.5 nm and for A2 is 577 nm to 578 nm. The magnitudes and widths of A1 and A2 are allowed to float during fitting. There is no restriction for the fitting process of A3.

It is important to note that, besides the bleaching of the first and second excitonic transition, electric field will slightly increase the absorbance value at the pump wavelength (532 nm, raw

data: 0 kV/cm: 0.1246; 263.89 kV/cm: 0.1262, the increase is $\sim 1.3\%$). This observation is also reported in ref. 20 in which the CdSe CQDs are negatively charged via photo-doping. The reason for this observation is a slight redshift of the absorption spectrum (as we can see easily in PL spectrum at different E-field and also in absorption peak). This absorption redshift is tentatively attributed to the reduced energy required for trion formation in our n-doped CdSe/CdS/ZnS CQDs rather than exciton formation. Thus, this observation could be another evidence to support the electron injection in our device.

Figure A9 Gaussian fitting (red dashed line) of absorbance spectra (black solid line). (a) Four Gaussian curves to fit absorbance of the CQD layer under zero electric field. (b-d) Four Gaussian curves to fit absorbance of the CQD layer in the electric field of 12.31 kV/cm, 42.52 kV/cm, and 263.89 kV/cm, respectively.

According to the above discussion, when the pump fluence (wavelength: 532 nm) is fixed, for larger applied electric field, the absorption cross-section will be slightly larger, and thus, the

ASE threshold could be reduced without any change in recombination dynamics. However, absorption cross-section increases by 1.3% at the maximum E field of 263.89 kV/cm; and our threshold reduction of more than 10% was achieved at very low E-field, with which the increase in absorption cross-section is negligible (when E-field is ~21 kV/cm, absorbance is 0.1250, the increase is only ~0.3%).

2.5 Kinetics model

a. Rate equations

Here, we modify the kinetic model proposed in ref. 7 and calculate the stimulated emission process in mix population of neutral and charged CQDs. **Figure A10** shows the transition processes which are responsible for stimulated emission. In neutral CQDs, we need biexciton to achieve the population inversion. For singly charged CQDs, the transitions involved in stimulated emission are only between $|X^{1-}\rangle$ and $|GS\rangle$. For doubly charged CQDs, due to the optical transparency, the transition involved in optical gain calculates are only $|X^{2-}\rangle$ to $|GS\rangle$ stimulated emission. All the multiple-exciton states in singly or doubly charged CQDs will non-radiatively recombine very fast and we consider them having no contribution to the process.

Figure A10. Optical transition processes in neutral CQDs (X), singly charged CQDs (X^{1-}) and doubly charged CQDs (X^{2-}). $|GS\rangle$ means the ground state.

We now consider the CQDs in our device under different electric field which is converted to charged CQD population in our model. Besides those transitions involved in the stimulated

emission, we take the waveguide photon losses, decay of exciton/biexciton and pumping laser into consideration and get the rate equations.

