Optical properties of single photon emitters with GaN, SiC, and perovskites quantum dots

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**OPTICAL PROPERTIES OF SINGLE PHOTON EMITTERS
WITH GAN, SIC, AND PEROVSKITES QUANTUM DOTS**

ZIYU WANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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WITH GAN, SIC, AND PEROVSKITES QUANTUM DOTS**

ZIYU WANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. 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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Authorship Attribution Statement

*(B) This thesis contains material from 2 papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 2 is published as Yu Zhou, Ziyu Wang, Abdullah Rasmita, Sejeong Kim, Amanuel Berhane, Zoltan Bodrog, Giorgio Adamo, Adam Gali, Igor Aharonovich, Wei-bo Gao Room-temperature solid state quantum emitters in the telecom range. Science Advances 4, 3, eaar3580 (2018). DOI: 10.1126/sciadv.aar3580

The contributions of the co-authors are as follows:

- Yu Zhou and I built the optical set-up and performed the optical measurements.
- Yu Zhou, Abdullah Rasmita, Sejeong Kim performed the data analysis.
- Bodrog Zoltan and Adamo Giorgio performed the wavelength modelling.
- Yu Zhou, Igor Aharonovich, and Weibo Gao designed the experiments and wrote the manuscript with contributions from all co-authors.

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Another paper from chapter 4 is accepted, correct?

The contributions of the co-authors are as follows:

- Junfeng Wang, Yu Zhou, and I built the optical set-up and performed the optical measurements.
- Junfeng Wang and Weibo Gao designed the experiments and wrote the manuscript with contributions from all co-authors.
- Xingji Li and Jianqun Yang performed electron irradiation of the samples.

- Junfeng Wang, Yu Zhou, Abdullah Rasmita, and Hans Jurgen von Bardeleben performed the data analysis.

Note: If published materials are not inserted as thesis chapters, students must acknowledge co-worker contributions in the acknowledgement section of their thesis.

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Abstract

Single-photon emitters (SPEs) have been taken as the building block for quantum information technologies. In recent decades, people have kept searching for the 'ideal' on-demand SPEs as the fundamental light resource for many proposed quantum information schemes: quantum key distribution, quantum teleportation, quantum computing, and et cetera. With the discovery of telecom range SPEs in GaN and 3C-SiC host materials, we made an effort to characterize many important optical properties and elucidated the quantum emitters' formation. We also expanded our scope to include the perovskite quantum dots (PQDs) and studied the complex physics of single CsPbBr₃ nanocrystal photoluminescence emission. Finally, we summarized the optical properties of PQDs, and telecom range SPEs in GaN and 3C-SiC, and our results indicate they can be applied to different quantum applications for their advantages in different perspectives.

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I have been pushing myself hard to complete writing this thesis for a long time, although I could only work on it intermittently. Generally, I must admit that it was hard to do so since the theoretical modeling for the last chapter about PQDs was just at the beginning when I decided to start writing the thesis. Thus, I was doing writing for thesis and paper and modeling at the same time. Furthermore, the pressure to find a job after graduation, to squeeze out time for my engaged girlfriend now and wife in the future, and to do other daily personal chores often made me really tired. Luckily, I managed to do all these and enjoyed working hard under pressure, and I felt my life became better and better. I would like to say that the most difficult time is not dealing with the obvious difficulties or pressures, but instead feeling depressed. Now, I have finished my thesis and must give thanks to the people who have helped me.

I, of course, should first thank my parents, my girlfriend, my paternal uncle, and the rest of my family. They have not only always given me encouragements but also warned me of potential negative outcomes of what I choose to do. I could not ask for a better childhood from my parents, a better soul mate than my girlfriend, or better support from my paternal uncle. I am so happy to be and to grow up with my parents in my small town.

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Much of the work presented in this thesis was conducted in collaboration with the support of my old group members: Yu Zhou, Abdullah Rasmita, Junfeng Wang, Oscar Garcia Garcia, and Ke Li. Ke Li was the post doctor teaching me the basic hands-on optical experiment skills and he spent a lot of time doing various experiments with me. Junfeng was a reliable friend and always enthusiastic about discussing problems and

solving issues with me. Yu Zhou was the first graduated Ph. D. student in our lab group. He completed his undergraduate study in the same university program as me, and thus we had many conversation topics in common during the time we were doing experiments till midnight. Abdullah was very good at modeling, and I always learned a lot of physical knowledge from him and got recommended books worthy of reading. He was really enthusiasm in learning physics, which also influenced me when discussing our experimental observations. I am so happy that I had the opportunity to work with these guys.

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Table of Contents

Abstract.....	1
Acknowledgements.....	2
Table of Contents.....	4
Chapter 1 Introduction	7
1.1 What is so great about a Single-photon emitter?.....	7
1.2 The candidates for single-photon emitters and the difference in our studied objectives.....	8
1.3 Hanbury-Brown and Twiss experiment.	11
1.4 Hong-Ou-Mandel experiment	15
1.5 Basic optical characterization tools for solid-state single-photon emitters.....	16
1.6 Thesis overview.....	18
Chapter 2 The quantum emitters in GaN	20
2.1 Sample description and Experimental setup details	20
2.2 Optical characterization for RT telecom range SPEs in GaN	22
2.2.1 PL spectrum characterization and $[g^{(2)}(\tau)]$ for proving an SPE	23
2.2.2 Power-dependent $[g^{(2)}(\tau)]$ and the three-level model	24
2.2.3 Study about the performance of the GaN SPE: Lifetime characterization, saturation curve, photostability, and polarization measurement.....	26
2.2.4 Photoluminescence statistics and photoluminescence under high power.....	28
2.3 Optical enhancement of the SPEs	30
2.4 The theoretical modeling for the possible source of the GaN SPEs	35
2.5 Outlook.....	36
Chapter 3 Room temperature single-photon emitters at telecom range based on silicon carbide.....	38
3.1 Optical characterization for the SPEs.....	38
3.1.1 Sample description and experimental setup.....	39
3.2 Basic Optical characterization for the SPEs.....	39

3.2.1 Locating the bright SPEs	40
3.2.2 Property characterization for SPE.....	41
3.3 The source of the 3C-SiC SPEs.....	45
3.4 Outlook.....	47
Chapter 4 Investigating single-photon source property of Perovskite quantum dots ..	48
4.1 Theoretical prediction for the bright triplet exciton states and dark singlet state in cesium lead halide perovskites.....	49
4.1.1 Four-band model and Fine structure	49
4.2 Synthesis Method and TEM measurement.....	52
4.2.1 Method 1: Synthesis of CsPbBr3 Nanocrystals from cesium oleate and PbBr2	52
4.2.2 Method 2: Synthesis of CsPbBr3 Nanocrystals from cesium and lead oleates and TOPBr2	53
4.2.3 Isolation and Purification process of PQDs	55
4.2.4 TEM result	55
4.2.5 Spin-coating PQDs on a silicon substrate	62
4.3 Experimental Setup	63
4.4 Observation of Super-bunching	64
4.4.1 Optically driven Super-bunching in individual single PQDs	65
4.4.2 Power-dependent behavior of the super-bunching	72
4.4.3 The Photon twins in the emission PL spectrum.....	76
4.4.4 Measuring the lifetime of single PQDs emitted photons	82
4.4.5 The temperature-dependent behavior of super-bunching	85
4.5 Theoretical model and simulation to explain the source of the giant super- bunching from the emission of single PQDs.....	88
4.5.1 General description of theoretical models	88
4.5.2 General expression for $g(2)(\tau)$ for PQD emission	91
4.5.3 Model 1: Three-energy-level system with all radiative decays	93

4.5.4 Model 2: Three-energy-level system with radiative and non-radiative decays ..	96
4.6 Outlook.....	97
4.6.1 Adding a shell surround the PQD	98
4.6.2 Electrically driven single PQDs.....	98
4.6.3 Resonant Polarized Photoluminescence excitation for analyzing the exciton fine structure of CsPbBr₃ QDs.....	102

Chapter 1 Introduction

1.1 What is so great about a Single-photon emitter?

When talking about single-photon emitters (SPEs), the first that comes to mind is the light-matter interaction that happens between a single-mode radiation field and a two-level structure [1]. As the scope of observation becomes smaller and smaller, the laws of quantum mechanics take the place of "the classical" and present some interesting phenomenon: the rabi-oscillation predicted in semiclassical theory or the phenomenon of collapse and revival predicted by fully quantum theory. The most distinguishing point is the existence of coherence between two atoms, two qubits, or a photon and a simple two-level structure [2-4], and the observation of this coherence is the same as quantum mechanics predicts before the happening of decoherence. These motivate people to manipulate the eigenstate's population of the quantized states of a single qubit [5, 6] or to generate entanglement [7-9]. Naturally, solid-state quantum emitters become one of the keys for realizing quantum applications.

Quantum key distribution (QKD): In the past decades, the development of quantum information has been amazingly fast [10-14], and the literature in this active research field is in rapid growth [15-17]. Many algorithms and protocols have been developed to use the quantum advantage to solve the advanced computing tasks [18, 19] which the supreme classical computer may never be able to complete. The quantum key distribution [20, 21] might be the most mature and fundamental technology out of these fantastic and revolutionary applications. Using the BB84 protocol [20] as an example for QKD, the on-demand emitters should have an ultra-single-photon purity, a single polarization mode, a high brightness, and a lifetime-limited linewidth (a signature of long coherence time and indistinguishability).

On-Chip quantum technology: For large-scale quantum photonic applications [21], the on-chip integration of electrically driven single-photon sources combined with

reconfigurable waveguide circuits shows a great potential [22, 23]. Relatively complicated quantum circuits have been demonstrated with mature experimental methods [24, 25], and the realization of electrically driven quantum light-emitting diodes has also been achieved [26-28]. The electrically driven single quantum emitter device is ideally designed to directly inject one electron and one hole in opposite directions and let them tunnel to the precise location of a quantum emitter [29-31]. Therefore, the material layer where the quantum emitter is buried would determine the actually achieved optical quality of the electrically driven quantum emission. Although quantum emitters' fabrication and integration technology, such as the material growth or site-specific emitter engineering, have been developed more and more over time [30, 32], the future application still requires further improvements [33]. The challenges we face are working at room temperature [36, 37], reducing the influence from the existing impurities, barring the holes tunneling through the transport path designed for electrons, and vice versa.

Quantum teleportation and computing: Using single optic qubits for quantum teleportation [34] and building the controlled-NOT (CNOT) gate [35] can enable photonic quantum information processing. The quantum CNOT gate would manipulate a qubit to any arbitrary accuracy, and the teleportation enables operations between the parallel computing processes. A few years ago, electrically driven biexciton (XX) exciton (X) cascaded emission from an InAs quantum dot was used to generate entangled photon pairs and demo the quantum teleportation [36]. Based on these, the on-demand SPEs would need near background-free single-photon purity emission and near-unity indistinguishability, and the electrical triggering would further reduce the relatively low spectral diffusion. In addition, we also need a combination with a photonic cavity structure to increase the photon extraction efficiency for enhancing the brightness, and thus fully unleash the potential in the operating mean photon number per pulse of $\langle n \rangle = 1$ compared to $\langle n \rangle \approx 0.5$ of attenuated laser source [37, 38].

1.2 The candidates for single-photon emitters and the difference in our studied objectives

Quantum dots and atomic defects: Over the years, various quantum emitters in different material systems have been investigated. The studies show that conventional III-V quantum dots (GaAs, InAs, etc.) [39-42] and atomic defects [43-46] are promising for their similarity to the atoms. They indeed show outstanding optical properties [35, 47] and the combination with the convenience and scalability of the solid-state system [35, 48]. However, the impurities in the atomic defect systems and the requirement of cryogenic temperature result in drawbacks [49] which lead to the inhomogeneous broadening of different emitters and homogeneous broadening of the same emitter [50]. Therefore, the indistinguishability of photons from the same SPE or between the tuned different SPEs decreased [51, 52]. Besides, the lifetime limited linewidth has been achieved for color centers [53-55] in diamond and recently for defects in hBN [56], but not in other systems due to the complexities of the mesoscopic environment. Recently, the perovskite quantum dots (PQDs) have been shown to exhibit tunable emission wavelength, single-photon emission, novel exciton energy levels, and being operatable at room temperature, but the emitters often blink and bleach [57-59]. Thus, more materials engineering is required to optimize these quantum emitters [60, 61].

SPEs discovered in two-dimensional and carbon nanotubes: In recent years, researchers have been searching for new material systems that host single-photon emitters (SPEs), and they have successfully increased the types to include two-dimensional (2D) materials, carbon nanotubes (CNTs), and single fluorescence molecules. Among these, the most attractive is the 2D materials system [62-67] whose natural source and mechanism in forming SPEs are still unclear in theory but are probably related to the strains based on experimental evidence [68, 69]. One outstanding 2D material host that shows a great advantage over other transitional metal dichalcogenides (TMD) for being workable at room temperature with high brightness and stability is the hexagonal Boron Nitride (hBN). As for the CNTs [70-72], the source is the molecule trapping the localized excitons attached to a single-walled nanotube acting as a high-quality one-dimensional mechanical resonator, but the poor emission intensity (several hundred photons per second) of it is a problem. Recently, researchers have tuned the zero-phonon line of the SPEs in CNTs to telecom range for improving the photon extraction efficiency and thus minimized the influence of the low emission count rate [73].

Our studied GaN, 3C-SiC, and PQDs: First, we studied the SPEs in GaN semiconductor system (refer to Chapter 2). It is possible that there exist telecom range

SPEs in GaN at RT, since researchers have observed the wide range zero-phonon line (ZPL) emission distribution covering from visible to near-infrared wavelengths [74]. Therefore, we used superconducting single-photon detectors to search the SPEs in the telecom range at RT, and we found the source was possibly the same as in [74], the cubic inclusion formed when the GaN semiconductor was growing,. We got a single photon purity about 95% (that is $g^{(2)}(0) = 0.05 \pm 0.02$), photon count rate 0.6 M counts per second when saturated, and emission polarization visibility 93% for the RT telecom range SPEs. These optical properties are really amazing compared to the conventional microcavity-embedded InAs/GaAs QDs, show single-photon purity > 99% at cryogenic temperature. However, the ZPL linewidths of our GaN SPEs vary from a minimum 3 nm (~ 741 GHz width) to a maximum 50 nm (~ 15 THz width), too wide to measure the indistinguishability property, and the exciton fine structures are not clear either. Thus, further studies are required to know the spectral diffusion [1] source and the exciton fine structure for GaN. Then, we can control the mesoscopic environment of these SPEs by using an electric field or laser radiation to make the resonance fluorescence linewidth compatible with the value of 20 GHz in InAs/GaAs QDs [47].

Second, we studied the SPEs in 3C-SiC (refer to Chapter 3). The RT telecom range SPEs in SiC was coincidentally observed when we used the optical setup for GaN to look at SiC samples. Therefore, we had no theoretical expectation for the existence of such SPEs. The SiC SPEs even showed a linewidth more than 180 nm, broader than that of our discovered GaN SPEs. Although such SPEs show single-photon purity about 95% with an ultra-bright count rate more than 1 M counts per second without optical enhancement structure, they can only be used in QKD, but not in other applications of quantum information processing due to the their huge FWHM values. The unclear formation mechanism of these SPEs and lack of experimental information on the SPEs' nature prevent us from improving the optical properties of these quantum emitters by materials engineering.

Third, we studied the perovskite quantum dots (PQDs) (refer to Chapter 4). The PQDs in our experiments show a good single-photon purities ~ 90%, which depends on the spectral isolation purity of exciton emission, 40 K counts per second under several hundred nanowatts continuous-wave (CW) excitation, and exciton linewidth varying from 0.3 ~ 1.0 nm similar to the reported by [58]. The drawback we found is that the

PQDs always blink and bleach after maintaining emission for more than 5 hours under CW excitation. Additionally, the spectral diffusion of the PQDs should be eliminated to make a lifetime-limited exciton emission FWHM value for high indistinguishability in the Hong-Ou Mandel measurement experiment, and thus enable constructing a controlled-NOT gate. Compared to the InAs\GaAs QDs, the PQDs are quite promising to gain good properties with materials developments [58, 61, 75]. Finally, we observed a giant super-bunching from the emission of a single PQD which is resulted from a biexciton-exciton cascaded emission similar to conventional QDs [76]. Therefore, the quantum teleportation scheme based on entangled photon pairs is possible to be realized in using the PQDs as in [13, 36] but at RT.

In sum, the GaN and SiC SPEs both show a good single-photon purity, ultra-bright emission, single-polarization mode of emission at RT, but we lack experimental information on their formation mechanisms and exciton-fine structure. These make them good candidates only for QKD application. Therefore, the single PQDs show a great potential to work at RT [75] with the same good property of conventional InAs\GaAs possible only at cryogenic temperature, but using PQDs would require further material development to stabilize and control the dielectric environment.

1.3 Hanbury-Brown and Twiss experiment.

The main concept of this section is given in more detail in [1]. Here, we show the simplified scheme and related formulas for the second-order correlation function $g^{(2)}(\tau)$ and present a discussion of $g^{(2)}(0)$ values for classifying quantum emission, coherent light, thermal light, and photon bunching.

The basic idea of the Hanbury-Brown and Twiss (HBT) experiment (Figure 1-1) is to use two photodetectors at two separate spatial positions that are located symmetrically to an ideal 50/50 beam splitter for measuring the photon counts independently and recording the relative arrival time between the photon incidents at the two photodetectors. Then, we can write the second-order correlation function calculating the joint probability of the photon events arrived at the two photodetectors with the field operators:

$$\begin{aligned}
G^{(2)}(\hat{r}_1, \hat{r}_2, \hat{r}_3, \hat{r}_4; t_1, t_2, t_3, t_4) &= \text{Tr}[\rho E^{(-)}(\hat{r}_1, t_1) E^{(-)}(\hat{r}_2, t_2) \times E^{(+)}(\hat{r}_3, t_3) E^{(+)}(\hat{r}_4, t_4)] \\
&= \langle E^{(-)}(\hat{r}_1, t_1) E^{(-)}(\hat{r}_2, t_2) \times E^{(+)}(\hat{r}_3, t_3) E^{(+)}(\hat{r}_4, t_4) \rangle
\end{aligned}$$

Equation 1-1

Where, $\hat{r}_i, t_i$ ($i = 1, 2, 3, 4$) refers to the vector of the two photodetectors at different times, $\rho = \sum_i P_i |i\rangle\langle i|$ is the density operator of the field, and the field operators are $E^{(+)}(\hat{r}, t) = \sum_k \hat{e}_k \epsilon_k a_k e^{-i\nu_k t + i\hat{k} \cdot \hat{r}}$, $E^{(-)}(\hat{r}, t) = \sum_k \hat{e}_k \epsilon_k a_k^\dagger e^{i\nu_k t - i\hat{k} \cdot \hat{r}}$.

Figure 1-1. Hanbury-Brown and Twiss experiment scheme. The input light beam goes to an ideal beam splitter placed at a 45° angle to the center coating surface and is separated into two outputs at a 1:1 ratio by the splitter. The filled and empty circles indicate having and having no photons, respectively. The arrows indicate the moving directions of photons. The left arrow indicates incoming light with the arrival time sequences of photons; for the outputs, the upper arrow indicates the start times (τ_0) and the right arrow indicates the stop times ($\delta\tau$: relative time delays to τ_0) recorded for the relevant photons.

As the two photodetectors are aligned to two separate beam paths from a 50:50 nonpolarizing beam splitter with the same distance, we can get $g^{(2)}(\hat{r}, \tau)$ as:

$$g^{(2)}(\hat{r}, \tau) = \frac{\langle E^{(-)}(\hat{r}, t) E^{(-)}(\hat{r}, t + \tau) E^{(+)}(\hat{r}, t) E^{(+)}(\hat{r}, t + \tau) \rangle}{\langle E^{(-)}(\hat{r}, t) E^{(+)}(\hat{r}, t) \rangle \langle E^{(-)}(\hat{r}, t + \tau) E^{(+)}(\hat{r}, t + \tau) \rangle}$$

Equation 1-2

Then, for the most simple and ideal situation: our radiation field is statistically stationary and consists of only a single mode, if we take the field operators into Equation 1-2, most factors cancel themselves out, and we then get:

$$g^{(2)}(\tau = 0) = \frac{\langle \hat{a}^\dagger(t) \hat{a}^\dagger(t + \tau) \hat{a}(t + \tau) \hat{a}(t) \rangle}{\langle \hat{a}^\dagger \hat{a} \rangle^2} \quad \text{Equation 1-3}$$

For further discussion about classifying the light sources, we list four main types of light, quantum emission, coherent light, thermal light, and ensembled photon pairs, that show different behaviors in the HBT experiment (Figure 1-2). First, we consider the correlation measurement result for the quantum emission. For simplifying, we assume a driving field is used to excite a number of ‘n’ single quantum emitters that ideally emit photons at the same frequency not affected by Heisenberg’s uncertainty principle. Thus, we have $g^{(2)}(\tau = 0) = \frac{n(n-1)}{n^2} = 1 - \frac{1}{n}$ at the zero-time delay. If the HBT is for a single quantum emitter $n = 1$, we would get Figure 1-2 (a) result as predicted $g^{(2)}(\tau = 0) = 1 - \frac{1}{1} = 0$. Since there are background noise and finite sharp energy levels for SPEs in real experiments [77, 78], the $g^{(2)}(\tau = 0)$ value will not be zero but between zero and 0.5 for a single quantum emission.

Second, we derive the normalized $g^{(2)}(\tau)$ for thermal and coherent radiation fields using the formula in [1] for the P-representations of the two fields:

$$P(\alpha, \alpha^*) = \frac{1}{\pi \langle n \rangle} \exp(-|\alpha|^2 / \langle n \rangle) \quad \text{Equation 1-4}$$

This is a Gaussian distribution describing the thermal radiation field.

We take Equation 1-4 into Equation 1-3 and get

$$g^{(2)}(\tau = 0) = \frac{\int P(\alpha, \alpha^*) |\alpha|^4 d^2 \alpha}{[\int P(\alpha, \alpha^*) |\alpha|^2 d^2 \alpha]^2} = \frac{\int P(\alpha, \alpha^*) (|\alpha|^2)^2 d^2 \alpha}{[\int P(\alpha, \alpha^*) |\alpha|^2 d^2 \alpha]^2} = 2 \quad \text{Equation 1-5}$$

Figure 1-2 (c) shows the theoretical predictions of the HBT experiment for the thermal light source, and the $g^{(2)}(\tau = 0)$ value is exactly 2 as calculated by Equation 1-5. The experiment on this was done in 1965 by researchers in Italy [79].

As for the coherent radiation field like lasing, the P-representation is a two-dimensional delta function:

$$P(\alpha, \alpha^*) = \delta^{(2)}(\alpha - \alpha_0)$$

Equation
1-6

Then, we can get $g^{(2)}(\tau) = 1$ for the representation is a delta function. This is also shown in Figure 1-2 (b), and the related experiment was carried out by the same group [79].

Finally, we think about the HBT experiment for the light source which emits light in the form of highly time-correlated photon twins [80]. Figure 1-2 (d) shows the super-bunching phenomenon in $g^{(2)}(\tau)$. The peak value at zero-time delay depends on the efficiency of generating paired photons, or in other words, the photon twins radiation field P-representations. Since there is no standard distribution statistics for a photon twins emission, we do not derive a $g^{(2)}(\tau = 0)$ value here. However, two models of generating the super-bunching phenomenon through biexciton-exciton cascaded emission in single PQDs are discussed in Section 4.5.2.

Figure 1-2. Classifying the types of light sources using the HBT experiment. (a) The single-photon source HBT result: the photons arrive as a well-separated distribution statistic of one photon at one time. (b) The lasing light source HBT result: the photon arrives as a delta distribution statistic. (c) The thermal light source HBT result: the photon arrives as a Gaussian distribution statistic. (d) The photon twins light source HBT result: the photons always arrive as ensembled groups.

1.4 Hong-Ou-Mandel experiment

The Hong-Ou-Mandel experiment is different from the HBT experiment in the input, as it has two beams for input and also two for output. The HBT experiment is used to classify the types of input light sources or to get the single-photon purity value of an SPE; the HOM experiment is used to check the quantum interference between the two input beams. Thus, the HOM experiment can check the indistinguishability of photons emitted by a quantum emitter [81].

Figure 1-3 is a simple scheme to show the HOM experiment for two identical photon sequences, and the photons are all the same in polarization and frequency. Since the

photons are bosons, they gather together in the two output beam paths. Therefore, there are no photons or photon pairs at any time point in each path. In other words, there would never be a coincidence for simultaneous detection of photons in the two paths. Thus, if the input photons are ideally indistinguishable, we would also see an antibunching as zero at zero-time delay in a second-order correlation function measurement for two output paths.

Figure 1-3. The simple scheme of Hong-Ou-Mandel experiment for two identical single-mode photons. The left and low arrows represent two identical input beams of photons moving to a nonpolarizing 1:1 beam splitter. Refer to Figure 1-1 captions for the meanings of the circles, arrows, $\delta\tau$ and τ_0 .

1.5 Basic optical characterization tools for solid-state single-photon emitters

Spectral characterization: Using a spectrometer to characterize the quantum emission is the most basic and very first step in all the experiments because we rely on it as a direct way to look at our localized emitters and get a photon intensity distribution versus

the energy or wavelength. Normally, we input our collected emission beam into the spectrometer through a home-built collimator that consists of an achromatic lens, an XY-transition stage, a precise XY-transition plate for fiber port, and a fiber port. Therefore, we connected the collection port of the optical setup and the collimator before the input slit of the spectrometer with single-mode fiber. If the whole system is in free space, we would need a pinhole between a pair of two extra lenses before the collimator taken off the fiber coupler part. As for the inner structure of a spectrometer, there are a pair of collimating and focusing mirrors, several selectable gratings, an entrance slit, an exit slit, and a CCD. Thus, the emission beam would be focused by the collimator to go through the entrance slit (the size is often set as 10 μm), and then it would be reflected by the collimating mirror, then by the diffraction grating, and finally by the focusing mirror to go through the exit slit and spatially distributed at different locations of the CCD corresponding to different wavelengths. Therefore, we measured the spectrum of a quantum emission by choosing suitable CCD and grating to get the photoluminescence spectroscopy with a good signal-to-noise ratio and resolution.

Polarization measurement: For the emission or excitation polarization visibility measurement of a quantum emission, we used a pair of linear polarizers and a half-wave plate in the excitation path to make a controllable linear polarization excitation radiation for the quantum emitter and used the other pair of a half-wave plate and a polarizer in the collection path to collect any selective polarized angle emission photons. Then, we rotated the half-wave plate at the excitation path for the excitation polarization measurement and vice versa the half-wave plate at the collection path for emission polarization measurement.

Saturation curve measurement: For maintaining the stability of the laser, we never tuned the laser intensity by changing the power of the laser but instead by using variable neutral density filter wheels. Therefore, we could measure the photon counts of the quantum emission versus the excitation power.

Photon stability test: This was done to check whether the quantum emitter would blink during the process of emitting or bleach after some time of excitation. Normally, we picked an excitation power and observed the photon count rate histogram of the quantum emission with a time bin size often set at 100 ms. If a quantum emitter was stable, it would show a gaussian distribution of shot noise with a mean value determined by the excitation power, indicating that the count rate fluctuations are at the shot-noise

limit. As reported by [82, 83], the stability is mainly affected by the dielectric environment around the SPE and can be tuned by an radiation field or electric field.

1.6 Thesis overview

In this introductory section, we discussed the importance of quantum emitters and their applications in quantum information. Moreover, we talked about the solid-state systems burying the SPEs, and the different types of SPEs. For a general view of the experimental objectives in this thesis, we showed our investigated quantum emitters belonging to which material system and their advantages and disadvantages in quantum applications. For the main experimental methods, we showed the derivation of $[g^2(\tau)]$ for the HBT experiment and listed four types of light sources that were different from each other in the HBT measurement. We also gave a short explanation for the HOM experiment which is very important for measuring the indistinguishability or interference of two lights. Then, we listed and discussed other basic optical characterization methods for quantum emissions to give a background for a detailed discussion of our objectives.

Chapter 2 presents our study on the discovered GaN SPEs that emit stably in the telecom range at RT. We did the optical characterizations both at RT and low cryogenic temperature (LT) 4K and analyzed the data. Our results show that the GaN SPEs are an excellent candidate, especially for QKD. Since the GaN semiconductor is mature in materials engineering, such as etching, device fabrication, and LED making, we believe our work provides valuable information for people interested in quantum applications based on the solid-state host. However, the source of the SPEs in GaN remains unclear even though we tried to find it by investigating the photoluminescence statistics in detail. Additionally, we demonstrated an enhancement of these SPEs by using optical structure - patterned structure sapphire substrate – to enhance the photon extraction efficiency and thus increase the count rate by three times. Because our data show that the formation mechanism of the GaN SPEs could make the quantum emission distribution over visible, near-infrared, and telecom range with a narrow linewidth of the zero-

phonon line, our collaborators built a quasi-one-chain numerical model to explain the cubic inclusion as the possible source of the SPEs.

Chapter 3 presents our study on 3C-SiC SPEs that also emit at telecom range at RT, and such SPEs were experimentally proved by us to be in the 3C-SiC epitaxy layer. The optical characterization results of these SPEs are similar to those in GaN, except the linewidth of the emission peak is broad, more than 180 nm. Therefore, the good single-photon purity, ultra-brightness, great photon stability, and good visibility of the single polarization mode of these SPEs make them promising candidates for QKD application. However, our results do not tell us how they are formed and which type of atomic defect they exactly belong to. We suggested further studies to be conducted in these areas.

Chapter 4 presents the optical characteristics of single perovskite quantum dots (PQDs) and shows the mechanism generating highly time-correlated photon twins resulting in a giant super-bunching in $[g^{(2)}(\tau)]$ for a single PQD emission. The observed super-bunching for the unfiltered emission was studied in detail by theoretical simulations with two models. We think the nonradiative path related to a dark state around the bright neutral exciton energy level is why the biexciton-exciton cascaded emission can generate photon twins with high efficiency. Therefore, the electrically driven entangled photon pairs from PQDs are quite promising for quantum information applications [13, 34, 36, 52], and we have already done some preparation works for making electrically triggered quantum emissions device from single PQDs.

Chapter 2 The quantum emitters in GaN

GaN semiconductor material has attracted people's attention for its potentials in quantum technologies [42, 84-90], because of the maturity in the fabrication and applications of semiconductors. The GaN defects were predicted [91] to contain single-photon emitters (SPEs) with a wide zero phonon line (ZPL) wavelength range covering from ultraviolet (UV) to infrared (IR), and the experimenters also found UV [92] and visible range [74] quantum emitters in GaN and did a lot of related works. Amazingly, we observed the GaN defect could also produce SPEs emitted at telecom range with a great photostability at room temperature (RT), and this shall open a new path toward the realization of electrically driven single-photon sources for on-chip quantum simulators [93, 94] and practical quantum communication technologies [36, 95, 96]. In the rest of this chapter, we will present the optical characterization for GaN telecom range quantum emitters and discuss the possible sources of them.

2.1 Sample description and Experimental setup details

The GaN sample for our study was a magnesium (Mg)-doped GaN layer on an undoped GaN layer that was grown on sapphire, and both layers were 2 μm thick. We built and used a confocal setup (Figure 2-1) for both the cryogenic and room temperature measurements, and the focus point to find the SPEs was about 2 μm below the sample surface but not reaching the undoped layer. At room temperature, we used an oil immersion objective with a numerical aperture of 1.35 (Nikon) and a two-dimensional nanopositioner (PI P-611.3S) for photoluminescence (PL) scanning and optimizing the

focal depth. Additionally, there was another XYZ crossed-roller bearing steel linear stage, with a maximum movable scale at the magnitude of cm, installed under the nano-positioner to move the sample under the objective. The continuous wave (CW) excitation was done by a diode laser with a center wavelength of 950 nm, and the pulse excitation was performed by a Titanium: Sapphire one picosecond laser (Spectra Physics) with a repetition rate of 80 MHz. To suppress the laser reflection, a 1000 nm long-pass filter was put in the collection arm, and another 1000 nm short-pass filter was inserted in the excitation beam path to clean up the residual laser intensity above 1000 nm. We used a single-mode fiber to connect the collection port with a spectrometer, a liquid nitrogen cooled InGaAs camera (Princeton Instruments), or a low jitter (~ 30 ps) super-conducting-single-photon-detector (Scontel SPD). The small core diameter of the single-mode fiber resulted in a small mode field diameter; thus, it could act as a pinhole to reduce the noise background from the environment. At cryogenic temperature, we used a pair of silver-coated galvo mirrors (Thorlabs, GVS012) to scan the beam with a fine resolution depending on the working distance of the selected objective, if $WD = 10$ mm, then minimum resolution was 150 nm, since the sample was in a closed-cycle cryostat (Montana Instruments) where only an atto-cube stepper could do non-repeatable rough scanning. For the second-order correlation measurements [$g^2(\tau)$], we used a fiber-based beam splitter to perform Hanbury Brown and Twiss measurement.

Figure 2-1. The optical setup scheme for telecom range SPEs in GaN. The setup is formed by connecting two arms with a dichroic mirror, a 980 nm edge long pass, loaded in a 30 mm cage cube. Which one of the two arms is the collection and the other is the excitation depends on the dichroic mirror positions. If we do experiments at RT, we do not need to use the Galvo scanning part but directly place an oil immersion lens below the 30 mm cage cube. Therefore, the dichroic mirror would be loaded in the diagonal position, making the right arm the excitation and the left arm collection. If we do experiments at cryogenic LT, we have to use the Galvo to scan the beam. Thus, we rotate the loaded dichroic mirror with a relative 90° to the previous diagonal position, making the right arm the collection and the left arm excitation. A dry objective would be below the Galvo beam port and inside the cryo chamber space.

2.2 Optical characterization for RT telecom range SPEs in GaN

To do the optical characterization, we first did the $[g^{(2)}(\tau)]$ for the unfiltered emission from a brightest SPE to confirm and show it had a good single-photon purity. Secondly, power-dependent $[g^{(2)}(\tau)]$ measurements were performed to investigate the SPEs in more details. Then, the saturation curve measurements, photostability test, lifetime, and polarization measurements were carried out for the same SPE. Furthermore, we did the same optical characterization measurements for other individual SPEs to study GaN infrared range quantum emitters' general statistics.

2.2.1 PL spectrum characterization and $[g^{(2)}(\tau)]$ for proving an SPE

Figure 2-2A shows our studied GaN sample with the corresponding lattice structure. Figure 2-2B presents the PL mapping containing a single-photon emitter with an emission ratio about 350 kcounts/s at the focal depth. Figure 2-2C shows the emission spectra of six emitters, three pairs of SPEs with ZPL located at similar wavelengths, demonstrating the ZPL linewidths decreasing from RT to cryogenic temperature. At RT, the full widths at half maximum (FWHM) of individual emitters vary from a minimum of 3 nm to a maximum of 50 nm. At cryogenic temperature, 4K, the FWHMs of the emitters decrease to a few nanometers. These indicate that cooling down can effectively weaken the broadening of linewidth due to the acoustic phonon coupling [97], but not enough to make the FWHM of ZPL reach the lifetime limit value, or the phonon coupling to the lattice in GaN defect is so strong that it still broadens the ZPL at 4K. Our data show that all the spectrums at RT or LT have asymmetric shapes for the ZPLs. As the temperature increases, the line shapes of SPEs deviate similarly from the expected Lorentzian line shape. These might be due to acoustic phonon broadening [97].

Our second-order correlation measurements for SPE1 show that $g^{(2)}(0)$ is 0.05 ± 0.02 and 0.14 ± 0.01 under CW (Figure 2-2D) and pulse excitations (Figure 2-2E), respectively. As both these $g^{(2)}(0)$ are less than 0.5, the SPE1 is a single-photon source. Usually, the pulse excitation results in a smaller $g^{(2)}(0)$ than CW excitation because the pulse not only can excite the quantum emitter but also add a time window for the emission signal detection. But if the SPE1 is ultra-stable with the excitation power increasing, the higher background noise of pulse excitation could result in higher $g^{(2)}(0)$ value than CW excitation the CW excitation.

Figure 2-2. Infrared single-photon emission in GaN. (A) Schematic illustration of gallium nitride crystal lattice structure and an image of the GaN wafer under white room light. (B) Confocal 2-dimensional PL mapping shows an SPE at almost the center location, and we labeled it as SPE1. (C) Photoluminescence spectra of 6 infrared SPEs reveal the ZPL ranging from 1085 to 1340 nm. PL spectra for three emitters are taken at 4 K (upper panel) and 300 K (low panel), respectively. Note that the emitters at 4K and RT are different. (D) $[g^{(2)}(\tau)]$ measurement of the unfiltered emission from SPE 1 under 950 nm CW laser excitation. The blue dots are the raw data without any background correction, and the red curve is fitted to a three-level system using Equation 2-1, yielding $g^{(2)}(0) = 0.05 \pm 0.02$. (E) $[g^{(2)}(\tau)]$ measurement of the unfiltered emission from SPE 1 excited by pulsed laser with one picosecond pulse width and 80 MHz repetition rate, yielding $g^{(2)}(0) = 0.14 \pm 0.01$. We did the $[g^{(2)}(\tau)]$ measurements at room temperature.

2.2.2 Power-dependent $[g^{(2)}(\tau)]$ and the three-level model

Near the zero-time delay (Figure 2-2D), there is a symmetrical bunching shoulder. To explain this, three energy levels with a shelving state [98] were considered. First, the following formula was used to fit the $[g^{(2)}(\tau)]$ data of Figure 2-2D to get a set of experimental values of β , τ_1 and τ_2 .

$$g^{(2)}(\tau) = 1 - \alpha \cdot e^{-\frac{|\tau|}{\tau_1}} + \beta \cdot e^{-\frac{|\tau|}{\tau_2}}, \quad \alpha = 1 + \beta \quad \text{Equation 2-1}$$

Where τ_1, τ_2 refer to the lifetime of excited and shelving state, respectively, and α, β are fitting parameters related to the excitation power.

The following formulas show how the four parameters here are related to each other and to the excitation power: β is bonded to τ_1 and τ_2 with k_{31} , and τ_1, τ_2 are determined by the decay ratios between all three energy levels:

$$\beta = \frac{1 - \tau_2 k_{31}}{k_{31}(\tau_2 - \tau_1)}, \quad \tau_{1,2} = \frac{2}{A \pm \sqrt{A^2 - 4B}} \quad \text{Equation 2-2}$$

$$A = k_{12} + k_{21} + k_{23} + k_{31}, \quad B = k_{12}(k_{23} + k_{31}) + k_{31}(k_{21} + k_{23}), \quad \text{Equation 2-3}$$

$$k_{12} = \eta P$$

Where, k_{xy} , $x = 1, 2, 3, y = 1, 2, 3$ means the decay ratio from level $|x\rangle$ to level $|y\rangle$, except the k_{12} , that is the excitation rate from energy level $|1\rangle$ to $|2\rangle$ and proportional to the power P with an unchanged value η . Through using Equation 3-1, the k_{31} can be directly calculated with $k_{31} = \frac{1}{[\beta(\tau_2 - \tau_1) + \tau_2]}$, because β, τ_1 and τ_2 are experimentally got with fitting the $[g^{(2)}(\tau)]$ by Equation 2-1. In principle, η, k_{13}, k_{21} , and k_{23} are independent parameters, and they together determine how β, τ_1, k_{31} , and τ_2 are correlated. Thus, we used a combined function of exponential decay and linear function as $\frac{a}{\exp(bx)} + \frac{dx}{(x+c)}$ (Figure 2-3), where η, k_{21}, k_{13} , and k_{23} are free parameters to be calculated in the fitting. Therefore, the fitting of the $[g^{(2)}(\tau)]$ would show how the four parameters τ_1, τ_2, β , and k_{31} vary with CW excitation powers. To avoid possible misunderstanding here, we emphasize that Figure 2-3C-F are never based on the assumption that no correlation exists between these four parameters, and the way we show how the four parameters varied with powers follows the standards in [98-100]. The ZPL emission lifetime can be calculated by $(k_{21} + k_{23})^{-1}$ and compared with the measured lifetime result using a pulse laser. Here, it gives the lifetime value around 776 ± 39 ps for the fitting (Figure 2-3C-F) based on three energy levels (Figure 2-3B) for the power-dependent $[g^{(2)}(\tau)]$ (Figure 2-3A).

Figure 2-3. Repeated $[g^{(2)}(\tau)]$ measurement for SPE1 emission with varied CW excitation power. (A) Zoom-out and the zoom-in pictures of four different CW excitation power $[g^{(2)}(\tau)]$. Normalization is done here far to the whole measurement time scale. (B) Scheme of the three-level model. (C), (D), (E), (F) The fitting results τ_1 , τ_2 , β , and k_{31} with the CW excitation powers. The fitting shown by the red curve is done through a combination of exponential decay and linear function as $\frac{a}{e^{bx}} + \frac{dx}{x+c}$.