$$\begin{aligned}
\frac{dP_{GS,0}}{dt} &= \frac{P_{ex,0}P_{ph}}{\tau_{sti}} + \frac{P_{ex,0}}{\tau_{ex,0}} - \frac{4P_{GS,0}P_{ph}}{\tau_{sti}} - P_{GS,0}R_{pump} \\
\frac{dP_{GS,1}}{dt} &= \frac{2P_{ex,1}P_{ph}}{\tau_{sti}} + \frac{P_{ex,1}}{\tau_{ex,1}} - \frac{2P_{GS,1}P_{ph}}{\tau_{sti}} - P_{GS,1}R_{pump} \\
\frac{dP_{GS,2}}{dt} &= \frac{2P_{ex,2}P_{ph}}{\tau_{sti}} + \frac{P_{ex,2}}{\tau_{ex,2}} - P_{GS,2}R_{pump} \\
\frac{dP_{ex,0}}{dt} &= \frac{P_{biex,0}}{\tau_{biex,0}} - \frac{P_{ex,0}}{\tau_{ex,0}} + \frac{4P_{GS,0}P_{ph}}{\tau_{sti}} - \frac{P_{ex,0}P_{ph}}{\tau_{sti}} + \frac{4P_{biex,0}P_{ph}}{\tau_{sti}} + P_{GS,0}R_{pump} - P_{ex,0}R_{pump} \\
\frac{dP_{ex,1}}{dt} &= -\frac{P_{ex,1}}{\tau_{ex,1}} + \frac{2P_{GS,1}P_{ph}}{\tau_{sti}} - \frac{2P_{ex,1}P_{ph}}{\tau_{sti}} + P_{GS,1}R_{pump} \\
\frac{dP_{ex,2}}{dt} &= -\frac{P_{ex,2}}{\tau_{ex,2}} - \frac{2P_{ex,2}P_{ph}}{\tau_{sti}} + P_{GS,2}R_{pump} \\
\frac{dP_{biex,0}}{dt} &= -\frac{P_{biex,0}}{\tau_{biex,0}} + \frac{P_{ex,0}P_{ph}}{\tau_{sti}} - \frac{4P_{biex,0}P_{ph}}{\tau_{sti}} + P_{ex,0}R_{pump} \\
\frac{dP_{ph}}{dt} &= -\frac{P_{ph}}{\tau_c} + \frac{4P_{biex,0}P_{ph}}{\tau_{sti}} - \frac{4P_{GS,0}P_{ph}}{\tau_{sti}} + \frac{P_{ex,0}\gamma}{\tau_{ex,0}} + \frac{P_{biex,0}\gamma}{\tau_{biex,r,0}} + \frac{2P_{ex,1}P_{ph}}{\tau_{sti}} - \frac{2P_{GS,1}P_{ph}}{\tau_{sti}} + \frac{P_{ex,1}\gamma}{\tau_{ex,r,1}} + \frac{2P_{ex,2}P_{ph}}{\tau_{sti}} + \frac{P_{ex,2}\gamma}{\tau_{ex,r,2}}
\end{aligned} \tag{A16}$$

Where P_{ph} is the photon density, τ_{sti} is the lifetime of stimulated absorption/emission, R_{pump} is the exciton pumping rate (proportional to the laser pump intensity), τ_c is the lifetime of cavity photons which represents all the potential losses for waveguide-coupling photons in our model. $P_{GS,0}$, $P_{GS,1}$ and $P_{GS,2}$ are the unexcited population fraction of neutral, singly and doubly charged CQDs, respectively. $P_{ex,0}$, $P_{ex,1}$ and $P_{ex,2}$ are the exciton population fraction of neutral, singly and doubly charged CQDs, respectively. $P_{biex,0}$ is the biexciton population fraction of neutral CQDs. $\tau_{ex,0}$, $\tau_{ex,1}$ and $\tau_{ex,2}$ are the exciton lifetime of neutral, singly and doubly charged CQDs, respectively. $\tau_{ex,r,1}$ and $\tau_{ex,r,2}$ are the radiative lifetime of biexciton in singly charged and doubly charged CQDs, respectively. $\tau_{biex,0}$ are the biexciton lifetime in neutral CQDs and $\tau_{biex,r}$ is the radiative lifetime of biexciton in neutral CQDs.

Figure A11 COMSOL simulation to determine the coupling efficiency. (a) The In-plane dipole inside the capacitor structure. (b) Calculated electric field distribution of the In-plane dipole. (c) The Out-plane dipole inside the capacitor structure. (d) Calculated electric field distribution of the Out-plane dipole.

Considering the direction of spontaneous emission is random and not all the spontaneous emission photons can contribute to the stimulated emission, γ is the coupling efficiency defined as the fraction of spontaneous emission photons which are coupled into the waveguide. COMSOL simulation is performed to determine the coupling efficiency, as shown in **Figure A11**. Basically, we put the dipole oscillating in Y direction (In-plane dipole, in **Figure A11a**) and Z direction (Out-plane dipole, in **Figure A11b**) inside the capacitor structure, and monitor the energy propagated along the Y direction (edge emission). A coupling efficiency of ~2% is

obtained for In-plane dipole and ~10% for Out-plane dipole as shown in the electric field distribution **Figure A11b**. According to R. Scott's works^[53], the population fraction in CdSe CQDs of In-plane dipole is 68% while for Out-plane dipole is 32%. Hence, we adopt the coupling efficiency of ~4.5% in our calculation.