2.2.3 Study about the performance of the GaN SPE: Lifetime characterization, saturation curve, photostability, and polarization measurement

The ZPL intensities for SPE1 increase as the CW excitation powers increase and reach saturation at about $P_s = 2.32$ mW (Figure 2-4A). The data can be well-fitted by $I_{(P)} = I_{\infty} \times P/(P + P_s)$, where $I_{(P)}$ is the ZPL intensity count, P is the CW excitation power, and P_s (saturation power) and I_{∞} (maximum count of ZPL) are two free fitting parameters. The results obtained are $P_s = 2.32$ mW, and $I_{\infty} = 0.69 \pm 0.01 \times 10^6$ counts per second for the SPE1 experimental data. Such a ZPL intensity count, reaching a million, is on a par with the brightest RT SPE buried in a bulk crystal [74, 84, 101]. Figure 2-4B indicates our discovered telecom range SPE1 is ultra-stable under three different CW excitation powers, as the count rate of SPE1 remains stable and no blinking or bleaching occurred in a run of 120 seconds with the time binning of 100 ms measurement.

The experimental polarization measurement results for the excitation (red) and emission (blue) are fitted with $\cos^2(\theta)$ (Figure 2-4D). The calculation shows polarization visibilities $\frac{I_{\max}-I_{\min}}{I_{\max}+I_{\min}} = 93.2\%$ and 55.4% for emission and excitation of SPE1, respectively. Additionally, we also got the lifetime of ZPL emission 736 ± 4 ps (Figure 2-4C) which is close to 776 ± 39 ps from our three-level model fitting in the last section.

Figure 2-4. Property characterization for the SPE1. (A) Saturation curve measurement for SPE1 emission presenting photon counts saturated around $P_s = 2.32$ mW, and indicating the maximum emission count as $I_{\infty} = 0.69$ M counts/s. (B) Photon counts for SPE1 emission is stable for high power 1.8 mW, medium power 0.5 mW, and low power 0.1 mW. (C) solid black line: the lifetime measurement result for SPE1 emission; solid blue line: the instrument response function (IRF). Since the lifetime measurement had a longer decay than the IRF, we did not deconvolute; instead, we used a single exponential decay to fit and get the lifetime value 736 ± 4 ps. (D) Polarization measurement data for excitation and emission are plotted in red dot and blue dot, respectively. The two sets of data points are fitted by $\cos^2(\theta)^2$.

2.2.4 Photoluminescence statistics and photoluminescence under high power

To use the discovered SPEs in quantum applications, we must study if 1) the emission polarization of the defect aligns with any of the crystal axes of the GaN host crystal, 2) all the defects show the same orientation, and 3) the defect emission peaks remain sharp, isolated, and free of background noise at high pump power. To do so, we characterized other individual telecom range SPEs, not only SPE1.

For 1) and 2), we measured the polarization of 25 emitters. Their emission polarization angles at maximum intensity indicate that not all the defects show the same orientation, and no clear relationship exists between the maximum emission angle and the crystalline axis of GaN (Figure 2-5A). To know whether there is a relationship between absorption and emission polarization, we measured both absorption and emission polarization patterns for nine other emitters. One of them has two nearly overlapped polarization patterns (Figure 2-5B), another shows almost orthogonal polarization patterns for emission and excitation (Figure 2-5C), and the rest seven have random distributions for the angle between maximum emission and absorption (Figure 2-5D). Thus, there is no relationship between the emission and excitation polarization patterns. For 3), we studied the ZPL positions of other 10 infrared single-photon emitters. Our data indicate that the ZPLs of discovered SPEs cover a wide spectrum range from around 1050 to around 1350 nm, and the FWHMs of ZPLs broaden as the emission wavelength moves from the near-infrared range to the telecom range (Figure 2-6A and B). We chose the narrowest linewidth emitters to study how the FWHM would vary with excitation power increases from 1 to 5 mW. We observed that the FWHM value remained 4.69 ± 0.06 nm, even if the noise background of its normalized PL spectrum increased (Figure 2-6C). Therefore, the linewidth of our discovered SPEs did remain sharp, isolated, and free of background noise with high excitation power.

In conclusion, the RT telecom range SPEs have near to one polarization visibilities, and their ZPLs remains sharp with excitation power increases. Thus, they are promising to be directly used in QKD [20, 102]. However, the random distributions of their emission and absorption patterns and having no relationships to GaN crystal axes make it hard to understand SPEs' formation and the physical mechanism of the exciton.

Figure 2-5. Polarization measurement for 25 emitters. (A) The histogram of maximum emission angles for the 25 emitters. (B), (C) Two representative emission and absorption polarization pattern results. The distributions of the data points are fitted by $\cos(\theta)^2$. (D) Random distribution of the angle between the maximum emission and absorption polarization of SPEs.

Figure 2-6. PL statistics study for 10 different emitters. (A) The RT PL spectra characterization for 10 individual emitters. (B) The distribution of linewidth versus the ZPL of the 10 emitters. (C) Normalized PL spectrum of SPE2 with CW excitation power varied from 1 to 5 mW, with 1 mW per increment step. The FWHM remains as 4.69 ± 0.06 nm and confirms that the ZPL emission peak is well isolated from the noise background even under high excitation flux intensity. The inset here shows the saturation curve of SPE2, yielding a saturation power $P_s = 1.59 \pm 0.1$ mW, and $I_{\infty} = 0.46 \pm 0.1$ M counts/s indicated by the fitting with $I(P) = I_{\infty} \cdot \frac{P}{(P+P_s)}$, where $I(P)$ is the detected count rate, P is the excitation power value, and P_s (saturation power) and I_{∞} (maximum emission count) are the parameters.

2.3 Optical enhancement of the SPEs

In Section 2.2, our SPEs have good qualities: near to one polarization visibility and the narrow linewidth robust to high excitation power; but their polarizations do not relate to GaN crystal lattice axes, and there is no relationship between the emission and excitation polarization pattern. Thus, we have no clue about, and it is difficult to find the physical source of them. However, as they show great potential in quantum applications [76, 93, 103] and the fabrication technologies in GaN semiconductors are mature, we decided to enhance the photon count rate of our SPEs anyway. As mentioned in Section 2.1, the sample structure we studied is one layer doping on one layer undoped GaN grown on sapphire. Thus, we used different refractive index layers to enhance the photon extraction efficiency based on the law of refraction. Since our focus was below the surface with a depth roughly 1~2 μm and an oil immersion objective was used, we thought the critical point to enhance the emission intensity was to recollect the lost emitted photons that were going to the bottom layer. Rather than using a top-down reactive etching technique to make an optical structure, we directly grew a separate GaN layer on a patterned structure sapphire substrate (PSS) to induce the optical structure without inducing any side effect from the etching. This mature PSS in GaN fabrication was used in improving the photon extraction efficiency for quantum dots-based light-emitting-diodes [104, 105]. The design of the PSS is shown in Figure 2-7B and C, the V-shaped depth between the nearest two cones leads to an increasing reflection area for the emission from SPEs buried in the upper GaN layer and therefore could enhance the photon extraction efficiency of our sample.

We build a model to study the influence of the PSS structure using 3D finite difference time domain (FDTD) optical simulation using Lumerical software [106]. The simulating model is based on an ideal assumption that the dipole of an SPE sits exactly at the center of the V-Shaped depth (Figure 2-7B, and C). For this GaN/PSS structure, the simulation as done including the patterned geometry; and the in-used refractive indexes of the GaN layer, the sapphire layer, and the oil environment are 2.33, 1.75, and 1.52, respectively. For the bare GaN sample, the refractive indexes are the same but without considering any geometry.

Figure 2-7. Model of SPE in GaN with PSS structure. (A) Polarization measurement for SPE1 emission, indicating a single polarization component for the SPE1. The red curve is fitted with $y = y_0 + A \cos^2(ax + \phi)$. (B) Vertical view to the dipole of SPE1 is prepared for the far-field radiation model built. The ideal case is presented here for the electric dipole locating right at the center of the surrounding PSS cones. (C) Side view of the far-field radiation model. From top to down: the oil used to immerse the high N. A. objective, two layers of doping and undoped GaN, and the final pattern structure sapphire (PSS) substrate.

Figure 2-8A shows the scanning-electron-microscopy picture for the GaN/PSS sample, and our PSS has a cone shape with a base diameter of about 2 μm . Figure 2-8B and C show the FDTD simulating results for the far-field radiation patterns for bare GaN and GaN/PSS samples, respectively. The collected intensities from inner to outer circles were calculated by varying the collection half angles from 100 to 900 for a 1.35 N. A. objective in an oil immersion environment. Comparing the intensities in GaN/PSS to the bare GaN samples in simulating (Figure 2-8B and C), the PSS structure did enhance the collection efficiency with the emission intensities two times of the bare GaN samples.

Afterward, we did the optical characterizations for SPEs in GaN/PSS sample. Interestingly, we accidentally found an SPE located at the center in the surrounding PSS (Figure 2-8D). Therefore, this SPE is a perfect experimental objective reference for the actual enhancement effect of PSS. To compare the enhancement of the photon extraction, we measured the saturation curve of this SPE and compared it with the SPE1, and the data and fitting are shown in Figure 2-8E. The saturated count rate for the enhanced SPE was 2.33×10^6 counts/s, two times of 1.13×10^6 counts/s of SPE1. This enhancement is consistent with our FDTD simulation results. To study if this would be common for all GaN emitters in the GaN/PSS sample, we repeated our experiments on other five more pairs of emitters with similar ZPLs. Our data show that

their average enhancement ratio of maximum count rates at saturation power is about 1.5 (Figure 2-8F).

For the five pairs of emitters, we also did the optical characterization to get a set of PL spectra together with $[g^{(2)}(\tau)]$ data (Figure 2-9, Figure 2-10, Figure 2-11, and Figure 2-12) that indicate they are single-photon emitters. Our data suggest that the $[g^{(2)}(\tau)]$ value at zero time delay for enhanced SPEs shows an obvious rise, from ~ 0.15 to ~ 0.25 , compared to the SPEs without PSS (comparing the $g^{(2)}(0)$ value in Figure 2-12 with Figure 2-10). We believe this results from the side effect of photon extraction efficiency increases compared to without PSS sample: the PSS also leads to a stronger excitation (the unabsorbed excitation beam would be reflected) than without PSS sample, which results in a worse signal to noise ratio for counts in the $[g^{(2)}(\tau)]$ measurement. As talked in Section 3.2.1, Equation 3-1 shows the background correction formula, which can be transformed as $(g^{(2)}(\tau) - 1) \cdot \rho^2 = g_{\text{raw}}^{(2)}(\tau) - 1$. Therefore, if the signal to noise ratio is very bad, then even the ideal antibunching $g^{(2)}(\tau = 0) = 0$ still result in a $\lim_{\rho \rightarrow 0} (g^{(2)}(\tau) - 1) \cdot \rho^2 = 0 = g_{\text{raw}}^{(2)}(\tau = 0) - 1$, and thus the experimental data $g_{\text{raw}}^{(2)}(\tau = 0) \rightarrow 1$. In conclusion, a worse signal to noise ratio caused by the PSS would result in a worse experimental $[g^{(2)}(\tau)]$ result with a smaller antibunching depth.

Figure 2-8. Enhancement of the infrared emission from SPEs in GaN using the PSS. (A) SEM image of the vertical cross-section for our GaN grown on a PSS. We can clearly see the PSS are generally in cone shapes. (B), (C): respectively for the far-field radiation simulations for the SPE emission with and without PSS. Refer to Figure 2-7 for the details of the model. The inner to outer circles correspond to the collection half angles ranging from 100 to 900. The Y-axis value in (C) is two times the value in (B).

Thus, the ideal enhancement of the emission flux intensity is two times. **(D)** We found an SPE perfectly sitting in the center of the surrounding PSS and used it to show the actual enhancement. **(E)** The saturation curve for the SPE in **(D)** is shown as blue dots, and fitting is by $I(P) = I_{\infty} \cdot \frac{P}{(P+P_s)}$. To compare, we found another SPE with a similar ZPL location to the SPE in **(D)**, and measured the saturation curve for it. The saturation curve for SPE with PSS shows an obvious enhancement about three times to the SPE without PSS, and the (I_{∞}) for SPE with PSS reaches 2.33×10^6 counts/s relatively higher than 1.13×10^6 counts/s for SPE without PSS. **(F)** To study if this was common, the emission intensities of the other five pairs of SPEs with and without PSS under maximum CW excitation power 10 mW of our diode laser were investigated. The enhancement is roughly three times.

Figure 2-9. PL spectra and saturation curves of five emitters without PSS. **(A)** Five located SPEs with ZPL ranging from 1080 to 1110 nm. **(B)** The saturation curves of the five emitters, with the CW excitation power increased from several μ W to the maximum 10 mW. The saturation is fitted using the $I(P) = I_{\infty} \cdot \frac{P}{(P+P_s)}$.

Figure 2-10. The $[g^2(\tau)]$ measurement to study if the five emitters in GaN sample without PSS were single-photon sources. The blue dots are without any background correction, and the solid red line is fitted by Equation 2-1. The $g^{(2)}(0)$ value is given in each graph.

Figure 2-11. PL spectra and saturation curves of five emitters with PSS. (A) Five located SPEs with similar ZPL ranging from 1080 to 1110 nm to the previous five SPEs in pristine GaN sample. (B) The saturation curves of the five emitters, with the CW excitation power increased from several μW to the maximum 10 mW. The saturation is fitted by $I(P) = I_{\infty} \cdot \frac{P}{(P+P_s)}$.

Figure 2-12. The $[g^2(\tau)]$ measurement to study if the five emitters in GaN sample with PSS were single-photon sources. The blue dots are without any background correction, and the solid red line is fitted by Equation 2-1. The $g^2(0)$ value is given in each graph.

Moreover, we also studied the lifetimes of the five pairs of emitters. Our lifetime data suggest that the enhanced SPEs are similar to that of the SPEs in the pristine GaN sample (Table 2-1). This means that the PSS improves the count intensities of the SPEs

only through enhancing the photon extraction efficiency, not by decreasing the lifetime of emitters to increase the decay ratio [107].

SPEs in pristine GaN	Lifetime (ps)	I_{∞} from saturation curve fitting	SPEs in GaN grown on PSS	Lifetime (ps)	I_{∞} from saturation curve fitting
A	484	0.89 M	a	482	1.4 M
B	448	1.13 M	b	442	1.17 M
C	348	1.67 M	c	405	2.13 M
D	456	0.89 M	d	348	2.33 M
E	265	1.19 M	e	396	2.45 M

Table 2-1. The summary of the five pairs of emitters. A-E are the five SPEs in the GaN sample without PSS, and a-e is the five SPEs in the GaN sample with PSS. When the I_{∞} is enhanced for averaged two times, the lifetimes are not significantly different between the SPEs with and without PSS.

2.4 The theoretical modeling for the possible source of the GaN SPEs

Although our PL and polarization statistics indicate the polarization of the discovered GaN infrared emitter is not related to any crystal lattice axis and the distribution of the ZPL is random and covers from 1000 to 1300 nm, to study the possible source of the SPEs, our collaborators built a material-based model that could generate a uniform set of PL which is the same as our experimentally observed single-photon emitters. Since the SPEs are excited when the excitation beam is focused at a depth of about 1.5 μm between the doping and undoped GaN layer, we think the defect may originate from the cubic inclusions [74].

The numerical modeling to explain the common source for all PL of SPEs is a simple quasi one-dimensional model. It is known that the fluorescence of a single photon must result from an exciton's recombination. Thus, the wide covering range of our SPEs would require the exciton binding energy to vary a lot from one defect to another defect and remain stable under high excitation flux for each defect. Therefore, we assumed the hole part of the exciton was tightly localized at the point defect that was shaped by the inhomogeneous stacking sequence of GaN bilayers, and the electron part was diffusely centered at the low-end part of the triangular potential of the cubic part. In our case, a three-bilayer part showing the cubic stacking pattern can locally break the translation

symmetry along the stacking axis, and the different stacking sequences here would determine the relative position of electrons to the tightly localized hole at the cubic inclusion (Figure 2-13B and C). Additionally, in the second-order, the binding energy of exciton is also a function of the shape of the electron wavefunction, resulting from conduction band maximum (CBM) and the hole's Coulomb potential.

Figure 2-13. Numerical modeling of the SPEs. (A), (B) Theoretical simulation of a simple quasi one-dimensional model to show the ZPL emission coming from the cubic inclusions. The arrow is to connect the possible defect position, where the hole is tightly localized, to the related ZPL emission location in the emission spectrum. ZPL can vary a lot, the relative electron position is diffusely centered at the three bilayer cubic GaN layer which is inserted into the continuous hexagonal GaN bilayers and caused the cubic inclusions. (A) is the 2 + 1 bilayer configuration, and (B) is the continuous 3 cubic bilayers configuration. (C) If the point defect only occurred at the interface of the cubic inclusions, the generated SPEs would only have two distinctive ZPLs at ~1100 and 1350 nm. CBM and VBM denote the conduction band minimum and valence band maximum, respectively.

2.5 Outlook

Electrically triggering the telecom range RT SPEs is the most direct application [29], since the GaN is a mature semiconductor material used to make blue LEDs for industrial applications. Such SPEs would surely open a new path for the on-chip quantum simulators [93, 94, 108-111] or other practical quantum technologies [15, 20, 95, 112-114]. Based on previous works done in the conventional InAs\GaAs quantum dots [29], the success of RT electrically driven GaN telecom range SPEs necessarily requires a p-doping and n-doping layer to form a hole transport layer and electron

tunneling layer, respectively, for a device. Thus, locating the observed SPEs in a certain depth is the first key to be obtained. Then, we can control the generating SPEs in GaN at a certain layer like in conventional quantum dots [115] and use the mature GaN semiconductor fabricating technology to make geometry structure to enhance the emission, even though it is going through several layers.

Since the source of the SPEs remains unknown, it is valuable to study the formation mechanism of the SPEs in GaN. We can prepare several samples with different parameters, such as the thickness of (Mg)-doped GaN layer or different doping components, to investigate the locating depth of the SPEs. Hopefully, more statistics such as the ZPL locations for the material-based experiments can give a clue for the origin of such SPEs.

The most interesting and the most difficult study might be observing the fine-structure splitting (FSS) of such SPEs. Previously, the research on the FSS of conventional InGaAs, or other III-IV quantum dots, opened a wide door and supplied information about the spin of quantum dots' energy levels [39, 40] in that field. We have also tried to use a technique called optically detected magnetic resonance (ODMR) to observe the energy splitting of the ZPL under the external field when scanning the add-on microwave frequency, but we did not see any resonance. Thus, direct detection based on spectral signal is the last tool for the FSS study. A tunable, covering 1000 to 1300 nm, and finesse, FWHM no larger than 250 MHz, laser is required to use as a resonant excitation source. Moreover, we need to use two sets of quarter waveplates and half waveplates to put in the excitation and collection path, and then the polarized resonant spectral measurement can be done. The GaN sample is better to be cooled to millikelvin level for narrowing the ZPL linewidth as best as we can, thus minimizing the scanning wavelength range of our laser to stabilize the excitation power.

Chapter 3

Room temperature single-photon emitters at telecom range based on silicon carbide

Single photon emitters play an essential role in a number of quantum information tasks [15, 116]. The most direct one is to use them as the high single photon purity light source in quantum key distributions. It is well-known that telecom wavelength photons are the most desired among UV, visible and infrared range photons due to their low transmission loss in long silicon fibers. This chapter presents a study of bright room temperature telecom range single-photon emitters discovered in cubic silicon carbide (3C-SiC). Similar to our previous work (Chapter 2) done in GaN infrared quantum emitters, these emitters are found to be photostable and bright at room temperature with a count rate of $\sim$ MHz.

3.1 Optical characterization for the SPEs.

The basic characterization was carried for RT telecom range SPEs in silicon carbide, and it included PL spectrum both at LT and RT, saturation curve, power-dependent $[g^{(2)}(\tau)]$, lifetime measurement, photostability, and the polarization of emission and excitation.

3.1.1 Sample description and experimental setup.

An epitaxial layer was used to grow the high-purity 3C-SiC on a silicon substrate for ensuring a low background level for single-photon emitters (SPEs) detection. It also provides a natural way to obtain thin membranes for photonics and micromechanics applications rather than the thinning of bulk crystals [117]. A homemade confocal microscopy system (Figure 2-1) was used for the optical experiments. For the room temperature experiments, a 950 nm diode laser was used to excite the emitters through a high-NA (1.35) oil objective (Nikon). We collected the emission passing through a 1000-nm dichroic mirror, and a 1000-nm long pass filter, by a single-mode fiber. The fiber was connected to a (Princeton) liquid nitrogen cooling spectrometer or to two-channel super-conducting-single-photon detectors (SSPD, Scontel) for PL spectrum characterization or a Hanbury-Brown and Twiss (HBT) experiment. For the cryogenic experiments, another confocal microscopy system with an infrared air objective with N. A. of 0.65 was used, and the 3C-SiC sample was loaded in a closed-cycle cryostat (Montana Instruments). Its setup was the same as the one for GaN emitters at LT (Figure 2-1), and it also used a pair of silver-coated Galvo mirrors to do the fine scanning when the sample was roughly moved and stably stopped by the attocube stepper. Thus, at LT, we first moved the localized SPEs inside the view scale of our objective, and then used the Galvo mirror to do a fine scanning for a whole area inside the view scale (diameter around 30 μm) to precisely locate the SPE that we meant to investigate.