All these three groups of rate equations are based on the following assumptions:

- (1) The exciton pumping rate are the same for all three cases. This is reasonable because the excitation photon is at high energy compared to band gap, so the absorption is not affected by charges in the CQDs which are at the band edge.
- (2) We do not consider the interaction among CQDs.
- (3) We do not consider the contributions from multiple excitons (≥ 3 for neutral CQD and ≥ 2 for charged CQDs) as they do not directly contribute to stimulated emission at the band edge and the enhanced Auger process will make them non-radiatively recombined significantly fast.

Below we list the initial conditions used for calculation:

- (1) when $t = 0$, the value of $P_{GS,0}$, $P_{GS,1}$ and $P_{GS,2}$ under different electric field used in the rate equation is from the PL dynamics analysis (main text, Fig. 4). And $P_{GS,0} + P_{GS,1} + P_{GS,2} = 1$.

At $t = 0$, the population fraction of exciton ($P_{ex,0}$, $P_{ex,1}$ and $P_{ex,2}$), biexciton ($P_{biex,0}$) and cavity photon (P_{ph}) are all zero.

- (2) $R_{pump} = \text{abs_cs} * \text{Pump_fluence} * \text{Laser_pulse_shape}$. Here, abs_cs means absorption cross section of CQDs. We should choose the abs_cs value which make the simulated threshold be consistent with $891.48 \mu\text{J}/\text{cm}^2$ (experimental result) for neutral CQDs. Laser_pulse_shape is Gaussian pulsed with 500 ps FWHM of our laser.

(3) τ_{sti} of 10 ps is cited the number in ref 6 and ref 7.

(4) τ_c of 13.3 ps is estimated which corresponds to a photon propagates 4 mm (our strip length) along the waveguide.

(5) Other lifetime data used here is from experimental results of PL dynamics (**Figure 5.8**).

b. Simulated population dynamics

Figure A12 Population dynamics under electric field of ~ 21 kV/cm and with pump fluence of $100 \mu\text{J}/\text{cm}^2$. Red solid line is the normalized laser pulse as a function of time. Blue solid line is the population dynamics.

After we plug the initial conditions into the modified rate equations, the population dynamics of ground state exciton, biexciton and cavity photon can be obtained. Two examples when the applied electric field is 21 kV/cm are presented to show the simulated dynamics (below the threshold: $100 \mu\text{J}/\text{cm}^2$, **Figure A12**; above the threshold: $1000 \mu\text{J}/\text{cm}^2$, **Figure A13**);

Figure A13 Population dynamics under electric field of ~ 21 kV/cm and with pump fluence of $1000 \mu\text{J}/\text{cm}^2$. Red solid line is the normalized laser pulse as a function of time. Blue solid line is the population dynamics.

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Chapter 6: Closing perspective

The robust, flexible properties of excitons in CLDNMs make them stand out as a promising candidate to develop next-generation excitonic devices. Motivated by the essential requirement of solid-state devices, that is the manipulation of certain properties in corresponding carriers (here, it refers to excitons, charger excitons or high-order excitons, etc.) to store, transport and process information, this thesis is concentrated on the developing of new methods to control/manipulate excitonic properties in CLDNMs, beyond the well-known chemical structure optimization and quantum-confinement engineering.

6.1 Conclusion

Our main works in terms of excitonic modulation included in this thesis can be sorted into two categories: synthetic and post-synthetic.