3.2 Basic Optical characterization for the SPEs.

We followed a sequence of steps to optimize our optical setup: basic alignment for the confocal microscopy system, 2D fluorescence mapping to locate the quantum emitters, PL check for the emission from the single emitters, $[g^{(2)}(\tau)]$ measurements to confirm the emitter at a single photon source level, and realigning to optimize to reach the maximum intensity from the located SPE. Then, we looked for the bright single-photon emitters and did the characterizations for them, including polarization and power saturation.

3.2.1 Locating the bright SPEs

Figure 3-1 (a) shows the two-dimensional photoluminescence mapping containing four single SPEs, SPE1, SPE2, SPE3, and SPE4, and the SPE4 intensity is optimized with the photon counts reaching around 580 K counts/s at the CW excitation power 2 mW. The white circles mark out the locations of the four SPEs. When we moved the excitation beam to the SPE4 location and took a $[g^{(2)}(\tau)]$ measurement under a smaller CW excitation power of 0.2 mW, we obtained $g^{(2)}(0) = 0.05 \pm 0.03$ (Figure 3-1 (d)), well below the nonclassical limit 0.5, indicating SPE4 has a good single-photon purity. Thus, SPE4 is a single-photon emitter. We repeated the $[g^{(2)}(\tau)]$ measurement under a pulse excitation at the power of 50 μ W and obtained $g^{(2)}(0) = 0.13 \pm 0.02$ (Figure 3-1 (e)). This is higher than that at 0.2 mW of CW excitation, and it might be caused by a stronger excitation triggered by the pulse laser, as the actually short pump time (pulse laser power was read out as an averaged value, and the 12.5 ns time window of the actual pump is much shorter than 1 second average time of the power meter). Therefore, the bunching becomes more obvious and $g^{(2)}(0)$ becomes larger as the CW power increases.

Similar to the simulation models used for $[g^{(2)}(\tau)]$ results of GaN defect SPEs (Figure 2-3B), we used a three-level mode to fit all the CW $[g^{(2)}(\tau)]$ measurements here. The formula for background correction is:

$$g^{(2)}(\tau) = [g^{(2)}(\tau) - (1 - \rho^2)]/\rho^2 \quad \text{Equation 3-1}$$

Where, $\rho = \frac{s}{s+b}$, s is the intensity of the SPE4 emission signal count, and the b is the background noise count [100, 117].

The equation for the three-level model is:

$$g^{(2)}(\tau) = 1 - (1 + a)e^{-\frac{|\tau|}{\tau_1}} + ae^{-\frac{|\tau|}{\tau_2}} \quad \text{Equation 3-2}$$

where a, τ_1, τ_2 are all power-dependent parameters.

Figure 3-1. 3C-SiC quantum emitters. (a) A two-dimensional fine scan for a $25 \times 25 \mu\text{m}^2$ area with the scale bar at $5 \mu\text{m}$ at RT. The CW excitation used was a 950 nm diode laser at 2 mW. SPE1, SPE2, SPE3, and SPE4 are four single-photon emitters. SPE4 is the brightest, with the count ~ 580 K counts/s. (b) Three representative PL spectra of the quantum emitters at RT. (c) Two typical PL spectrum of other two single emitters at cryogenic LT. (d) Second-order correlation measurement for SPE4 unfiltered wide emission with $g^{(2)}(0) = 0.05 \pm 0.03$ under 0.2 mW CW excitation. The black data points are dealt with background correction with Equation 3-1 and normalization. The solid red curve is the fitted using Equation 3-2. (e) Second-order correlation measurement for SPE4 emission when exchanged to pulse excitation at 50 μW . At zero-time delay, $g^{(2)}(0) = 0.13 \pm 0.02$.

Moreover, the PL characterizations were done for the emitters at the telecom range (Figure 3-1(b) and (c)). The three representative PL for SPEs at RT show the center wavelength at 1085, 1188, and 1250 nm, with a broad linewidth. Additionally, we measured other emitters at RT and found that the center wavelength of different SPEs at the telecom range varied from 1080 to 1265 nm, with the corresponding FWHM range from 180 to 194 nm. Figure 3-1 (c) represents two typical PL of single emitters at cryogenic temperature 4K, and the linewidths of them are both around 100 nm. Therefore, PL of SPEs is still broad and show no sizable decreasing of linewidth compared to those at RT. These indicate that the broad linewidth of our discovered telecom range SPEs is not caused by the phonons. Figure 3-1c shows that the PL of an SPE can have multiple sharp peaks at LT, and we think this might be attributable to the emission coupling to the phonon modes.

3.2.2 Property characterization for SPE

We characterized SPE4 in detail by investigating its saturation behavior, lifetime and photon stability. Figure 3-2 (a) shows the PL of SPE4 emission, and the FWHM is 180

nm. Figure 3-2 (b) shows the lifetime measurement result, and the lifetime value is estimated to be around 1 ns. Thus, the IRF, in the order of ps, is undoubtedly much shorter than it. Therefore, instead of using a convoluted IRF function for fitting, we just used a single exponential decay to fit the lifetime data, and the result is 0.81 ± 0.01 ns. Figure 3-2 (c) shows the curve is the fitted result by $I(p) = \frac{I_s}{1 + \frac{p}{P_0}}$, where I_s is the maximum emission photon counts and P_0 is the saturation power. Based on the fitted curve, we obtained 1.36 Mcps for I_s and 3.0 mW for P_0 . Finally, Figure 3-2 (d) shows the stability measurement result of SPE4 emission at 1.5 and 8.5 mW with the sapling time bin size of 100 ps. As there is no photon bleaching or blinking ever appeared in the histogram, the SPE4 is quite stable at room temperature.

Figure 3-2. Optical characterization for the SPE4. (a) RT PL spectrum of SPE4. (b) The lifetime measurement was done by using the pulse laser with a repetition ratio of 80 MHz. (c) Saturation curve measurement of SPE4 emission count, with the CW power increasing from microwatts to a maximum 10 mW. (d) Photostability data for SPE4 emission under two different CW excitation powers of 1.5 and 8.2 mW are plotted in solid black and blue lines, respectively. The time bin for 1.5 mW is 100 ms, and for 8.2 mW is 400 ms. All the data are acquired at RT.

The power-dependent $[g^{(2)}(\tau)]$ measurements were done for SPE4 at CW excitation powers of 0.2, 1.1, and 2.7 mW, with time resolution 256 ps. Our power-dependent $[g^{(2)}(\tau)]$ results were similar to those in SiC [100, 118-120], and there exists a metastable state [100, 118-120] between exciton and ground state of SPE4 (Figure 3-3

(a)). The three-energy-level model scheme is shown in Figure 3-3 (a): levels 1, 2, and 3 are the ground, excited state, and metastable states, respectively. The k_{ij} means the pump or decay ratio from level i to level j , and it is related to the three key power-dependent parameters, a , τ_1 , and τ_2 , through the following equations:

$$a = \frac{1 - \tau_2 k_{31}}{k_{31}(\tau_2 - \tau_1)} \quad \text{Equation 3-3}$$

$$\tau_{1,2} = \frac{2}{A \pm \sqrt{A^2 - 4B}} \quad \text{Equation 3-4}$$

Where $A = k_{12} + k_{21} + k_{23} + k_{31}$, $B = k_{12}(k_{23} + k_{31}) + k_{31}(k_{21} + k_{23})$.

Figure 3-3. Power-dependent CW correlation measurement of SPE4 emission and the three-level model scheme. (a) $|1\rangle, |2\rangle$ refers to the ground and excited states of the SPE4, respectively, and $|3\rangle$ refers to a metastable state that provides a non-radiative decay path to the ground state. $k_{ij}, i, j = 1, 2, 3$ means the ratio for electrons to go from $|i\rangle$ to $|j\rangle$. (b) Second-order correlation measurements of SPE4

emission under three CW excitation powers 0.2, 1.1, and 2.7 mW. (c), (d), and (e) refer to the changes of the three key parameters, a , τ_1 , and τ_2 , with the different CW excitation powers. The red curve is the fitting result by the combination of an exponential decay and a linear function.

Through fitting the $[g^{(2)}(\tau)]$ by Equation 3-2 under three different powers (Figure 3-3 (b)), a , τ_1 , and τ_2 , were obtained for different CW powers (Figure 3-3 (c), (d), and (e)). Then, k_{21} and k_{23} can be calculated in using Equation 3-3 and Equation 3-4. Therefore, the lifetime of SPE4 emission was derived from the $[g^{(2)}(\tau)]$ fitting parameters: $\tau = (k_{21} + k_{23})^{-1} = 0.7 \pm 0.05$ ns that is close to our experimntally measured lifetime value 0.81 ± 0.02 ns (Figure 3-2(b)).

Lastly, we did the polarization measurement for SPE4. We fixed the excitation beam as a linearly polarized light and measured the collected emission intensity with different linear polarization angles to check the emission polarizability. Vice versa, the polarization of the excitation was measured when fixing the collection linear polarization. A half-wave plate and a polarizer were used to ensure the light passing through was a linear polarized light.

Figure 3-4a and b show the polarization of the emission and excitation of SPE4, and the fitting patterns indicate that the SPE4 consists of a single polarization dipole. The fitting formula was $I = \alpha + \beta \sin^2(\theta + \phi)$, where α , β , and ϕ are the fitting parameters. The polarization visibilities for SPE4 in emission and excitation calculated by $\eta = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min})$ were around 98% and 97%, respectively. Not only for SPE4 but also for the other SPEs, the degrees of polarization all exceed 95%. These indicate that the infrared emitters in 3C-SiC have a single linearly polarized dipole transition. However, the linear polarization angles of excitation and emission dipole show random distribution (Figure 3-4 (c)).

Figure 3-4. Polarization characterization of SPEs. (a) The polarization measurement results of SPE4's emission and excitation. The blue data points are for the excitation and the red for the emission. The data were fitted using $\cos(\theta)^2$, and the fitting patterns show single-polarization dipoles in both excitations

and emissions. (c) The angles between the maximum emission and maximum excitation polarizations for the other twelve SPEs were measured, and they show a random distribution.

3.3 The source of the 3C-SiC SPEs

Because it is certain that the SPEs in 3C-SiC were related to some unknown defects that existed, we tried to find the origination of the SPEs in two steps: first was to locate the layer where the SPEs are formed, and the second was to change parameters of ion irradiation to influence the telecom range SPEs in 3C-SiC.

For the first, we tried to locate the exact layer containing telecom range SPEs in 3C-SiC by repeating fluorescence mappings for the samples that were etched in the usage of reactive ion etching technique at different depths of 200, 300, and 1 μm . We found that only the sample etched at 1 μm showed no PL emission counts. This indicates that the SPEs are right in the 3C-SiC epitaxy film.

For the second, we irradiated the samples with 1 MeV electrons at a range of fluences (1e^{15} to $1\text{e}^{16} \text{ cm}^{-2}$), and annealed them at 800°C under vacuum for 0.5 hour. The 2D PL mappings we obtained for the samples (Figure 3-5) show that the quantum emitters' emission intensities are similar: the highest counts are the same at 100 K counts per second in APD, and the single ones emit photons at 50 ~100 K counts per second. We also checked the PL spectra for single-photon emitters under different doses of irradiations and observed that the center wavelengths of them did not show an obvious difference, either.

Figure 3-5. 2D PL mapping obtained using the same confocal setup for different doses of ion irradiations. All four samples have the same range for the count intensities, which indicate the ion irradiations did not influence the infrared SPEs in 3C-SiC

The Photoluminescence Excitation (PLE) spectrum measurement [121, 122] was also performed for another SPE to see whether we could detect the fine energy level structure. The PLs (Figure 3-6) shows the SPE emission centered at around 1275 nm (0.97 eV) with linewidth 181 ± 3 nm. Thus, we set the scanning range from 940 to 990 nm to cover the broad PL peak while keeping the power of this tunable excitation laser at 0.5 mW. Our data show just a simple broad peak (Figure 3-6), which indicates that the SPE does not have a fine energy level structure. Therefore, the PLE spectrum of this SPE is asymmetric, and we believe this originated from the complex form of the vibronic bands [123]. Additionally, the maximum wavelength position in the PLE spectrum shows a blue shift (refer to the drawings in the left compared to the right of Figure 3-6) compared to the PL (Figure 3-6), which can be explained by Frank-Condon principle [124].

A simple energy level model of the SPE (refer to the drawings in the middle of Figure 3-6) is shown here: the SPE has three energy levels, two excited (E_1 , E_2), and one

ground (E_g); it is off-resonant excited from E_g to E_2 ; then, it relaxes to E_1 ; and during its return from E_1 to E_g , it emits a photon.

Figure 3-6. PLE spectra measurement result. The left side is the raw data of photon counts versus the tuning wavelength of the CW excitation laser diode. The power remained stable at 0.5 mW during the measurement. The right side is the PL spectrum of the tested SPE. There is only one broad peak observed in the PLE spectra, which can be fitted with a Lorentz waveform similar to the solid blue curve of PL. Thus, it is just a simple two-level of the SPE, and we always did the above bandgap excitation to the SPE, from E_g to E_2 , and collect emission from E_1 , relaxed from E_2 , to E_g .

3.4 Outlook

For our 3C-SiC infrared SPEs, the polarization degrees are high ($>95\%$), the single photon purity ($g^{(2)}(0)=0.05\pm0.03$) is good, and the maximum count can reach more than 1 M counts per second. These suggest that they are ideal candidates for the QKD [15, 125]. However, the source of this kind of SPEs remains unclear even after our experiments in Section 3.3 were done, and it must be found before real applications. Theoretical modeling is further required to explain how the SPEs are formed and what mechanisms control their formation and properties. The electrically driven of SPEs in 3C-SiC is also worth trying because the fabrication technology for SiC is not complicated.

Chapter 4 Investigating

single-photon source property of

Perovskite quantum dots

It is well-known for conventional III-V quantum dots that the singlet states are radiative, and the triplet states are nonradiative due to the spin selection rule [40, 126-129]. Additionally, Hund's rule [130, 131] predicts that the lowest-energy exciton is a poorly emissive triplet state for organic semiconductors. Thus, it seems certain that the triplet states are dark for both organic and inorganic semiconductor quantum dots. However, the perovskite quantum dots (PQDs) break this rule with a bright triplet state and a dark singlet state, which is because the spins of electrons are strongly coupled to orbital momentum and result in an s-symmetry of the valence band [57]. Therefore, PQDs have attracted people to study their unknown features distinguished from the other semiconductor nanocrystals. Up to now, debate still exists in whether the triplet state is really below the singlet state, and the experiment result contradicts the theory prediction [57, 132]. Thus, we began the study with basic optical characterization for our own synthesized CsPbBr₃ quantum dots, and we observed a giant super-bunching in second-order correlation measurement for the unfiltered emission of a single PQD, which had never been observed for the conventional III-V quantum dots. Interested in the mechanism behind the super-bunching, we carried out power and temperature-dependent measurements for the bunching [$g^{(2)}(\tau)$]. We hypothesized the bunching was caused by the correlated pair of exciton and biexciton, and we did cross-correlation [$g^{(2)}(\tau)$] for differently isolated emission photons. Furthermore, we observed the bunching was directly bond to the correlated pair of excitons at the main peak and biexcitons in the lower energy tail. Finally, we built two theoretical models to simulate the results using a three-level cascaded emission of a single PQD, and the simulation indicated one model was physically reasonable: the generation of photon twins of exciton and biexciton was caused by another nonradiative path. Besides, the

temperature-dependent $[g^{(2)}(\tau)]$ and time-resolved measurement for biexciton and exciton also supported that model experimentally. Therefore, we believed there was a related dark state that made the nonradiative path dominate for neutral exciton's decay and thus enhanced the probability of generating timely entangled exciton and biexciton pair, at low excitation power and cryogenic temperature. In the rest of this chapter, we will present our studies, and at the end, we will discuss about the potential experimental explorations to be done for real-world applications of PQDs.

4.1 Theoretical prediction for the bright triplet exciton states and dark singlet state in cesium lead halide perovskites

Based on the theoretical works [133-138] about the conventional III-V semiconductors, a multi-band effective-mass Hamiltonian describing the electrons and holes bandgap edge energies of the bulk crystals was used to obtain effective energy-band parameters via the first-principle description. Then, all the key characteristics, such as optical transition energies, fine structure, polarization properties, and the radiative lifetime, could be calculated.

4.1.1 Four-band model and Fine structure

It is well-known that the R-point of the Brillouin zone is isomorphic to the Γ -point in a cubic semiconductor crystal [133], which leads to the dispersion of electrons and holes at the R-point. A familiar $8 \times 8 \mathbf{k} \cdot \mathbf{p}$ Hamiltonian matrix characterizing the band edge of direct-gap at the Γ -point is used here to describe the dispersion.

Notation: The derivation of Hamiltonian is given below using standard notations [136, 137],

- $|\uparrow\rangle_e$: spin-up electron states
- $|\downarrow\rangle_e$: spin-down electron states
- $|\uparrow\rangle_h$: spin-up hole states

- $|\downarrow\rangle_h$: spin-down hole states
- $|X\rangle, |Y\rangle, |Z\rangle$: shorthand notations for the $\mathcal{J}_3$ wavefunctions
- $|S\rangle$: wavefunction of s-symmetry
- $\hat{p}_i$: the momentum operator, thus $\hat{p}_x, \hat{p}_y$ and $\hat{p}_z$ correspond to three crystal axis directions
- P : $P = -i\langle S|\hat{p}_z|Z\rangle$ is the Kane matrix element
- $E_{c,v}$: the band-edge energies
- $\gamma_{e,h}$: the remote band contributions to the effective mass value of electron and hole
- E_g : energy band gap between conduction band minimum and valence band maximum

Becker *et al.* [57] developed a four-band model specifically for perovskite nanocrystals: the description of carrier dispersion is obtained by extracting the 4×4 Hamiltonian related to the Γ_6^- and Γ_6^+ bands of the conduction and valence bands due to large spin-orbit coupling.

The Bloch wavefunctions of the electron and hole band-edge states are written as:

$$\begin{aligned} |\uparrow\rangle_e &= -\frac{1}{\sqrt{3}}[\{|X\rangle + i|Y\rangle\}|\downarrow\rangle + |Z\rangle|\uparrow\rangle] \\ |\downarrow\rangle_e &= \frac{1}{\sqrt{3}}[|Z\rangle|\downarrow\rangle - \{|X\rangle - i|Y\rangle\}|\uparrow\rangle] \\ |\uparrow\rangle_h &= |S\rangle|\uparrow\rangle \\ |\downarrow\rangle_h &= |S\rangle|\downarrow\rangle \end{aligned} \quad \text{Equation 4-1}$$

The 4×4 Hamiltonian applicable to our perovskite nanocrystal is similar to but different from the one used in [134]:

$$\hat{H} = \begin{pmatrix} E_c + \gamma_e \frac{p^2}{2m_0} & 0 & -\frac{1}{m_0} \frac{iP}{\sqrt{3}} p_z & -\frac{1}{m_0} \frac{iP}{\sqrt{3}} p_- \\ 0 & E_c + \gamma_e \frac{p^2}{2m_0} & -\frac{1}{m_0} \frac{iP}{\sqrt{3}} p_+ & \frac{1}{m_0} \frac{iP}{\sqrt{3}} p_z \\ \frac{1}{m_0} \frac{iP}{\sqrt{3}} p_z & \frac{1}{m_0} \frac{iP}{\sqrt{3}} p_- & E_c - \gamma_e \frac{p^2}{2m_0} & 0 \\ \frac{1}{m_0} \frac{iP}{\sqrt{3}} p_+ & -\frac{1}{m_0} \frac{iP}{\sqrt{3}} p_z & 0 & E_c - \gamma_e \frac{p^2}{2m_0} \end{pmatrix} \quad \text{Equation 4-2}$$

In contrast to the conventional III-V semiconductors, the band structure of PQDs is reversed, for the valence band is s-like symmetry. Since the energy spectrum of the carrier is isotropic at the R-point of the Brillouin zone, we can take p as in the z axis and change the 4×4 matrix to consist of two identical 2×2 blocks decoupled from each other:

$$\begin{pmatrix} E_g - \varepsilon + \frac{\gamma_e}{2m_0} p^2 & \frac{i}{\sqrt{3}} \frac{p}{m_0} p \\ -\frac{i}{\sqrt{3}} \frac{p}{m_0} p & -\varepsilon - \frac{\gamma_h}{2m_0} p^2 \end{pmatrix} \quad \text{Equation 4-3}$$

This leads to the final result for the dispersion relation:

$$\varepsilon_{\pm} = \frac{1}{2} \left[E_g + (\gamma_e - \gamma_h) \frac{p^2}{2m_0} \right] \pm \sqrt{\frac{1}{4} [E_g + (\gamma_e + \gamma_h) \frac{p^2}{2m_0}]^2 + E_p \frac{p^2}{6m_0}} \quad \text{Equation 4-4}$$

For the selection rules, Fermi's Golden rule [139] is applied together with the notations in [57]:

$$\begin{aligned} \langle 0 | \hat{P} | \Phi_{0,0} \rangle &= \int d^3r \frac{1}{\sqrt{2}} ((\hat{K}|S\rangle|\uparrow\rangle) \hat{P} \frac{1}{\sqrt{3}} [|Z\rangle|\downarrow\rangle - (|X\rangle - i|Y\rangle)|\uparrow\rangle] \\ &\quad - (\hat{K}|S\rangle|\downarrow\rangle) \hat{P} (-\frac{1}{\sqrt{3}} [|Z\rangle|\uparrow\rangle - (|X\rangle + i|Y\rangle)|\downarrow\rangle]) \end{aligned} \quad \text{Equation 4-5}$$

Here, we used the property of the time-reversal operator $\hat{K}$: $\hat{K}|\uparrow\rangle = |\downarrow\rangle$ and $\hat{K}|\downarrow\rangle = -|\uparrow\rangle$ to calculate optical transition rate from the singlet state to the ground:

$$\begin{aligned} \langle 0 | \hat{P} | \Phi_{0,0} \rangle &= \frac{1}{\sqrt{6}} \int d^3r (\langle S | \langle \downarrow | \hat{P} [|Z\rangle|\downarrow\rangle - (|X\rangle - i|Y\rangle)|\uparrow\rangle] \\ &\quad + \langle S | \langle \uparrow | \hat{P} [|Z\rangle|\uparrow\rangle - (|X\rangle + i|Y\rangle)|\downarrow\rangle]) = 0 \end{aligned} \quad \text{Equation 4-6}$$

As the result is zero, the singlet state shall be optically passive and can be called a dark state.

We also did calculations for the optical transitions from triplet states to the ground state:

$$\begin{aligned} \langle 0|\hat{P}|\Phi_{1,0}\rangle &= \frac{1}{\sqrt{6}} \int d^3r (\langle S|(\langle \downarrow|\hat{P}[[Z]|\downarrow\rangle - (|X\rangle - i|Y\rangle)|\uparrow\rangle) \\ &\quad + \langle S|(\langle \uparrow|\hat{P}[[Z]|\uparrow\rangle + (|X\rangle + i|Y\rangle)|\downarrow\rangle)) = \frac{2}{\sqrt{6}} \langle S|\hat{P}|Z\rangle \end{aligned} \quad \begin{array}{l} \text{Equation} \\ 4-7 \end{array}$$

$$\langle 0|\hat{P}|\Phi_{1,1}\rangle = \int d^3r \langle S|(\langle \downarrow|\hat{P}[[Z]|\downarrow\rangle + (|X\rangle + i|Y\rangle)|\uparrow\rangle) = \langle S|\hat{P}|Z\rangle \quad \begin{array}{l} \text{Equation} \\ 4-8 \end{array}$$

$$\langle 0|\hat{P}|\Phi_{1,-1}\rangle = \int d^3r \langle S|(\langle \uparrow|\hat{P}[[Z]|\uparrow\rangle + (|X\rangle + i|Y\rangle)|\downarrow\rangle)) = \langle S|\hat{P}|Z\rangle \quad \begin{array}{l} \text{Equation} \\ 4-9 \end{array}$$

The result tells that the triplet states are all optically active, and they should form the fine structure for the bright excitons of a single PQD.

4.2 Synthesis Method and TEM measurement

We synthesized CsPbBr₃ nanocrystals using two different methods: Method 1 [140] to produce ensembled nanocrystals, and Method 2 [141] to made single high-quality cubic shape nanocrystals.

4.2.1 Method 1: Synthesis of CsPbBr₃ Nanocrystals from cesium oleate and PbBr₂

According to [140], the synthesis was done in two separate steps: first to prepare the Cesium oleate and lead oleate solution, and second to mix the Cesium oleate with Lead oleate to make the reaction and crystallization of PQDs happen.

Materials (Chemicals purchased and used): Oleic acid (technical grade 90%), lead bromide (PbBr₂, 98%), octane (98%), Cesium carbonate (Cr₂CO₃, 99.995%, metal

basis), and octadecene (ODE), technical 90% were purchased from Sigma-Aldrich. Toluene (HPLC grade) was purchased from Honey Burdick & Jackson. All chemicals were used directly without further purification.

Cesium oleate solution: Cs_2CO_3 (0.814 g) was loaded into a 150 mL 2-neck flask in a glovebox environment. Then, we added ODE (30 mL) and oleic acid (2.5 mL) in the flask, evacuated the mixture at room temperature until the first gas evolution subsided, and then further evacuated for 1 hour at 120°C. Then, the flask went through purging with N_2 for 10 min and then evacuation for 15~20 min at 120°C alternately 3 times to remove moisture and O_2 . Then, the solution was heated under N_2 until all Cs_2CO_3 reacted with Oleic acid (OA). Finally, the solution was kept at 150 °C to avoid solidification before injection.

Synthesis of CsPbBr_3 QDs: 100 mL of ODE, 10 mL of OAm, 10 mL of OA, and 1.38 g of PbBr_2 were loaded into a 250 mL flask inside a glovebox environment. Then, the flask was evacuated at RT until the first gas evolution subsided and vacuumed again at 120°C for 30 min. As in cesium oleate solution preparation, the flask went through purging with N_2 for 10 min and then evacuation for 15~20 min at 120°C alternately 3 times to remove moisture and O_2 . Next, the solution was heated to 180°C under nitrogen flow, and 8 mL of cesium oleate solution (0.08 M in ODE) was quickly injected into it. After 5 seconds, the reaction mixture was immediately cooled in an ice-bath.

4.2.2 Method 2: Synthesis of CsPbBr_3 Nanocrystals from cesium and lead oleates and TOPBr_2

The method followed [141] requires three components - Cesium and lead oleates, and TOPBr_2 - prepared for the reaction to produce CsPbBr_3 quantum dots.

Chemicals purchased and used: Lead(II) acetate trihydrate, OA (oleic acid 90%), triethylamine, cesium carbonate (Cs_2CO_3), Br_2 , ethyl acetate (anhydrous, 99.8%), ODE (1-octadecene), TOP (trioctylphosphine), C_3 -sulfobetaine (3-(N,N-dimethyloctadecylammonio) propanesulfonate) >99% and toluene(anhydrous, 99.8%) were purchased from Sigma Aldrich.

TOPBr_2 solution: It was prepared by mixing TOP (6 mL, 13 mmol, 1eq) with Br_2 (0.6 mL, 11.5 mmol, 0.88 eq) in a 50 mL Schlenk flask under N_2 . Since the reaction

between the two components is exothermic and requires vigorous stirring due to the final product being highly viscous (white, not jelly, almost solid), and the flask was immersed in an ice-water bath during the whole reaction process. After the reaction completed, the product was dissolved in 18.7 mL toluene to produce a 0.46 M light orange stock solution to use as a precursor for injection.

Cesium Oleate solution: Cs_2CO_3 (1.628 g, 5 mmol, containing 10 mmol Cs, 1eq), oleic acid (5 mL, 16 mmol, 1.6 eq), and ODE (20 mL) were mixed in a three-neck flask and evacuated at room temperature until the first gas evolution subsided and then heated up to 120°C while kept under vacuum for 1 hour. Afterward, the flask was purged with N_2 for 10 min and then placed back under vacuum until first gas evolution subsided, and this process of alternately applying vacuum and N_2 was repeated 3 times to remove moisture and O_2 . Finally, this yielded a 0.4 M solution of Cs-oleate in ODE. The solution turned solid when cooled to room temperature, and we stored it under nitrogen.

Lead(II)-oleate solution: Lead(II) acetate trihydrate (4.6066 g, 12 mmol, 1 eq), oleic acid (7.6 mL, 24 mmol, 2eq), and ODE (16.4 mL) were evacuated in a three-neck flask at room temperature until first gas evolution stopped and then heated up to 120°C while kept under evacuation for 1 hour. Afterward, the flask was purged with N_2 for 10 minutes and then placed back under vacuum until first gas evolution subsided, and this process of alternately applying vacuum and N_2 was repeated 3 times to remove moisture and O_2 . This yielded a 0.5 M solution of Pb-oleate in ODE. The solution turned solid when cooled to RT and we stored it under nitrogen.

Synthesis of CsPbBr_3 NCs: For a synthesis of CsPbBr_3 NCs covered with zwitterionic ligands, N-(dimethyloctadecylammonio)-propanesulfonate (0.2415 g, 0.5 mmol), lead oleate (5 mL, 0.5M in octadecene, 1.6 eq), Cs-oleate (4 mL, 0.4 M in octadecene, 1 eq), and octadecene (50 mL) were added into a 150 mL three-neck flask. Before this, the oleate solutions were heated up to 120°C to become homogeneous and transferred into the reaction flask. Then, mixed solution in the flask went through the same alternately vacuuming (3~5 mins for our system) and N_2 purging processes (1 min for our system) 3 times at temperature 100-180°C to ensure the remove of moisture and O_2 before the final crystallization of PQDs. To obtain NCs with a cubic size of $12 \times 12 \times 12$ nm, the mixture was heated to and kept the temperature at 180°C before the injection of TOPBr_2 . Once we injected trioctylphosphine-bromine adduct (TOPBr_2 , 5

mL, 0.5 M in toluene), we gave 5 seconds for crystallization, and then the reaction flask was immediately cooled to room temperature in an ice-bath.

4.2.3 Isolation and Purification process of PQDs

Isolation: The synthesized CsPbBr₃ QDs solutions from the two methods were centrifuged at 29464 g for 10 minutes. Next, the supernatant was isolated, and the precipitate was discarded, because the excess Cs-oleate and Pb-oleate precipitated while the QDs dissolved in ODE at room temperature. Afterward, it was mixed with 12 mL of ethyl acetate, acting as a low polarity non-solvents, to wash QDs from the reaction solution ODE, and the mixture was centrifuged at 29464 g for another 10 minutes. Then, we collected and added the precipitates to a 3 mL toluene while discarded the supernatant. Additionally, a method in [58] to further purified CsPbI₃ QDs were applied to our CsPbBr₃ QDs. We kept the solution of colloidal CsPbBr₃ QDs at 4°C for 48 hrs to precipitate excess Cs-Oleate and Pb-Oleate solidified at low temperatures and isolated PQDs in the supernatant.

Purification: To purify PQDs, we repeated precipitation in ethyl acetate and redispersion in toluene with the ratio of toluene to ethyl acetate at 1:2 by volume. In the first run, 6 mL ethyl acetate and 3 mL toluene were used, and centrifugation was at 29464 g for 10 minutes. In the second and the third run, centrifugation times were 3 minutes and 1 minute, and the volumes of ethyl and volume were half of the those in the first run, respectively.

4.2.4 TEM result

We did transmission electron microscopy (TEM) to check the synthesis's product and to obtain an insight into the crystalline structures of the CsPbBr₃ nanocrystals. A droplet of the purified final product of purified PQDs in Section 4.2.4 was transferred to a copper grid coated with a very thin amorphous carbon film, the TEM grid. We inserted the sample into the microscope chamber after the solvent was evaporated at room temperature, and we obtained the images (Figure 4-1). By using appropriate

image analysis software [142], we measured the lateral sizes of 65 different nanocrystals and calculated their mean value to be 10.61 nm.

Figure 4-1. TEM image of CsPbBr₃ QDs at an acceleration voltage of 100 kV and in a normal operation mode for two different magnifications. (A) The bright-field view to the PQDs with the scale bar 100 nm. (B) The bright-field view to the PQDs with the scale bar 50 nm. In addition, the high dose here is due to that the solution was not diluted to a single quantum dot level prior to the TEM analysis.

The microscope equipped with an X-ray spectrometer and an electron beam was used to perform energy dispersive spectroscopy (EDS). Generally, if a sample is bombarded with a high-power electron beam, at least one electron is inevitably ejected from the inner shell of an atom. Then, the same atom's outer shell electrons would fill the vacancy left at the inner shell through a decay, which produces an electromagnetic radiation in the X-ray range [143]. As the X-ray radiation's energy is dictated by the fine structure of the atom, which is unique for every material, we can get a spectroscopic analysis of the emitted radiation that provides qualitative information about the composition of the sample. Figure 4-2A shows a TEM micrograph of the CsPbBr₃ nanoparticles, and Figure 4-2B, C, and D show the detected intensities of the characteristic X-ray emission lines of Cs, Pb, and Br, respectively. These results indicate that the product of our synthesis has the correct chemical composition Cs, Pb, and Br. We detected copper and carbon traces, and the photos are not shown here but available upon request. The copper was attributed to the structure of the TEM grid, and the carbon to both the thin carbon film of the TEM grid and the organic capping ligand. Therefore, our EDS results suggest that our synthesis and purification to get CsPbBr₃ QDs were successful.

Figure 4-2. EDS signal analysis with comparison to the original TEM image for the same view to an ensemble of our produced PQDs. (A) TEM image with the scale bar 50 nm. (B) Cesium EDS signal. (C) Lead EDS signal. (D) Bromine EDS signal.

Then, we zoomed in and got the atomic resolution ADF-STEM imaging of our PQDs synthesized with Method 2. Since only two shapes, cubic and orthorhombic, are possible for the CsPbBr_3 nanocrystals, and we could calculate the lattice spacing distances between the planes from the related parameters [57, 141]. Then, we compared these theoretical lattice spacing values with our actual measured distances to know which one, the cubic or orthorhombic scenario, would match with the experimental results.

The formula [57, 141] used for our calculations is:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \text{Equation 4-10}$$

with h ; k ; l are the Miller indices of the corresponding plane [144].

We got the fast Fourier transform (FFT) of the TEM image for our CsPbBr₃ nanocrystals as in [145] to compare with the simulated predictions for the cubic and orthorhombic cases. Figure 4-3 shows three different TEM images with the corresponding FFT results; the bright dots mean the heavy atoms that scatter electrons in the lattice. The values of lattice parameters for cubic CsPbBr₃ QDs were $a = b = c = 5.86 \text{ \AA}$ [146], and for orthorhombic $a = 8.25 \text{ \AA}$, $b = 8.19 \text{ \AA}$, and $c = 11.77 \text{ \AA}$ [60].

Figure 4-3. High-angle annular dark-field scanning TEM micrograph. (A), (C), and (E) Zoom-in pictures with scale bar 5 nm for different quantum dots. (B), (D), and (F) The corresponding FFTs for (A), (C), and (E).

Our measured data and the related plane for the three different nanocrystals in Figure 4-3 are summarized in Table 4-1, Table 4-2, and Table 4-3.

Point	Measured interplanar distance (Å)	Measured angle (°)	Corresponding cubic plane	Corresponding orthorhombic plane
1	5.989	0	[1 0 0]	[1 1 0]
2	6.095	88.97	[0 1 0]	[1 $\bar{1}$ 0]
3	4.312	43.97	[1 1 0]	[2 0 0]
4	2.995	89.92	[0 2 0]	[2 2 0]
5	2.678	83.19	[1 2 0]	[3 1 0]
6	2.156	44.70	[2 2 0]	[4 0 0]

Table 4-1. Distances and angles between the planes of the nanocrystals shown in Figures 3A, and 3B. Only cubic phase shows right plane families [x y z] set to the measured interplanar distance, and orthorhombic phase presents wrong plane families [x y z] set, not corresponding to actual plane measured.

Point	Measured interplanar distance (Å)	Measured angle (°)	Corresponding cubic plane	Corresponding orthorhombic plane
1	5.974	0	[100]	[1 1 0]
2	5.973	91.13	[010]	[1 $\bar{1}$ 0]
3	4.304	45.01	[110]	[2 0 0]
4	2.960	90.00	[020]	[2 2 0]
5	2.404	64.6	[120]	[3 1 0]
6	2.142	44.80	[220]	[4 0 0]
7	1.160	101.24	[-150]	

Table 4-2. Distances and angles between the planes of the nanocrystals shown in Figures 3C, and 3D. Only cubic phase shows right plane families [x y z] set to the measured interplanar distance, and orthorhombic phase presents wrong plane families [x y z] set, not corresponding to actual plane measured.

Point	Measured interplanar distance (Å)	Measured angle (°)	Corresponding cubic plane	Corresponding orthorhombic plane
1	5.988	0	[1 0 0]	[1 1 0]
2	0,6082	88,280	[0 1 0]	[1 $\bar{1}$ 0]

3	0,4194	44,703	[1 1 0]	[2 0 0]
4	0,3059	89,095	[0 2 0]	[2 2 0]
5	0,2490	61,670	[1 2 0]	[3 1 0]
6	0,2207	44,289	[2 2 0]	[4 0 0]

Table 4-3. Distances and angles between the planes of the nanocrystals shown in Figures 3E, and 3F. Only cubic phase shows right plane families [x y z] set to the measured interplanar distance, while and orthorhombic phase presents another wrong plane families [x y z] set, not corresponding to actual plane measured.

As for the theoretical predictions, we calculated the interplanar distances [57, 141] for different planes set: [1 0 0], [0 1 0], [1 1 0], [0 2 0], [1 2 0], [2 2 0], and [-1 5 0], and we summarized the results in Table 4-4.

Plane	Cubic phase interplanar distance (Å)	Orthorhombic phase interplanar distance (Å)
[1 0 0]	0.6017	0.8260
[0 1 0]	0.6017	0.8210
[1 1 0]	0.4255	0.5823
[0 2 0]	0.3009	0.4105
[1 2 0]	0.2691	0.3676
[2 2 0]	0.2127	0.2911
[-1 5 0]	0.1180	0.1610

Table 4-4. Theoretically calculated parameter values. The calculated interplanar distances of cubic and orthorhombic phase configurations are presented. In total, there are generally seven directions for the CsPbBr₃ nanocrystal lattice structure.

The measured interplanar distances of our PQDs are compatible with the predicted cubic lattice values and incompatible with the orthorhombic values (Table 4-1, Table 4-2, Table 4-3, and Table 4-4). Therefore, our PQDs have cubic phase lattice structure. In addition, the edges of our PQDs are merged and connected with each other (Figure 4-1A, C, and E). This may be attributed to a lattice distortion created by the highly energetic electron beam [147], particularly when using TEM to scan. Similar phenomena were observed solely due to exposure to ambient light [148]. Moreover, oxygen and humidity are detrimental to the photoemission properties due to the activation of trapping defects at the surface of the nanocrystal [149]. Therefore, even with zwitterionic ligands, CsPbBr₃ nanocrystals are unstable under atmospheric

conditions. Thus, we kept everything under a nitrogen environment and low light exposure throughout the synthesis.

4.2.5 Spin-coating PQDs on a silicon substrate

At the end of purifications in Methods 1 and 2, the concentration of PQDs was 0.25 M in toluene. We diluted them in the following 3 steps, because single nanocrystal spectroscopy required QDs concentration in nM. The first step was transferring 20 μ L purified QDs 0.25 M in toluene solution, into 5 mL toluene, and then mixing the CsPbBr₃ nanocrystals in solution using a magnetic stirrer bar. The second step was transferring 5 μ L solution from the first step into 5 mL toluene and mixing them using another stirrer bar. The third step was transferring another 5 μ L solution from the second step into 5 mL 3% polystyrene in toluene by weight. The polystyrene was to form a protecting layer to prevent the PQDs from direct contact with water and oxygen in the environment.

we used the 1 nM CsPbBr₃ PQD solution for spin-coating at 5000 rpm on a 3- μ m-thick silicon wafer with a 285 Å $\pm$ 5%-thick SiO₂ layer to make a thin layer for single quantum dot characterization at cryogenic temperature. The cut-off size of the silicon substrate was about 0.7 $\times$ 0.7 cm, and the corresponding drop volume of the final PQDs solution was 10 μ L.