For synthetic modulation, instead of conventional optimization of stoichiometry and geometry of CLDNMs, we have shown that through introducing the foreign atoms into the host CLDNMs, the excitonic properties of CLDNMs can be dramatically changed (**chapter 2**). Our experiments reveal that the spectrally-separable, room temperature biexciton emission with continuous-wave excitation (pump intensity as low as $\sim 10 \text{ W/cm}^2$) can be achieved in copper-doped four mono-layer CdSe Colloidal quantum wells. Benefitting from the new Coulomb interaction environment created by the doped transition metal ions (copper) for band-edge excitonic resonance, we have reached and showed proof of sustained, well-resolved biexciton emission in a long-sought “all solution processable regime”- enabling the easy integration of quantum emitters into almost any optoelectronic quantum architectures. Suppressed Auger loss in 1D quantum confinement and reduced Coulomb screening assisted by dopant-host interaction enables a biexciton binding energy of $\sim 64 \text{ meV}$, a factor of 2 greater than the

values reported in other colloidal nanomaterials and comparable to the value reported in atomically thin transition metal dichalcogenides (TMDs). The biexcitons are robust, optically and mechanically in ways that have no parallel in the reported literature in terms of colloidal nanomaterials.

Furthermore, utilizing the copper-doped CQWs, we have solved a challenging problem for optical gain performance in CLDNMs: ensuring the preferred four-level system (biexcitons) rather than two-level system (electro-hole plasma) being the primary lasing mechanism even when Mott carrier density is exceeded. Leveraging the optical gain arising from pure biexcitons, single-mode lasing with very low threshold ($\sim 4.1 \mu\text{J}/\text{cm}^2$) in the vertical cavity surface-emitting laser structure has been demonstrated. These observations supplement the possible optical gain mechanism in CLDNMs and set copper-doped CQWs as an excellent candidate for achieving low-threshold, solution processable lasing devices.

For post-synthetic modulation, we started by using Förster resonance energy transfer (FRET) to control the exciton flow in a binary CLDNM complex (**chapter 3**). The **first** conducted work is to break the unidirectional limitation of exciton flow in conventional FRET. Benefiting from the *d* orbital electrons in copper dopants, we have proposed and demonstrated that the excitation energy can flow back and forth between the two components in a binary complex made of colloidal quantum wells (CQWs). Through analysing the steady state emission intensity, time-resolved PL (trPL) and photoluminescence excitation (PLE) spectroscopies, we find that band-edge excitons in copper-doped 3 mono-layer (ML) CQWs transfer the excitation to excitons in 4 ML CQWs, whose energy is simultaneously harvested backwards by the dopants in 3ML CQWs. The proposed binary CQW complex that offers unique mutual FRET may boost the new design for biophysics, by offering a cross-check configuration to precisely probe the dynamics in biomolecules, and energy optoelectronics, through enabling more external control parameters.

The **second** conducted work is inspired by the concept that FRET is significantly dependent on the donor and acceptor populations, we have proposed and demonstrated the stimulated emission-controlled exciton flow in a binary colloidal quantum well (CQW) complex consisted of 4 mono-layer core-only CdSe CQWs and 8 ML core-shell CdS/CdSe/CdS CQWs. Specifically, in spontaneous emission regime, nearly 50% of the exciton population in donor outflows into acceptor via FRET. When acceptor exhibits stimulated emission, the enhanced population overlap between donor's excited state and acceptor's ground state almost shut down the excitonic emission in donor. Upon further increasing excitation, stimulated emission in donor totally switches off the exciton flow process since lasing occurs much faster than FRET. Our results which demonstrate a prototype of controllable exciton flow with multiple modulation stages and exceptional contrast ratio, may lead to the novel design of all-optical excitonic circuits.

For post-synthetic modulation, we then investigated how charged excitons can influence the optical amplification of CLDNMs (**chapter 4**). By embedding the quasi type-II CQDs (CdSe/CdS/ZnS core/shell/shell) into the Sawyer–Tower circuit to apply a potential that is experienced as an electric field by the CQDs, we have reached and showed tunable amplified spontaneous emission (ASE) threshold in a long-sought practical device where the CQDs sandwiched between two dielectric layers to retain their high quantum efficiency as in parent solution (quantum yield of $> 70\%$). Singly-charged CQDs help building up population inversion due to pre-existing electrons while strongly enhanced Auger recombination in multiple-charged CQDs stymies the optical amplification. In addition to experimentally demonstrating threshold tunability, we also developed a kinetic equation model to systematically analyse the electric field dependent ASE threshold. The kinetic model not only confirms our experimental results but also presents to be a reliable tool for accessing the requirements of charging level to achieve nearly zero-threshold in CQDs. This practical

device allows us to fine-tune and achieve the optimal charging level to utilize the advantages of singly charged CQDs and avoid the adverse effect of doubly charged CQDs. The ASE threshold of CQD gain media are robust, reproducibly controllable and environment-undependable in ways that may enlighten the demonstration of electrically-pump CQD lasing device.