Additional information: Based on [141], the purities of our PQDs from the purification should be about 70%, and the size of CsPbBr₃ nanocrystal can be tuned between 10 and 15 nm. The sizes of the PQDs correspond to the neutral exciton emission lines from 470 to 530 nm. Therefore, we can tune the PQDs exciton emission line by changing the reaction temperature from 130-180°C to influence the grown size of PQDs.

For the single-photon property optical experiment, the dissolved CsPbBr₃ QDs in toluene was re-dispersed in solutions of 3% polystyrene in toluene by weight, to dilute to nanomolar concentration as stated previously. Then, the solution was spin-coated at 5000 r.p.m on the Silicon substrate.

4.3 Experimental Setup

To analyze the exciton fine structure of CsPbBr₃ QDs, we had to find a single QD first. Therefore, we used a confocal setup (Figure 4-4) to do photoluminescence mapping and find out the dots singly located. Additionally, we set two collection arms: one directly went to the spectrum and the other one to the APD, or both to two APDs for doing a second-order correlation function measurement. We used two 50/50 visible (400-700 nm) non-polarizing cube beam splitters: one to split two collection arms before the tunable filters, and the other to separate the collection and excitation path.

Figure 4-4. The Optical Set-up Scheme. Three beam-splitters used are all non-polarizing 400-700 nm with a 30 mm cage. A CW laser with a center wavelength of 402 nm or a pulse laser with an 80 MHz repetition ratio centered at 394 nm is ready to use by connecting the excitation arm's fiber port to different coupler ports. There is more than a short pass filter in excitation path and a bandpass filter before collection arms to suppress the laser reflection, and other three tunable dichroic filters with a sharp edge are loaded in two collection arms to do a high freedom spectral selection. The sample is loaded into a cryogenic temperature environment at 4K by using our insert. At the first beam splitter, a CCD camera checks the focus point and our alignment for the whole setup.

We mounted the spin-coated sample from Section 4.2.5 using GE-varnish or N-grace on the attocube stepper inside the chamber where it was cooled to and kept at 4K by a closed-cycle cryostats attoDRY system. The objective we used inside the low temperature (LT) chamber was Olympus, MPLN100X. The attocube stepper had five

stages, three of them were LT steppers to move the sample in a maximum XY-plane region of $1350 \times 1350 \mu\text{m}^2$ with a $500 \mu\text{m}$ in the z-direction, and the other two were ANSx150/LT x-scanner that could precisely walk at a step resolution from 100 to 500 nm.

For the excitation (Figure 4-4), we prepared three lasers: one CW 402 nm laser to do the off-resonant excitation, one picosecond laser centered at 394 nm with a repetition rate of 80 MHz for lifetime measurement, and another widely tunable C-Wave laser to do polarized photoluminescence scanning from 500 to 520 nm. Before the setup optimization, we collimated the laser light at 532 nm to two fiber couplers of collections and the light at 405 nm to the coupler of excitation.

The collection is the most crucial part of this hands-on optical aligning experiment, since the emission photons from single PQDs are weak and an excellent signal-to-noise ratio is required. We input two identical laser lights with a sharp linewidth of about 0.1 nm and a center wavelength at 520 nm through the collimated collection fiber port to demo the real collection path in our setup. Then, we could view how the two laser beams coming from two collection paths going in the whole setup, by looking at the CCD or directly inserting alignment plates at different locations in the paths. Afterward, we operated the differential drivers to overlap perfectly the two independent paths and made the beams in CCD show an ideally circular diffusion when focusing and defocusing. Besides, we improved the collection efficiency again by adjusting one beam path dependent on the other based on the feedback from photon counters. To do so, we first picked up one collection arm as the reference, secondly added a neutral density (ND) filter in the referred one, thirdly connected the other path to an APD, and then maximized the photon counts by operating the differential drivers for this path. Finally, we aligned the excitation path by overlapping it with the collection path. These optimization steps would locate the best distance between the quantum dot and the objective and the system's perfect collection path by the law of reversibility.

When measuring the spectrum for the PLs of PQDs, our Andor spectrometer settings were exposure time 200 s, grating 300 lines/mm, and the blaze selected as 760 nm.

4.4 Observation of Super-bunching

We used a CW 402 nm laser to excite the PQDs and took the spectrum for the PL at LT. Then, we measured the second-order autocorrelation $[g^{(2)}(\tau)]$ for the emission from single PQDs. Interestingly, the single PQDs all showed a giant super-bunching with a ratio of more than 18 at 30 nW CW excitation power for the unfiltered emission photons. Similar to [58, 150, 151], we also observed the anti-bunching well below 0.5 when X emission was isolated under CW and Pulse excitation to ensure a single PQD was being studied. Based on our experimental and theoretical results, we concluded that the highly-time-correlated exciton and biexciton pairs led to this giant super-bunching. We thought the possible reasons for the photon twins generated might be 1) the abnormal higher pumping ratio from neutral exciton to biexciton than from the ground to exciton, and 2) there were two decay paths, one radiative and the other non-radiative, from exciton to ground. We build two models with the three-level to isolate the simulation results for these two possibilities. With the temperature-dependent $[g^{(2)}(\tau)]$ results and XX lifetime around two times to X lifetime, we concluded that the non-radiative path was the exact reason for the highly correlated photon twins.

4.4.1 Optically driven Super-bunching in individual single PQDs

Figure 4-5 shows the data of PQD1. In, Figure 4-5A, we converted the wavelength unit 'nm' to energy unit 'eV' and plotted PL intensities versus energy for its spectrum. The red LT spectrum data points of PQD1 and the fitted line through them (Figure 4-5A) show three Lorentz peaks, and two of them are prominent sharp peaks: the exciton (X) peak corresponding to neutral exciton and the trion (T) peak, with a 19 meV offset, to charged exciton. This offset value is consistent with those published in [58, 150]. Additionally, the line widths of X and T were both about 5 meV.

We filtered out the single X emission of PQD1 from the full spectrum by tilting the tunable laser-line filter. The corresponding spectral selection result is presented as the blue dots (Figure 4-5A) which were fitted with a single Lorentz peak shown as the blue line (Figure 4-5A).

The $[g^{(2)}(\tau)]$ result (Figure 4-5B) of PQD1 X emission shows a clear anti-bunching below 0.5 at CW excitation. The blue data points were obtained in two steps: normalizing the raw data to the average intensity in 200 ns, and correcting the

normalized data through extracting the background noise counts by using the following function [46, 101, 152]:

$$g^{(2)}(\tau) = [g^2(\tau) - (1 - \rho^2)]/\rho^2 \quad \text{Equation 4-11}$$

where $\rho = s/(s + b)$, s and b are the signal and background intensities, respectively. Since this $[g^{(2)}(\tau)]$ shows a bunching shoulder near the anti-bunching depth at zero-time delay, we thought there was a three-level system for PQD1. Thus, we fitted through the blue data points using the following function:

$$g^{(2)}(\tau) = 1 - (1 + \alpha)e^{-|\tau|/\tau_1} + \alpha e^{-|\tau|/\tau_2} \quad \text{Equation 4-12}$$

where α , τ_1 , τ_2 are power-dependent fitting parameters[101]. The fitting result shows that PQD1 exhibits anti-bunching, $g^{(2)}(\tau = 0) = 0.33 \pm 0.11$, indicating a high single-photon purity for the X emission.

When swapped CW excitation to pulse excitation for PQD1 X emission correlation $[g^{(2)}(\tau)]$, we observed an anti-bunching with $g^{(2)}(0) \approx 0.15$ (Figure 4-5D). In summary, both CW and pulse excitation $[g^{(2)}(\tau)]$ indicate that the PQD1 is a single quantum dot with good single-photon purity for its X emission.

However, without spectral selection for the PQD1 emission photons, the $[g^{(2)}(\tau)]$ under CW excitation showed a super-bunching with a ratio of about 7.5 at zero-time delay (red line in Figure 4-5C), but the second correlation result for unfiltered photons under pulse excitation shows $[g^{(2)}(\tau)] \approx 1$, suggesting neither bunching nor anti-bunching. The reason for the disappearance of super-bunching under pulse excitation might be that a pulse excitation acted as a short occurrence in a continuous ultra-high CW excitation. If this is true, the super-bunching may gradually disappear when the CW excitation power increases to a certain level. Thus, it is a must for us to study the power-dependent behavior of the super-bunching in $[g^{(2)}(\tau)]$ at CW excitation.

Figure 4-5. PL characterization and $[g^{(2)}(\tau)]$ results for Perovskite quantum dot1 (PQD1). (A) Red dots are the Low Temperature (LT) photoluminescence (PL) spectrum, and blue dots are the raw data of isolated exciton peak of PQD1 emission under CW excitation. The red line is the fitted line with three Lorentz peaks, the main two of them are labeled as X and T, and the blue line is the fitted line with a single Lorentz peak. CW excitation power was 200 nW. (B) Background-corrected and normalized second-order correlation measurement $[g^{(2)}(\tau)]$ for spectrally selected X peak under CW excitation. Data were corrected by using Equation 4-11. Fitting with Equation 4-12, CW $[g^{(2)}(\tau)]$ solid red line gives $g^{(2)}(\tau = 0) = 0.33 \pm 0.11$. (C) $[g^{(2)}(\tau)]$ for PQD1 unfiltered emission under CW and pulse excitations without any background correction. The red and the blue lines are for CW and pulse excitation data, respectively. (D) Normalized second-order correlation measurement $[g^{(2)}(\tau)]$ for PQD1 emissions under pulse excitation. With normalization, pulse excitation $[g^{(2)}(\tau)]$ shows $g^{(2)}(\tau = 0) \approx 0.15$.

We did the LT PL spectrum characterization and Hanbury-Brown and Twiss (HBT) autocorrelation measurements for the other three PQDs (PQD2, PQD3, and PQD4) to study if the super-bunching was common. Figure 4-6A shows that the solid red line for the PL of PQD2 has more peaks than X and T, as in the case of PQD1. All the single peaks are in Lorentz fitting shapes, spectrally selectable and shown in solid black, orange, and blue lines. Since the correlation exists only between the emission of neutral excitons (X peak emission) and charged excitons (T peak emission), we used this to identify X and T peaks. There is an obvious anti-bunching well below 0.5 at zero-time delay (Figure 4-6C, D) between Peaks 2 and 3, and a $[g^{(2)}(\tau)] = 1.0 \pm 0.5$ (Figure

4-6E) with $[g^{(2)}(\tau = 0)] \approx 1$ for Peaks 2 and 1. These indicate the correlation only exists between Peaks 2 and 3. Thus, Peaks 1, 2, and 3 are labeled as X', X, and T, respectively.

The $[g^{(2)}(\tau)]$ for PQD2 exciton emission (Figure 4-6B) shows an expected anti-bunching below 0.5 under pulse excitation. Additionally, PQD 2 also generated photon twins, which is confirmed by the $[g^{(2)}(\tau)]$ for unfiltered emission from CW excited PQD2 (Figure 4-6F). Moreover, a lower power would lead to an increment in super-bunching peak (the bunching peak in blue line for 140 nW CW excitation is clearly higher than that in the red line for the 500 nW (Figure 4-6F) at the zero-time delay).

Figure 4-6. The PL characterization and $[g^{(2)}(\tau)]$ for PQD2. (A) The LT full spectrum of PQD2. Here are three main peaks marked as Peak 1, Peak 2, and Peak 3. The correlation measurement results between the three peaks indicate peak 2 belongs to X emission of PQD 2, Peak 3 to T emission of PQD2, and Peak 1 to X emission from another quantum dot nearby. (B) The $[g^{(2)}(\tau)]$ measurement for spectrally filtered out Peak 2 in both detection channels under pulse excitation. (C) The $[g^{(2)}(\tau)]$ measurement for spectrally isolated Peak 2 and Peak 3 in detection channels 0 and 1, respectively, under pulse excitation. (D) The $[g^{(2)}(\tau)]$ measurement for spectrally isolated Peaks 2 and 3 in detection channels 0 and 1, respectively, under CW excitation. (E) The $[g^{(2)}(\tau)]$ measurement for spectrally isolated Peaks 1 and 2 in detection channels 0 and 1, respectively under CW (solid blue line) and pulse excitation (solid red line). (F) The $[g^{(2)}(\tau)]$ measurement for unfiltered emission from PQD2 without any background correction. The blue and red lines are for results obtained at 140 and 500 nW CW excitations, respectively.

Figure 4-7 shows the repeated PL characterization and second-order correlation experiments results of PQD3, and the spectrum of PQD3 expectedly contains X and T peaks only. We labeled the higher one as the X, and the lower one as T. Second-order autocorrelation measurement shows good single-photon purity results since we observed $g^{(2)}(0) = 0$ and $g^{(2)}(0) = 0.059$ for X and T emission photons under pulse excitation, respectively. A bunching peak at zero-time delay for unfiltered PQD3 emission was observed with $g^{(2)}(0) \approx 5.5$. Moreover, we took PL spectrum of the PQD3 when increasing the CW excitation power and observed an expected gradual enhancement of T emission due to a stronger photo-charging (trion formation) process.

Figure 4-7. The PL characterization and $[g^{(2)}(\tau)]$ for PQ3. (A) LT spectrum of PQD3 characterization under 200 nW CW excitation contains two peaks, one is X, and the other is T with an offset 16 meV. The orange line is the spectrally selected X result, and the red line in the upper panel is the original spectrum. The blue line is the isolated T peak, and the red line is for the full spectrum. X and T are named as Peak 1 and Peak 2. (B) $[g^{(2)}(\tau)]$ measurements for X emission photons in two channels. (C) $[g^{(2)}(\tau)]$ measurements for T emission photons in two channels. (D) $[g^{(2)}(\tau)]$ measurements for unfiltered PQD3 emission photons in two channels without any background correction. (E) PL intensities at CW excitation powers 200, 250, and 300 nW. As CW excitation power increases, the obvious increase of trion peak intensity to exciton peak intensity indicates a stronger charging with power increases.

Figure 4-8 shows the results for PQD4. Figure 4-8A shows the spectrum of PQD4 that contains X and T emission peaks. Figure 4-8B shows the gradual enhancement of T emission with CW power increases from 20 to 180 nW. The trions related to T peak did not exist at minimum power but appeared at medium power and became relatively more apparent at higher excitation intensity, which is consistent with the photon-charging process. When X emission peak (solid blue line in Figure 4-8A) was spectrally isolated in both detection channels, we obtained an antibunching with $g^{(2)}(0) = 0.055$ that suggests a good single photon purity for PQD4. In addition, there is a spectral jump at 200 nW excitation intensity (Figure 4-8D). Our data showed that PQD4 produced highly correlated photon twins and a bunching peak at zero-time delay for its unfiltered emissions.

In summary, all PQD1, PQD2, PQD3, and PQD4 generate highly correlated photon twins with a bunching peak at zero-time delay in the second-order autocorrelation measurement, which indicates that super-bunching may be a universal phenomenon for the single CsPbBr₃ PQDs. Besides, we observed that the photon charging resulted in trion emission for PQD3 and PQD4, and the consistent Hanbury Brown-Twiss effect for fermion statistics for the correlation between X and T peak in all four PQDs. Therefore, we believe that the emission from a single PQD could contain a highly correlated photon pair, and the photon charging process would lead to two prominent peaks – the X (neutral exciton) and T (charged exciton) – in the spectrum.

Figure 4-8. LT PL spectrum and $[g^{(2)}(\tau)]$ characterization for PQD4. (A) LT PL intensity result under 180 nW CW excitation for the original spectrum (solid orange line) and isolated X peak (solid blue line) of PQD 4. (B) LT PL of PQD4 under 20, 100, and 180 nW are presented from top to bottom panels. (C) Pulse excitation $[g^{(2)}(\tau)]$ measurements for X emission photons of PQD4. (D) Three LT PL of PQD4 under high excitation intensity at 200 nW. There is a clear spectral jump between the X and T. (E) $[g^{(2)}(\tau)]$ for the original PQD4 emission spectrum photons without any background correction at 100 nW CW excitation.

4.4.2 Power-dependent behavior of the super-bunching

We tried to study power-dependent super-bunching under CW excitation using ten other single PQDs, and all but two (PQD5 and PQD6) of them became unstable to produce the same emission brightness for us to complete the whole power-dependent

$[g^{(2)}(\tau)]$ measurements since they gradually became blinking and ended up bleached after five hours CW excitation. For example, within the first 5 hours under pulse excitation, the intensity of PQD3 or PQD4 was stable to complete the $[g^{(2)}(\tau)]$ measurement for spectrally selected X emission, but in the next 0.5 hour, the intensity became about 10% to the mean count in the previous 5 hours. As the minimum CW excitation power of 30 nW would require the integral time of $[g^{(2)}(\tau)]$ to be more than 10 hours, the PQD3 and PQD4 were not suitable for this power-dependent study. Therefore, the stability of the single PQDs acted as a key to finish the power-dependent super-bunching study.

Figure 4-9A1 and Figure 4-9B1 present the PL spectra of PQD5 and PQD6, respectively. Both quantum dots contain an X and a T peak in the PL. However, the PL spectra of PQD5 contain another very small X' peak, which is similar to the multi-peaks spectrum of PQD2 (Figure 4-6A). The offset between the neutral exciton (X peak center) and charged exciton (T peak center) energy is around 17 meV, similar to the data in [58, 150].

Figure 4-9A2 and Figure 4-9B2 show the power-dependent super-bunching results for PQD5 and PQD6, respectively. There is a sharp decrease of the bunching peak with the increase of the CW excitation power from $[g^{(2)}(\tau = 0)] = 30$ at 33 nW to $[g^{(2)}(\tau = 0)] \approx 1.0$ at 1 μ W. Figure 4-9A3 and Figure 4-9B3 show the zoom-in $[g^{(2)}(\tau)]$ results at four different CW excitation powers for PQD5 and PQD6, respectively. Figure 4-9A5 and Figure 4-9B5 show the second-order correlation function values at zero-time delay versus the CW excitation powers for PQD5 and PQD6, respectively. These data indicate that the generation of photon twins from single PQDs exponentially decayed as the excitation power increased.

To better understand the relationship between CW power and super-bunching height, we used "true coincidence" — the events that only occur at zero-time delay in correlated photons, and "accidental coincidence" — the events that may appear at any relative time delay in uncorrelated photons to characterize unnormalized integral $[g^{(2)}(\tau)]$ results as a function of CW excitation intensity. They were calculated from raw data by the following two formulas [153]:

$$\text{Accidental Coincidence} = \frac{\sum_{i=1}^{i=N} \text{Count}_i}{N \cdot T} \quad \text{Equation 4-13}$$

$$\text{True Coincidence} = \frac{\text{Count}_{\tau=0}}{T} - \text{Accidental Coincidence} \quad \text{Equation 4-14}$$

Figure 4-9A6 and Figure 4-9B6 show the log-log plots of true and accidental coincidences versus excitation powers, and the fitting of two linear lines for PQD5 and PQD6, respectively. They indicate that there is a power-law relationship between correlated photon counts and excitation power and no saturation phenomenon until 1 μW .

Moreover, we loaded a Laserline filter, LL01-532-25 Semrock, to act as a grating with an FWHM equal to 1 nm to isolate the X emission peak to check the single-photon purity of PQD5 and PQD6. The $[g^{(2)}(\tau)]$ results are shown in Figure 4-9 A4 and Figure 4-9 B4, and the well below 0.5 antibunching depth at zero-time delay is consistent with our expected single-photon emitter's scenario.

In summary, the super-bunching peak at zero-time delay shows an exponential decrease with the CW excitation power increases, which indicates that the stronger CW laser excitation would weaken the correlated photon twins generation from a single PQD. This explains why the super-bunching was gone for pulse excitation presented in Section 4.4.1.

Figure 4-9. Power-dependent behavior study of super-bunching in PQD5 and PQD6. (A1) LT PL spectrum of PQD5. The solid orange and blue lines are for two single peak isolation results, and solid red line is for the original full spectrum. (A2) $[g^{(2)}(\tau)]$ measurements results without any background correction for PQD5 unfiltered emission photons under CW excitation powers: 33, 60, 100, 150, 200, 300, 400, 600, 800, and 1000 nW. (A3) Four sets of $[g^{(2)}(\tau)]$ function results to show the decrease of super-bunching with increasing CW excitation powers. (A4) $[g^{(2)}(\tau)]$ measurements for PQD5 X emissions. (A5) Plot of PQD5's $[g^{(2)}(\tau = 0)]$ versus CW excitation powers. (A6) Log-log plot of true and accidental coincidences of PQD5 versus CW excitation intensity. (B1) LT PL spectrum of PQD6. The solid orange and blue lines are for two single peak isolation results, and solid red line is for the original full spectrum. (B2) HBT $[g^{(2)}(\tau)]$ measurements results without any background correction for unfiltered PQD6 emitted photons under CW excitation powers: 30, 50, 70, 105, 200, 300, 400, 600, 800, and 1000 nW. (B3) Four sets of $[g^{(2)}(\tau)]$ function results to show the decrease of super-bunching with increasing CW excitation powers. (B4) $[g^{(2)}(\tau)]$ measurements for PQD6 X emission. (B5) Plot of PQD6's $[g^{(2)}(\tau = 0)]$ versus CW excitation powers. (B6) Log-log plot of true and accidental coincidences of PQD6 versus CW excitation intensity.