For post-synthetic modulation, we lastly explored the interaction between excitons in CLDNMs and plasmons in open nanocavity (**chapter 5**). For the first time, our scientific achievement unambiguously shows that the ultra-strong exciton-plasmon coupling (Rabi energy larger than 400 meV) and high cooperativity (exceeding 11) can be achieved using Wannier Mott excitons. By using a hybrid structure system consisted of high aspect ratio colloidal quantum wells (HARCQWs) and an individual plasmonic silver nano-cube, the enhanced binding energy caused by another quantum confinement and less efficient homo-exciton tunnelling due to the non-stacking properties, as well as the enhanced spatial overlap ensured by the face-down geometry, ensures the largest Rabi splitting (corresponding to ~ 0.1 fs⁻¹ energy transfer rate) observed in any Wannier Mott exciton and plasmon system.

Overall, the finding of this thesis gives fundamental insights and indicates new possibilities in the field of excitonic modulation in CLDNMs, which advances current understanding and stimulates further studies. We deeply hope that our works can be helpful to attain the overarching goal: solid-state excitonic devices.

6.2 Outlook

Inspired by the experimental observations and knowledge acquired in the conducted studies, there are plenty of perspective works that are attractive and valuable which can both boost our current understanding on excitonic modulation and tackle the daunting challenges in developing solid-state excitonic devices.

6.2.1 Photoluminescent Anisotropy Amplification

Photoluminescent Anisotropy or emission polarization of CLDNMs is critical for various applications, for example, directional emission is highly preferable to increase the radiative outcoupling efficiency of light-emitting diodes and CNDNMs with anisotropic emission can boost the performance of current liquid crystal display (LCD) technology^{[1][2]}. However, colloidal quantum dots (CQDs), which are the most mature CLDNMs with the highest photoluminescence quantum yields, colour purity and chemical stability, are lacking the photoluminescent anisotropy due to the spherical quantum confinement environment^[1].

Figure 6.1 Photoluminescent anisotropy amplification of colloidal quantum dots. (a) Polar plots of angle-dependent emission (green frame) and excitation (blue frame) of CQWs, together with theory curves. The figure is reproduced from reference^[1]. (b) Polar plots of angle-dependent emission (green frame) and excitation (blue frame) of CQDs, together with theory curves. The figure is reproduced from reference^[1]. (c) FRET is used to amplify the emission anisotropy of CQDs. The schematic is reproduced from reference^[2]. The highly anisotropic dipoles in donor will transfer to the acceptor without changing the orientation.

To address this issue, we propose that colloidal quantum wells, whose emission is highly anisotropic with more than 95% out-of-plane direction due to the basic anisotropy of the electronic Bloch states^{[3][4]}, can be used to amplify the emission anisotropy of colloidal quantum dots by Förster resonance energy transfer. A schematic of this idea is shown in **Figure 6.1**: this amplification effect benefits from the efficient light-harvesting energy transfer process in the mixed donor-acceptor pairs, in which the highly anisotropic donor (CQWs with green emission) absorbed photons from the excitation sources and funnelled the excitation energy to the acceptor (CQDs with red emission) in a polarized form^{[5][6]}.

6.2.2 All optical control of lasing emission

Figure 6.2 Controlling the lasing emission in CdSe/CdTe CQWs. (a) The carrier transition processes in CdSe/CdTe CQWs. Without modulation, the charger transfer (CT) will dominate the recombination process due to its ultrafast dynamics (~ 1 ps)^{[7][8]}. The figure is reproduced from reference^[7]. (b) The distributed feed-back (DFB) cavity with gradually changed duty cycle is used to change the cavity resonance. (c) Different location of the DFB cavity will result in different lasing emission. The figure is reproduced from reference^[9].