4.4.3 The Photon twins in the emission PL spectrum

To locate where the paired photons that we previously discussed at the beginning of Section 4.4 fall in the related PL spectrum, we did cross-correlation $[g^{(2)}(\tau)]$ experiments for photons in the two collection channels. Since bunching occurs only if the photons in the two collection paths are highly correlated, the $[g^{(2)}(\tau)]$ can be used to check whether there is a pairing process between the isolated photons in the two collection channels.

The PL spectrum of a single PQD contains three parts: low energy tail (left side of the X and T), X peak (excitons) and T peak (trions), and high energy tail (right side of the X and T). We named them areas 1, 2, and 3 for simplicity, respectively. Thus, there are five possible cases for the correlated photon pairs to form: Case 1: in area 1 and area 2, Case 2: area 2 and area 3, Case 3: area 1 and area 3, Case 4: area 1, and Case 5: area 3. We used FF01-554/23-25 and LL532-01 to isolate the spectrally selected photons in cross-correlation measurements for checking these five cases.

We luckily found PQD7 to be tough enough for going through the cross-correlation experiments of five cases, and thus this section presents results for it only. Figure 4-10A shows that it has an X emission and a T emission under 280 nW CW excitation in the spectrum, and the $[g^{(2)}(\tau)]$ of its unfiltered emission shows a bunching peak around 2.7 at zero-time delay. The $[g^{(2)}(\tau)]$ for isolated X emission photons from PQD7 shows an expected anti-bunching $[g^{(2)}(0)] = 0.2$, and the cross-correlation between the X and T emission also shows an anticipate anti-bunching $[g^{(2)}(0)] = 0.25$ in a large time scale of about 1000 ns.

Figure 4-10. PQD7 characterization data sets. (A) LT PL spectrum characterization of PQD7. (B) $[g^{(2)}(\tau)]$ for unfiltered emission photons of PQD7. (C) Isolated X emission in PicoHarp detection channels 0 and 1. The solid orange and blue lines are for spectrum characterization, and the red line is for the original full spectrum of PQD7. (D) $[g^{(2)}(\tau)]$ for spectrally selected X emission photons in both two collection paths. (E) The solid orange and blue lines are for isolated X and T emissions in PicoHarp detection channels 0 and 1 spectrum characterization, and the red line is for the original full spectrum of PQD7. (F) $[g^{(2)}(\tau)]$ for cross-correlation between X and T emission photons from PQD7. The spectral selection tasks were completed by using the laserline filter LL01-532.

Figure 4-11B shows the correlation measurement, run overnight, for photons in areas 2 and 3 of both channels (Case 2 and Case 5), and the corresponding photon isolation results and the full spectrum data of PQD7 are presented in the lower and upper panels of Figure 4-11A, respectively. They indicate there is no correlation between the photons in area 2 and area 3 (Case 2), or for area 3 (Case 5). Therefore, Case 2 and Case 5 are not possible to generate the photon pairs. Figure 4-11D shows the correlation measurements for photons collected in area 1 of both channels (Case 4), and Figure 4-11C shows the corresponding photons isolation results. They indicate that there is a bunching peak $[g^{(2)}(0)] = 3.2$, which means the photons in area 1 can pair between themselves. Thus, Case 4 is possible to generate photon pairs.

Our data suggest that the signal to noise ratio for photons collected in area 1 of both channels (Figure 4-11D) was not as good as for photons in areas 2 and 3 of both channels (Figure 4-11B), because the counts per second in the former were only around

1 K but more than 10 K in the latter, with the background noise remaining about 200 counts per second.

Due to the poor stability of the PQD, we could not take the risk to let the cross-correlation measurement for area 1 and area 1 of PQD7_run for more than 3 hours, because the signal-to-noise ratio in Figure 4-11D is worse than the ratio in Figure 4-11B and would require more than 5 hours to suppress the noise in $[g^{(2)}(\tau)]$ (because the Figure 4-11B measurement run overnight and showed suppressed noise after 5 hours). However, the bunching peak at zero-time delay still shows itself, since the thermal light source is only able to result in $[g^{(2)}(\tau)] \leq 2$ (Section 1.3). We believe the bunching did exist in Figure 4-11D, and Case 4 indeed generates photon pairs but in a small amount (the signal intensity here is quite low ~ 1 K, compared to the total emission intensity ~ 10 K of PQD7).

Figure 4-11. Photon correlation measurements $[g^{(2)}(\tau)]$ at fixed CW excitation power 280 nW for PQD 7 with the varied spectral selection but the same in two collection channels. (A) Spectral isolation result for the range 2.352 - 2.459 eV in both two collection arms. The actual isolation spectral result in two detection channels is shown in the solid blue line in the low panel. The corresponding ideal filtering result is framed up with two blue dash lines in the upper panel, and the orange line is for the full spectrum. (B) $[g^{(2)}(\tau)]$ for photons in areas 2 and 3 of both channels. There is no bunching for the photons in X, T, and high energy tail areas. (C) Spectral isolation result for the range 2.296 - 2.352 eV in both collection arms. The actual isolation spectral result in two detection channels is shown in the solid blue line in the low panel. The corresponding ideal filtering result is framed up with two dashed blue lines in the upper panel, and orange line is for the full spectrum. (D) $[g^{(2)}(\tau)]$ for photons collected in area 1 of both channels. There is a bunching peak at zero-time delay for photons in low energy tail area between themselves.

Figure 4-12 shows the $[g^{(2)}(\tau)]$ measurement results with spectral selection in channel 1 but without spectral selection in channel 0. There is bunching for each scenario (Figure 4-12B and D): between photons in area 1 and full emission area (containing Case 1, Case 3, and Case 5), and between photons in areas 1, 2 and full emission area (containing Case 1, Case 2, Case 3, and Case 4). The bunching peak in Figure 4-12D is lower than that in Figure 4-12B, which is because the correlation of fermion statistics between area 2 and itself would only result in an antibunching (Figure 4-10D and F). Combining the previous cross-correlation results - no correlation between photons in areas 2 and 3 (Case 2) or in area 3 (Case 5), the bunching here (Figure 4-12) is only possible to result from the photon twins in area 1 and area 2 (Case 1), area 1 and area 3 (Case 3), or area 3 (Case 5). Since the intensity in area 1 consists of less than 10% and area 3 less than 1% of the whole emission intensity, these results indicate that the correlation of bosons statistics for the highly correlated photon pairs is probably generated as one photon in area 1 (low energy tail), and the other photon in area 2 (X, T main peaks, Case 1).

Figure 4-12. Photon correlation measurements $[g^{(2)}(\tau)]$ at fixed CW excitation power 280 nW for PQD 7 with the varied spectral selections in collection channel 1 while no filtering in channel 0. (A) Spectral isolation result for the range 2.296 - 2.352 eV in channel 1. The actual isolation spectral results are presented in solid blue line in the low panel. The corresponding ideal filtering result is framed up

with two dash blue lines in the upper panel, and the full spectrum is plotted in an orange line. **(B)** $[g^{(2)}(\tau)]$ between photons in areas 1 and full emission area. There is a bunching ($g^{(2)}(\tau = 0) \approx 2.5$) for the cross-correlation between photons in low energy tail and photons in full emission. **(C)** Spectral isolation result for the range 2.296 - 2.373 eV in channel 1. The actual isolation spectral result is presented in solid blue line in the low panel. The corresponding ideal filtering result is framed up with two dash blue lines in the upper panel, and orange line is for the full spectrum. **(D)** $[g^{(2)}(\tau)]$ between photons in areas 1, 2 and full emission area. There is a bunching ($g^{(2)}(\tau = 0) \approx 2.0$) for the cross-correlation between photons in X, T, and low energy tail area and photons in full emission.

There is a bunching for cross-correlation measurements between photons in areas 2 and 3 and the full emission (Figure 4-13D) (containing Case 1, Case 2, Case 3, and Case 5), and there is no bunching for cross-correlation measurements between photons in area 3 and the full emission area (containing Case 2, Case 3 and Case 5) (Figure 4-13B). Therefore, it is reconfirmed that case 1 is the only reason for the photon twins generation. In other words, the highly correlated photon twins, resulting in the giant super-bunching, are mainly constituted of one photon in area 1 and the other one in area 2 (Case 1).

Figure 4-13. Photon correlation measurements $[g^{(2)}(\tau)]$ at fixed CW excitation power 280 nW for PQD 7 with the varied spectral selections in collection channel 1 and without selection in channel 0. (A) Spectral isolation result for the range 2.37 - 2.48 eV in channel 1. The actual isolation spectral results are presented by the solid blue line in the low panel. The corresponding ideal filtering results are framed up with two dash blue lines in the upper panel, the orange line is for the full spectrum. **(B)** $[g^{(2)}(\tau)]$ between photons in area 3 and photons in full emission area. There is no bunching for the cross-correlation between photons in high energy tail area and photons in full emission area. **(C)** Spectral isolation result for the range 2.352 - 2.459 eV in channel 1. The actual isolation spectral results are presented by the

solid blue line in the low panel. The corresponding ideal filtering results are framed up with two dash blue lines in the upper panel, the orange line is for the full spectrum. **(D)** $[g^{(2)}(\tau)]$ between photons in areas 2, 3, and photons in full emission area. There is a bunching ($g^{(2)}(\tau = 0) \approx 2.0$) for the cross-correlation between photons in X, T, and high energy tail area and photons in full emission area.

Figure 4-14 shows the $[g^{(2)}(\tau)]$ cross-correlation measurement when isolating X emission photons in channel 1 and isolating area 1 or area 3 photons in channel 0 (we use Figure 4-11B and Figure 4-14D results to double-check for Case 2 and Case 1, respectively). Figure 4-14B confirms again there is no correlation between photons in area 3 and photons in area 2 (Figure 4-11B and Figure 4-13B also indicate this before), and Figure 4-14D indicates again that highly correlated photon twins originate from photons in area 1 and photons in area 2 (Figure 4-12B, D, and Figure 4-13D). Although the background noise is quite high in Figure 4-14D and some timing points even reach the same height 4.0 as at zero-time delay, these noise peak points only show as sudden jumps with one step (0.256 ps) linewidth. In principle, the true bunching can never show itself with such a linewidth (bunching peak FWHM ~ 1.02 ns). Thus, we believe only the bunching at zero-time delay is true, and the others are all just noise.

Figure 4-14. Photon correlation measurements $[g^{(2)}(\tau)]$ at fixed CW excitation power 280 nW for PQD 7 with the varied spectral selection in both channels 1 and 0. (A) Spectral isolation results for the X emission in channel 1 and high energy tail area photons in channel 0. The actual isolation spectral results are presented in solid orange and blue lines in the low panel for channels 0 and 1, respectively.

The corresponding ideal filtering result is framed up with two dash blue and orange lines in the upper panel, and the red line is for the full spectrum. **(B)** $[g^{(2)}(\tau)]$ between photons in area 2 and photons in area 3. There is no bunching ($g^{(2)}(\tau = 0) \approx 1.0$) for the cross-correlation between photons in high energy tail area and X emission. **(C)** Spectral isolation results for the X emission in channel 1 and low energy tail area photons in channel 0. The actual isolation spectral result is presented by the solid orange and blue lines in the low panel for channels 0 and 1, respectively. The corresponding ideal filtering result is framed up with two dash blue and orange lines in the upper panel, and the red line is for the full spectrum. **(D)** $[g^{(2)}(\tau)]$ between photons in area 2 and photons in area 1. There is bunching ($g^{(2)}(\tau = 0) \approx 4.0$) for the cross-correlation between photons in X emission and photons in low energy tail area.

Our experimental results in this section indicate that the photon twins in single PQD originate from the highly correlated photon pairs – one photon in area 1 pairs with the other one in area 2. Combining with data reported by [154, 155], we believe that the excitons and charged excitons constitute the photons in area 2, and the emission of biexcitons mainly contributes to the photon counts in area 1. We think the highly correlated pair of one photon from X emission and the other photon from XX emission in the lower energy tail is the source of the super-bunching observed for the unfiltered emission of our single CsPbBr₃ PQDs.

4.4.4 Measuring the lifetime of single PQDs emitted photons

We did the lifetime measurements for three PQDs, PQD4, PQD5, and PQD6, studied previously. Figure 4-15 shows the lifetime measurement result of PQD6 X emission and the instrument response function (IRF). The IRF was measured when no change was made to the setup alignment, but all filters (520BH, laserline filter, or FF01-334/23-25) were removed in the collection path; in other words, the IRF was obtained by measuring the reflection of the pulse laser. Our data indicate that the lifetime of PQD6 X emission is relatively short, almost as short as the IRF. Therefore, we use the combination of deconvoluting the IRF and single exponential fitting. The fitting details are described in Section 4.5.1.

Figure 4-15. The lifetime measurement together with IRF for PQD6. The solid gray line is the IRF, and the orange data points are the lifetime measurement result for PQD6 X emission. The photon counts are normalized and shown in a log scale. The X emission of PQD6 is labeled as isolated Peak1 in use of 532Laserline filter for unity, refer to Section 4.4.3. The fitting result is 122 ps for the PQD6 X emission. More fitting details are given in the theoretical simulation Section 4.5.1.

The red and green dots in Figure 4-16 show the lifetime measurements of X emission from PQD4 and PQD5, and the fitting results show the exact lifetime values 146 and 153 ps for them, respectively. We also measured the lifetime of trion emission from PQD5, and it is 87 ps (Figure 4-16).

Figure 4-16. Lifetime measurement results for PQD4, PQD5, and PQD6. All the lifetime results are fitted with a single exponential decay of the deconvolution of IRF. From the top to the bottom, the data points and the related lines are the first two for X emissions of PQD4 and PQD6, and the next 2 for the T and X emissions of PQD5, respectively. X (neutral exciton emission) lifetime of our PQDs varies from 122 to 153 ps, and the T (trion or charged exciton emission) lifetime of PQD5 is about 87 ps.

In summary, the lifetimes of the X emission from individual single PQDs vary from 122 ps to 153 ps. The trion emission lifetime from PQD5 is 87 ps, shorter than X emission lifetime 153 ps. The shorter lifetime and higher decay ratio of the trion than those of neutral X emission from our single perovskite quantum dots were also observed in conventional InAs QDs [156, 157]. This is probably due to the existence of the dark-state that is optically forbidden and thus a long lifetime. If a QD is at a neutral state, and the dark-state is below the bright exciton state, it would lead to a transition from a bright state to the dark-state and result in a low repetition rate for this QD. Therefore, a singlet charged state of QD would break the maximal achievable emission rate for the charged dark state is nonexistent.

Figure 4-17. The time-resolved measurement for the emission of a single PQD. All the lifetime results are fitted with a single exponential decay of the deconvolution of IRF. The XX emission hardly visible in the low energy tail shows a lifetime roughly two times of the X emission lifetime.

In addition, we measured the lifetime of XX emission by spectral isolating the photon counts in the low energy tail for the collection path. One result shows the XX emission lifetime is 210 ps, and X emission lifetime is 101.5 ps (Figure 4-17).

4.4.5 The temperature-dependent behavior of super-bunching

Our simulation model 2 in Section 4.5.2 predicts that the phonon interaction that can trigger the nonradiative state's excitons back to the bright radiative state would increase with the temperature increases. Thus, we used a PQD to check whether the $[g^{(2)}(\tau)]$ correlation measurement of its unfiltered emission would show a temperature-dependent behavior or not. To do so, we installed a heater between the sample holder and the fine scanner and placed a temperature sensor nestled right in the sample holder. Then, we reloaded the sample into our cryogenic system to cool down and redid the setup's alignment as in Section 4.3.

Figure 4-18 shows the normalized correlation measurements of our PQD's unfiltered emission at temperatures of 4.9, 20, 40, 60, 80, and 100 K under a stable CW excitation

power 100 nW. The bunching peak values $g^{(2)}(\tau = 0)$ are 1.83, 1.94, 1.31, 1.084, 0.892, and 0.558 for the corresponding temperatures from 4.9 to 100 K, indicating a decreasing trend for the peaks with increasing temperatures. Therefore, the bunching is gradually transforming to an antibunching, when the PQD is heated up by the installed heater through the Proportional-Integral-Derivative (PID) closed-loop. This means even when the PQD is loaded into a neutral dark state, the phonon interaction can pump it directly back to the neutral bright exciton state without the requirement of spin-flip or pump through the biexciton (XX) state to the bright state. We observed the effects of such phonon interaction became stronger and stronger with the temperature increases, which is consistent with the phonon effect in theory [158].

With temperature increases from 4.9 to 20 K, $g^{(2)}(0)$ increases slightly from 1.83 to 1.94, which is inconsistent with the general decreasing trend of $g^{(2)}(0)$ from 4.9 to 100 K. However, the full width at the half maximum (FWHM) of the bunching peak is ~ 1.28 ns at 4.9 K, and ~ 1.024 ns at 20 K. We doublechecked the accumulation time of $[g^{(2)}(\tau)]$ at 4.9 K and 20 K, and we found that it took about 2 and 12 hours to finish the $[g^{(2)}(\tau)]$ experiment measurements at 4.9 and 20 K, respectively. Therefore, it is probable that this abnormal observation may result from the experimentally integral time of $[g^{(2)}(\tau)]$ measurement not enough at 4.9 K.

Figure 4-18. $[g^{(2)}(\tau)]$ second-order correlation measurements of a single PQD with varying temperatures. The temperatures range from the lowest 4.9 K to the highest 100 K that our system could stably hold, with an increment about 20 K per step. The CW excitation power was kept at 100 nW. The $[g^{(2)}(\tau)]$ data were normalized but without any background correction. The bunching peaks decrease from ~ 2.0 to 1.0 with the temperature increases from 4.9 to 60 K. From 80 to 100 K, an antibunching is about to appear at zero-time delay. The $[g^{(2)}(\tau = 0)]$ values were 1.83, 1.94, 1.31, 1.084, 0.892, and 0.558 for 4.9, 20, 40, 60, 80, and 100 K, respectively.

The antibunching peak in 80 and 100 K are hard to see, and the fluctuations of $[g^{(2)}(\tau)]$ near zero-time delay can overlap with the antibunching depth completely. During the experimental processes, we noticed the emission intensities of the single PQD would drop with the temperature increases: averaged avalanche photodiodes (APD) counter decreased from ~ 10000 per second at 4.9 K to ~ 1500 per second at 100 K, while the noise background remained all the same, robust to temperature and excitation power. Therefore, the decreasing signal-to-noise ratio would result in a worse $[g^{(2)}(\tau)]$ measurement result with a smaller depth or peak indistinguishable from the noises, which might be why that the antibunching was hardly observable in our experimental case.

In summary, our data show the $[g^{(2)}(\tau = 0)]$ decreases with the temperature increases, which is consistent with model 2 about dark-state in Section 4.5.4. Therefore, the

signal-to-noise ratio can become too small for $[g^{(2)}(\tau)]$ measurements to show a clear antibunching depth at zero-time delay above a certain temperature. Furthermore, model 2 (Section 4.5.4) is physically reasonable for explaining our giant super-bunching observation.

4.5 Theoretical model and simulation to explain the source of the giant super-bunching from the emission of single PQDs

We used two possible models to explain the giant photon bunching from a single PQD emission and simulate the observed super-bunching phenomenon presented from Section 4.4.1 to 4.4.4. As we observed that the photon twins are formed by one photon from X emission and another from XX emission, there are two models that can generate such photon twins but through different theoretical mechanisms. Both models are 3-level models involving ground, exciton (X), and biexciton (XX) states. In the first model, the giant photon bunching is attributed to a great pumping rate from X to XX ~ 690 times greater than the pumping rate from the ground to X. In the second model, the giant photon bunching is attributed to a non-radiative decay path resulting from a dark-state_below the bright exciton state. However, the parameter $\frac{\beta_2}{\beta_1}$ in Model 1 is unreasonably large as nearly 700, and $\frac{\gamma_2}{\gamma_1}$ is only around 1.5 in order to simulate the experimental data well. Thus, we believe that Model 2 is more appropriate to explain the giant photon bunching. Besides, the observed bunching peak generally transformed into an antibunching in temperature-dependent $[g^{(2)}(\tau)]$ (refer to Section 4.4.5), which supports there is a dark-state related non-radiative path in Model 2. Further details on the models will be discussed in the followings.