Micro- and nano-lasers play a vital role in various applications ranging from on-chip communication to integrated circuit sensing^{[10][11]}. The critical requirements of solid-state devices on information density and bandwidth makes lasing emission wavelength switching highly urgent in the design of micro- and nano-lasers. Until now, lasing emission wavelength switching is mostly relying on integrating multiple gain media, manipulating the dielectric environment of gain materials or cavity size. However, in principle, these switchable micro- and nano-lasers suffer from limited tuning range and slow response. An optical control of lasing emission which is robust, wide-range and ultrafast is desirable.

To address this issue, we propose two ideas. The first idea is to exploit the carrier recombination competition in the core-crown CdSe/CdTe CQWs. As shown in **Figure 6.2**, if the cavity confinement (Q-factor) is good enough to suppress the charge transfer process, we scan the DFB with gradually changed duty cycle with various pump fluence, we should be able to see the lasing from the crown (CdTe), the shell (CdSe) and the CT process. As a result, a micro lasing device with continuous lasing transition is achieved.

The second idea is to use the optical cavity as the spectral filter to switch the single-mode lasing emission^[11]. As shown in **Figure 6.3**, two specially designed optical cavity (one is a whisper-gallery-mode cavity and another one is a Fabry-Pérot cavity; the position of the whisper-gallery-mode cavity is exactly matching the position of one mode in the Fabry-Pérot cavity) is close enough to ensure the effective optical coupling. Thus, we can utilize the strong optical coupling between these two optical cavities to achieve single-mode lasing switching: when pumped at port 1, the lasing mode of WGM cavity will couple into the waveguide and be collected at the output port; when pumped at port 2, the lasing mode of FP cavity which matches the resonance in WGM cavity will be filtered and the remaining mode be collected at the output port.

Figure 6.3 Switchable single-mode lasing device. A coupled whisper-gallery-mode cavity and Fabry-Pérot cavity is used to switch the laser emission wavelength. Pumping at different ports will result in different single-mode lasing emission due to the coupling effect.

6.2.3 Hot electron modulated Photoluminescence

Recently, using hot electrons generated from non-radiative decay of surface plasmon to modulate the emission properties of CLDMNs has attracted tremendous research interests due to its ultrafast response speed and active, all-optical characteristic^{[12][13]}. In chapter 2, we have already reported several interesting excitonic properties in copper doped CQWs. Here, benefiting from the widely distributed energy level of copper dopants, we can similarly achieve an active light control of copper emission, as shown in Figure 6.4: Gold nanorods are uniformly distributed on top of 3 ML Cu: CdSe CQWs. Without the gate pumping laser (800 nm CW laser), the emission collected from the drain is just the copper emission with intensity

quenching. However, if the architecture is excited with the gate source, the hot electron generated in Au nanorod will transfer into copper dopants and shift the fermi level of copper dopants: more Cu^{2+} (dark state) is changed to Cu^{1+} (bright state)^[14]. Considering the copper emission is coming from the electron in the conduction band of CdSe host and the hole localized in copper dopants: $\text{Cu}^{1+} + e \rightarrow \text{Cu}^{2+} + h\nu$. As a result, we can expect that: the copper emission will be dramatically modulated by the gate signal, with the 800 CW excitation and different pump intensity, the copper emission will become broader and red-shifted compared to the scenario in the pure Cu:CdSe CQWs.

Figure 6.4 Hot electron transfer between gold nanorod and Cu:CdSe nanorod. Based on the absorbance curve of Au nanorod, only around 800 nm, the significant absorption can generate hot electrons and 400 nm excitation can only cause negligible doping effect in our experiment^[15]. The hot electron transfer will lift the fermi level of copper dopants and increase the population of Cu^{1+} (bright state).

6.2.4 4-level systems enable continuous-wave lasing

CLDNMs are highly desirable gain media for lasing devices due to the solution processability, tunable band gap and efficient emission^{[16][17]}. However, the practical application of CLDNMs as gain media is limited by degenerated band-edge states, as a result, to achieve population inversion, each nano-particle must contain more than one excitons on average, which leads to increased optical gain threshold and rapidly Auger loss in the multiple carrier environment^{[16][18]}.