4.5.1 General description of theoretical models

Figure 4-19 shows how the theoretical parameters relate to the experimental setup that consists of different filters for various photon modes in collection arms to do spectral isolation for intensity time correlation [$g^{(2)}(\tau)$] measurements. The effect of filtering on PQD's emission spectrum is represented by the mode and arm dependent collection efficiency (η_{ij} for j^{th} mode in i^{th} arm), which results in different electric field operator in each arm ($\hat{E}^{(i-)}$ for i^{th} arm). The collection arms 1 and 2 are for start and stop signals, respectively. Each photon mode corresponds to a unique transition in the PQD. Generally, the filtering mechanisms should include:

- Spatial filtering: Emissions from different QD transitions can have different beam profiles
- Spectral filtering: The optical components (including filters, lenses, and APD) have a wavelength-dependent optical response

Figure 4-19 Theoretical model of the experimental setup. Here, η_{ij} is the collection efficiency for j_{th} mode in i_{th} arm, and $\hat{E}^{(i-)}$ is the electric field operator at i_{th} arm.

The experimental results for individual PQDs' spectra and the intensity time-correlation measurements are summarized in Figure 4-20. They indicate that:

- The bunching decreases as the pumping power increases
- The bunching involves the exciton emission (X) and emission having lower energy than X other than trion (T)

Figure 4-20. PQR4 spectrum and intensity time correlation measurement. (a) A typical spectrum of PQR4 emission is shown in the use of PQR5 data from section 4.4.2. The X and X' peaks correspond to 2 different exciton emissions, and the T peak corresponds to trion emission. (b) The $[g^{(2)}(\tau)]$ at different CW excitation powers. (c) Summary of photon bunching and anti-bunching. The left, right, X, T, and X' refer to the labeling in (a). 'Y' means this phenomenon was observed.

Additionally, lifetime measurements were done for the X emission peaks of three different PQRs (Figure 4-15 and Figure 4-16). The IRF in linear-linear scale and linear (x-axis)-log (y-axis) scale are shown in Figure 4-21 (a) and (c), respectively. The raw QDs pulse responses in linear-linear and linear-log scales are shown in Figure 4-21 (b) and (d), respectively. Since the IRF pulse width is at the same magnitude as the width of the QD pulse response is for the practice, the deconvolution is needed. To do this, we used the fitting function, $F(t + t_{\text{shift}}) = [e^{-t/\tau}H(t)] \otimes \text{IRF}(t) + y_0$ [83], where $H(t)$ is the unit step function with $H(t \geq 0) = 1$, and τ , y_0 , and t_{shift} are fitting parameters. The fittings for all lifetime data are quite good (Figure 4-21) as the R^2 values are around ~ 0.9952 . We obtained τ values between 122 to 153 ps for the X emission and ~ 87 ps for T emission (Figure 4-21 (b) and (d)).

We know that:

- ❖ The deconvolution method is only valid for a linear system [159] (i.e., pulse response has a linear relationship with excitation power), but the PQD system is not strictly linear.
 - ❖ While we attribute the parameter t_{shift} to the possible delay between pumping pulse and X emission, it can also indicate that multiple exponentials are needed.
- Regardless of these problems, the lifetime obtained here should be the lifetime of the lowest possible for X or T transition.

Figure 4-21. Lifetime measurement. (a) The instrument response function (IRF). (b) PQD Pulse response. The black line is fitted with the convolution function. (c, d) lifetime data plotted in log scales for data in (a, b), respectively.

4.5.2 General expression for $g^{(2)}(\tau)$ for PQD emission

We assume the following three assumptions are valid:

- ❖ The single QDs can be modeled as a system with multiple discrete energy levels with transitions allowed only between adjacent energy levels (refer Figure 4-22); in the far-field, the electric field operator for photon mode corresponding to $(i \rightarrow i - 1)$ transition can be expressed as $\hat{E}_i^{(-)} \propto \sqrt{\gamma_i} \sigma_i^\dagger$ with $\sigma_{ij} = |i - 1\rangle\langle i|$ and γ_i is the spontaneous emission rate from $|i\rangle$ to $|i - 1\rangle$ [1].
- ❖ There are no coherent terms in the light-matter interaction Hamiltonian density matrix, hence, the matrix of the PQDs can be approximated as entirely diagonal.
- ❖ The Quantum regression theorem is valid.

Then, we can derive the following expression of $g^{(2)}(\tau)$

$$g^{(2)}(\tau) = \frac{\sum_{i,j} [\eta_{mi} \eta_{nj} \gamma_i \gamma_j \rho_{ii}^{ss} \sum_{k \in \{0, i-1\}} B_{jk}(\tau)]}{[\sum_i \eta_{1i} \gamma_i \rho_{ii}^{ss}] [\sum_j \eta_{2j} \gamma_j \rho_{jj}^{ss}]}, \quad \text{Equation 4-15}$$

where $m = 1(2), n = 2(1)$ for $\tau \geq 0 (\tau < 0)$, η_{ij} is the collection efficiency of j^{th} mode in i^{th} arm, γ_i is the spontaneous emission rate from $|i\rangle$ to $|i - 1\rangle$, ρ_{ii}^{ss} is the steady-state population density of state $|i\rangle$ and $\langle \sigma_i^\dagger(t + \tau) \sigma_i(t + \tau) \rangle = B_{i0}(\tau) + \sum_{k>0} B_{jk}(\tau) \rho_{kk}(t)$.

Our particular interest is a system like above with three energy levels (i.e., biexciton (level 2), exciton (level 1), ground (level 0)) with the same collection efficiency for any mode in any arm. Thus, Equation 4-15 becomes:

$$g^{(2)} = \frac{\gamma_1 \rho_{11}^{ss} (\gamma_1 B_{10}(\tau) + \gamma_2 B_{20}(\tau)) + \gamma_2 \rho_{22}^{ss} (\gamma_1 (B_{10}(\tau) + B_{11}(\tau)) + \gamma_2 (B_{20}(\tau) + B_{21}(\tau)))}{[\gamma_1 \rho_{11}^{ss} + \gamma_2 \rho_{22}^{ss}]^2}, \quad \text{Equation 4-16}$$

There are four terms in the nominator with the same $\gamma_i \gamma_j$ corresponding to the consecutive emissions of (from left to right): (1-1), (1-2), (2-1), and (2-2), where (p-q) means the emission of mode p followed by the emission of mode q. For example, (1-1) means the simultaneous occurrences of two decay events from $|1\rangle$ to $|0\rangle$; in other words, the neutral exciton decays twice of a sudden. The term $B_{i0}(\tau)$ and $(B_{i0}(\tau) + B_{i1}(\tau))$ can be obtained from the time-dependent population density of state $|i\rangle$ with initial condition $\rho_{00}^{ss} = 1$ (c 1, see Figure 4-22b) and $\rho_{11}^{ss} = 1$ (c 2, see Figure 4-22c) for c 1

and c_2 , respectively. Equation 4-16 can also be obtained by calculating the probability of detecting consecutive emissions for each of the four possible events is mutually exclusive, based on our second assumption above.

One important parameter is $g^{(2)}(0)$, Equation 4-17 can be derived from Equation 4-16 for $B_{10}(0) = B_{20}(0) = B_{21}(0) = 0$ and $B_{11}(0) = 1$. This results in:

$$g^{(2)}(0) = \frac{\gamma_2 \gamma_1 \rho_{22}^{ss}}{[\gamma_1 \rho_{11}^{ss} + \gamma_2 \rho_{22}^{ss}]^2}, \quad \text{Equation 4-17}$$

Therefore, only the (2, 1) event contributes to $g^{(2)}(0)$.

Figure 4-22. The general model of QD emission. (a) Multiple energy levels with transition are only allowed between adjacent energy levels. (b) c 1. Relevant for (1-1) and (1-2) consecutive emissions. (c) c 2. Relevant for (2-1) and (2-2) consecutive emissions.

4.5.3 Model 1: Three-energy-level system with all radiative decays

In the first model, the transitions between the states are illustrated in Figure 4-23. Based on Equation 4-17, one direct way to understand the bunching peak at zero time delay is a large population of XX ($\rho_{22}^{ss}/\rho_{11}^{ss} \gg 1$), which is achievable if β_2 is much larger than β_1 while γ_1 is similar to γ_2 .

This is possible because at low excitation power $\beta_1 P$, $\beta_2 P \ll 1$ and $\gamma_2/\gamma_1 \approx 1$, and thus, Equation 4-17 becomes as below:

$$g^{(2)}(0) \approx \frac{\beta_2(1 + \beta_1 P)}{\beta_1 (1 + \beta_2 P)^2} \approx \frac{\beta_2}{\beta_1} \gg 1 \quad \text{Equation 4-18}$$

While at high excitation power $\beta_1 P, \beta_2 P \gg 1$ and $\gamma_2/\gamma_1 \approx 1$, Equation 4-17 becomes:

$$g^{(2)}(0) \approx \frac{\gamma_1}{\gamma_2} \approx 1, \quad \text{Equation 4-19}$$

Figure 4-23. Scheme of model 1. All decay processes are radiative. Here, P is the excitation power, β_1, β_2 are the pumping ratio between X and ground, and XX and X ; respectively, γ_1, γ_2 are the decay ratio for the two radiative paths corresponding to XX emission and X emission, respectively; and $\rho_{22}, \rho_{11}, \rho_{00}$ are the densities of population at XX, X and ground state, respectively.

The model 1 fitting results for PQD4 are shown in Figure 4-24a-c. Figure 4-24a shows the experimental data of $[g^{(2)}(\tau)]$ at some powers in red, blue, and solid green lines; and the calculated results obtained from model 1 are in black dash line. Figure 4-24b shows the $g^{(2)}(0)$ at different pumping powers obtained from the experiment and the fitted line through them by model 1. The fitting parameters' values and their 95% confidence intervals are shown in Figure 4-24c. Here, the X lifetime is directly obtained from the pulse response fitting result (Figure 4-21b, d), and the decay ratio would be reciprocal for it.

In Figure 4-24c, the high value of β_2/β_1 can be explained by Equation 4-18 $\lim_{P \rightarrow 0} g^{(2)}(0) = \beta_2/\beta_1$. Hence, a high bunching at low power means that β_2/β_1 must be very big. On the other hand, the saturation at high power can be explained by considering at high power for Equation 4-19 $\lim_{\beta_1 P, \beta_2 P \gg \gamma_1, \gamma_2} g^{(2)}(0) = \gamma_1/\gamma_2$.

In simulation result, there is a dip with an FWHM within the bin size 256 ps near $\tau = 0$, which is quite visible in a high-power regime. However, if the experimental resolution time bin size is 256 ps, we would not see this ideal dip experimentally. We have checked this by calculating the expected experimental value $g_{\text{meas}}^{(2)}(\tau) = \text{Average}(g^{(2)}(\tau - 128\text{ps}) \text{ to } g^{(2)}(\tau + 128\text{ps}), 11 \text{ points})$ and found no dip.

Figure 4-24. Simulation result of model 1 for QD4. (a) Fitting result of $g^{(2)}(\tau)$ at 33, 60, and 100 nW. The black dashed line is the fitting result. (b) Fitting to power dependence of $g^{(2)}(0)$. Red dots are the actual experimental results, and the solid black line is the fitted. (c) Fitting parameters.

In conclusion, model 1 can fit well the experimental $[g^{(2)}(\tau)]$ results, but it lacks data to support the core condition: the abnormal 700 times higher pumping ratio from X to XX than the ratio from ground to X. Since the precondition of this model 1 is abnormal and no experimental data in single PQDs from our data or published by others, the model 1 is not very convincing.

4.5.4 Model 2: Three-energy-level system with radiative and non-radiative decays

The other way to help us understand the experimental results is to build a model with a large population of XX, a bigger γ_1 than γ_2 , and β_2 is similar to β_1 . However, if all decays are radiative, this would result in a weak XX emission. To make the X and XX decay ratio maintain close to each other, we add a non-radiative path, which makes γ_1 have two components γ_1^r and γ_1^{nr} . Therefore, the γ_1 can be much bigger than γ_2 , and the γ_1^r (X emission decay ratio) is still similar to γ_2 (XX emission decay ratio). In conclusion, we still use a three-level model but include three decay paths shown in Model 2 (see Figure 4-25).

Figure 4-25. Scheme of model 2. All decays with the solid lines are radiative, and the one with the dash line is non-radiative. Here, P is the excitation power. Since we assume the pumping ratio for the ground to X and X to XX are the same, we only use one parameter β as the parameter. We set another decay parameter here as γ^{nr} . The population densities at the three states are set the same as in model 1.

The model 2 fitting results for PQD4 are shown in Figure 4-26a-c. Figure 4-26a shows the experimental data of $[g^{(2)}(\tau)]$ and the calculated results obtained from the model at three different powers 33, 60, and 100 nW. Figure 4-26b shows the experimental data of $g^{(2)}(0)$ and the model-fitted line through them. The fitting parameters' values and their 95% confidence intervals are shown in Figure 4-26c, and the X lifetime obtained from the pulse response fitting result is shown in Figure 4-26b, d.

Our data indicate that the value of γ_2 is about 185 times of that of γ_1^r (Figure 4-26c), which would lead to about 0.3 times of the total decay rate ($\gamma_1 = \gamma_1^{nr} + \gamma_1^r$) of X. Hence, the lifetime of XX is around three times of the lifetime of X, and the lifetime of XX emission from PQD4 is ~ 400 ps by calculation.

Figure 4-26. Simulation result of model 2 for PQD4. (a) Fitting result of $g^{(2)}(\tau)$ at 33, 60, and 100 nW. (b) Fitting to power dependent of $g^{(2)}(0)$. Red dots are the actual experimental results, and the solid black line is the fitted. (c) Fitting parameters.

In summary, model 2 is more convincing than model 1, based on the experimental observations for the temperature-dependent bunching in Section 4.4.5 and the experimental results that XX lifetime is longer than X lifetime in Section 4.4.4. A recent report [154] about the correlated photon pairs from single CsPbI₃ PQDs showed similar experimental observations to ours, and they also mentioned there was a long-lived dark-state below the bright X state.

4.6 Outlook

Based on our work so far on the PQDs, we have initiated a few related promising studies. They are pending to be completed in the future and can be divided into three main areas: improvements on material quality, electrically triggered PQDs, and the experimental explorations in the PQDs' fine exciton structure.

4.6.1 Adding a shell surround the PQD

Based on the developments and studies of III-V inorganic semiconductors QDs [160-162], the ideal QDs for applications should be non-blinking, bright at room temperatures, and stable in moist air [163-165], and these also apply to our single PQDs [61, 166]. Based on [166, 167] about core/shell nanocrystal synthesis method, it is a promising method to produce stable PQDs by overcoating the PQDs with another shell that has a wider bandgap than the core. Also, the outside zwitterionic ligand capping of PQDs can be replaced by pure single ions, and the charging process that happened to our single PQDs would be diminished [61]. Thus, we can improve our PQDs' quality by adding the core/shell structure to endure less spectral jumping [58] and possibly to have the narrowest FWHM of a single X emission peak reaching the lifetime limit.

After the lifetime limited linewidth of X emission from single PQDs is achieved, we can design and directly use the mature technology for the cavity that is made with DBR mirrors [17, 168, 169], as done in conventional III-V inorganic semiconductors QDs [52, 170]. In summary, we need to make the PQDs with high qualities with a suitable cavity structure to form a light source device in the real quantum applications [84], and it is possible for us to do so.

4.6.2 Electrically driven single PQDs

To date, optically driven single-photon emission has been achieved and well-studied for single PQDs, and only one work [171] attempting electrically driven single PQDs but without any confidential proof for success at a single photon level has been done. It is known that single-photon sources are electrically driven in a very similar manner as other semiconductor light sources, such as light-emitting diodes [172]: charge carriers are injected in a direct bandgap semiconductor. When carriers' wavefunctions

overlap, they undergo a recombination process, which emits a photon, at the overlapping spatial area. In general, semiconductor light-emitting diodes have three main regions engineered to boost photon emission efficiency. They are the active region, the hole transport layer (HTL), and the electron transport layer (ETL) [173]. The active region is where charge carriers accumulate and undergo the recombination process. The HTL injects holes into the active region but prevents the electrons from leaking out. Similarly, the ETL brings electrons into the active regions but blocks the holes. Thus, avoiding the poor charge injection and providing a charge-free clean environment become the key to successfully trigger PQDs at a single quantum dot level.

Up to now, we have just successfully enlightened the PQDs by DC voltage, with the device scheme in Figure 4-27. Since the polymer layer can act as a good electron and hole tunneling layer [59, 140, 174], we diluted the PQDs in a 10% PMMA in toluene by weight for spin coating a conductive layer containing well-distributed individual PQDs. Based on [175], we think that a polymer layer with a thickness of around 20 nm would do the best for an electrically driven PQDs device. Moreover, the electron and hole recombination process in the polymer layer is predicted to happen for a minimum transport distance around 50 and 10 nm at RT and LT, respectively [176]. Thus, we chose 10000 RPM to spin-coat PQDs layer and used the atomic force microscopy (AFM) to check the layer thickness. The thinnest possible layer we obtained was about 35 nm thick, after we tried different densities of PMMA 950K prepared by dissolving it in anisole in various proportions by weight, A5 (5%), A4 (4%), A3 (3%), A2 (2%), A1 (1%), and A0.5 (0.5%).

To prepare the other layers, we just followed the steps reported in [61, 140, 148]. From top to bottom of our device (Figure 4-27), ZnO nanoparticle dilute in water as an electron tunneling layer, single PQDs dilute in PMMA layer, PVK layer as an electron block layer, PEDOT: PSS layer as a hole tunneling layer, and the thin ITO coated on a glass with a high optical transmission.

Figure 4-27. The scheme of electrically driven single PQDs device. The detailed information of each layer is written clearly on the left side of the figure, and the arrow connects the description of the layer with the layer's position. A part of our spin-coated layer would be wiped out because the ITO film must be exposed for evaporation.

The details for the band alignment of the different spin-coating layers are presented in Figure 4-28. We found that spin-coating n doped ZnO nanoparticles in IPA would remove the PQDs layer in the device-making process, because the IPA has a side-effect of dissolving the PMMA and washing the PQDs layer almost entirely. Therefore, we purified the ZnO nanoparticles from the IPA solution and mix them into deionized water for spin-coating use. Additionally, the ITO film was cleaned three times by sonicating first in acetone, second in IPA, and finally in deionized water, and then was baked at around 150°C in the cleanroom.

Figure 4-28. Details of the device with the energy level of CBM and VBM. The left side presents the electron is tunneling from the CBM of n doped ZnO nanoparticle layer to PQDs layer, and the hole is transporting through the VBM of ITO, PEDOT:PSS, PVL, and finally PQDs layer. The right side shows the positive and negative evaporated electrodes related to the electrons and holes injection.

Coating the first layer of PEDOT:PSS requires an ultra-clean and active layer. Thus, we treated the right side of ITO film with oxygen plasma at a power of 100 W for five minutes. The PEDOT:PSS layer was then spin-coated in the first twenty minutes after the plasma.

Since the device must be loaded into our cryostat system for basic characterizations, we plan to use a leadless chip carrier and use wire bonding to connect the electrodes to the outer feet. Because the ITO film with the coated side is to be used for hole tunneling and the uncoated side is to transmit light, we will have to reverse the device upside down. However, there will be no space for a direct wire bonding from the evaporated gold electrodes of the PQDs device to the conductive feet of the chip carrier. Therefore, we will make another PCB board, designed to have negative and positive pads, to let the device directly sit on. Then, an electrically driven single PQDs device (Figure 4-29) will be made.

Besides, the quantized electrons or holes charged single PQD can also be probably achieved using this same device. Based on [156, 157, 175], the promising emission enhancement and polarization tunability are also valuable to explore.

Figure 4-29. The scheme of the on-chip electrically driven PQDs device. The size of the ITO film is designed as 5×5 mm, and the PCB board is cut into a 7×7 mm piece.

4.6.3 Resonant Polarized Photoluminescence excitation for analyzing the exciton fine structure of CsPbBr₃ QDs

It is clear that the triplet states of PQDs due to large spin-orbit coupling are bright [57]. Still, debate remains whether the singlet dark state is truly lower or higher than the bright states between the theoretical calculations and the actual experimental observations [132, 177]. A combination of strong magnetic field tuning the singlet dark state into a low emission and resonant polarized photoluminescence excitation spectrum measurement should resolve this debate by visualizing all quantized splitting states with different spins. Only then will it be possible for us to manipulate the spins in PQDs through optical methods like the works done for the conventional III-V quantum dots [5, 178, 179] and to use single PQDs as single qubits in applications [84].

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