Figure 6.5 The 4-level system in Cu:CdSe CQWs can be utilized to achieve continuous-wave pumped lasing. (a) Concept of the 4-level system in Cu:CdSe CQWs. The figure is reproduced from reference^[17]. (b,c) Cu:CdSe CQWs used for gain media are suffering from slow recombination and ultra-broad emission band. The figure is reproduced from reference^[19]. (d) Nano photonic crystal can be used to accelerate recombination and concentrate the transitions in copper-related emission. The figure is reproduced from reference^[19].

A four-level system which can automatically achieve the population inversion is undoubtedly a good method to enhance the optical gain performance of CLDNMs. In Cu:CdSe CQWs, as shown in **Figure 6.5a**, the localized hole in copper dopants is optically active and can radiatively recombine with the electron in the conduction band of CdSe^{[17][20]}. This ensuing 4-level system can be used to realize the concept of zero-threshold optical gain. Unfortunately, the copper dopants related transitions are suffering from the wide-spreading energy distribution and slow recombination dynamics: the lifetime of copper-related recombination is several hundred nanoseconds and the range of allowed energy transition is ~ 200 nm which significantly dilutes the density of preferred

stimulated transitions (see **Figure 6.5c**). To address this issue, we can use resonant photonic crystal to accelerate the recombination process in copper related emission and narrow down the allowed transitions by Purcell effect. As a result, we may achieve continuous-wave pumped stimulated emission in Cu:CdSe CQWs.

6.2.5 Memory-Erasable Field-Effect Transistor

Using an all-optic method to write and erase the memory of field-effect transistor (FET) is ultra-attractive for information/data process considering this ‘photo-induced’ recovery/control mechanism is high response speed, high sensitivity and low-power consumption^{[21][22]}. Utilizing the copper dopants which play the role as the hole trapper, we have proposed an idea to realize the light-erasable memories in FET, as shown in **Figure 6.6**: the copper-doped CdSe CQWs based FET is an unipolar n-type FET since the copper sites will trap the holes injected into the valence band of the CdSe host, as a result, when negative gate bias is applied (according to our architecture and the drain-source bias is fixed at a small value), if the hole concentration is not high enough to saturate the copper sites, the hole will not flow in these CQWs and the current between Source/Drain will be close to zero^{[23][24]}.

If we apply a negative writing voltage before the measurement (the writing voltage will inject holes and fill partial of the copper sites), we will expect that the minimum conduction point (MCP) will shifted to the left side (small voltage value)^{[21][25]}. Also, this memory effect caused by the writing voltage can be easily erased by the UV illumination: the CdSe CQWs will absorb the pumped photon and the stored holes induced by the writing energy will recombine with the photo-generated electrons in the conduction band of CdSe CQWs. We need to be aware that the controllable range or the characteristics of the memory effect is highly depending on the concentration of copper dopants. Therefore, the slow recombination of copper-related emission, which is typically ~500 ns, may results in a slow response speed and small photo-switching amplitude.

Figure 6.6 The field-effect transistor (FET) using copper-doped CQWs. (a) A schematic of the FET structure. (b) The carrier transitions in copper-doped CQWs. (c) The current flow between Source and Drain with positive (top panel) and negative (bottom panel) gate voltage. (d) The current flow between Source and Drain with different writing voltage.

6.2.6 Triplet Energy Transfer

Figure 6.7 Triplet energy transfer in CLDNMs. (a) A schematic of the reversible triplet energy transfer between colloidal CQDs and attached PCA. The figure is reproduced from reference^[26]. (b) The trapped excitons in CuInS colloidal quantum dots is beneficial to increase the efficiency of triplet energy transfer. The figure is reproduced from reference^[27].

The efficient emission from CLDNMs have been demonstrated to be partially enabled by the strong and fast band-edge recombination of excitons. The lifetime of excitons' recombination is typically sub- or several nanoseconds^[26]. However, this relatively short lifetime of carriers in CLDNMs limits the applications in charge separation related or energy transfer related applications. Triplet energy transfer, which can expand the lifetime of excitons to microseconds or milliseconds and store the energy in transition-forbidden triplet states, is an

effective mean to solve this problem. Moreover, triplet–triplet-annihilation is probably the only practical way to realize photon up-conversion under incoherent and continuous-wave illuminations, since the second/third harmonic generation in nonlinear crystals or up-conversion using lanthanides ions requires coherent laser excitation with high intensity^[27].

Since the first observation of triplet energy transfer has been demonstrated in CdSe CQDs^[26], tremendous research interests have been focused on how to improve the efficiency of the triplet energy transfer. Very recently, Wu and co-authors^[27] have reported that the self-trapped exciton in CIS CQDs which shows slow recombination is highly desirable for improving the efficiency of triplet energy transfer (in this report, the efficiency is as high as 90%). Considering the similar carrier dynamics between CIS CQDs and copper-doped CQWs, the trapped excitons in our Cu:CdSe CQWs maybe also a good candidate for triplet energy transfer study.

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1. **Junhong Yu**, Sushant Shendre, Weon-kyu Koh, Baiquan Liu, Songyan Hou, Chathuranga Hettiarachchi, Savas Delikanli, Pedro Hernández-Martínez, Muhammad Danang Birowosuto, Hong Wang, Hilmi Volkan Demir, Cuong Dang. Electrically control amplified spontaneous emission in colloidal quantum dots. *Science Advances* 2019, 5, eaav3140.
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4. **Junhong Yu**, Manoj Sharma, Mingjie Li, Savas Delikanli, Ashma Sharma, Muhammad Taimoor, Yemliha Altintas, James R. McBride, Thomas Kusserow, Tze-Chien Sum, Hilmi Volkan Demir, Cuong Dang. Copper dopants enable low-threshold biexciton lasing in colloidal quantum wells beyond Mott carrier density. *Applied Material today (under review)*.
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Co-author:

1. Baiquan Liu, Manoj Sharma, **Junhong Yu**, Sushant Shendre, Chathuranga Hettiarachchi, Ashma Sharma, Aydan Yeltik, Lin Wang, Handong Sun, Cuong Dang, Hilmi Volkan Demir. Light-Emitting Diodes with Cu-Doped Colloidal Quantum Wells: From Ultrapure Green, Tunable Dual-Emission to White Light. *Small*, 1901983.

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1. **Junhong Yu**, Sushant Shendre, Weon-kyu Koh, Baiquan Liu, Songyan Hou, Chathuranga Hettiarachchi, Savas Delikanli, Pedro Hernández-Martínez, Muhammad Danang Birowosuto,

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4. Junhong Yu, Songyan Hou, Manoj Sharma, Landobasa YM Tobing, Zhigang Song, Savas Delikanli, Chathuranga Hettiarachchi, Daohua Zhang, Weijun Fan, Muhammad Danang Birowosuto, Hong Wang, Hilmi Volkan Demir, Cuong Dang. Giant Rabi splitting observed in colloidal quantum wells interacting with silver nanocube. *SPIE Photonics West 2020*.

5. Junhong Yu, Manoj Sharma, Savas Delikanli, Muhammad Danang Birowosuto, Hilmi Volkan Demir, Cuong Dang. Back and forth Förster resonance energy transfer in a binary nanomaterial complex. *SPIE Photonics West 2020*.

Conference poster presentations

1. Junhong Yu, Sushant Shendre, Weon-kyu Koh, Baiquan Liu, Songyan Hou, Chathuranga Hettiarachchi, Savas Delikanli, Pedro Hernández-Martínez, Muhammad Danang Birowosuto, Hong Wang, Hilmi Volkan Demir, Cuong Dang. Controlling Light Amplification of Colloidal Quantum Dot in Actively Operating Device. *CLEO 2019*.

- 2. Junhong Yu**, Manoj Sharma, Mingjie Li, Pedro Ludwig Hernández-Martínez, Savas Delikanli, Ashma Sharma, Yemliha Altinas, Chathuranga Hettiarachchi, Tze-Chien Sum, Hilmi Volkan Demir, Cuong Dang. Continuous-Wave Pumped Biexciton Emission in Copper-Doped Colloidal Quantum Wells. *MRS 2019*.
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