Exciton photon coupling in all-inorganic cesium lead halide perovskite microcavities

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**NANYANG
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**EXCITON PHOTON COUPLING IN ALL-INORGANIC
CESIUM LEAD HALIDE PEROVSKITE MICROCAVITIES**

SU RUI

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2019

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CESIUM LEAD HALIDE PEROVSKITE MICROCAVITIES**

SU RUI

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2019

Statement of Originality

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

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SU RUI

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

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Prof. Xiong Qihua

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals where I was the first author.

Chapter 3 and 4 is published as “High Quality Whispering Gallery Mode Lasing from Cesium Lead Halide Perovskite Nanoplatelets.” Q. Zhang#, **R. Su**#, X.F. Liu#, J. Xing, T. C. Sum and Q. H. Xiong. *Adv. Funct. Mater.* 26 (34), 6238-6245, 2016. (# Equal contribution)

The contributions of the co-authors are as follows:

- Prof. Xiong and Prof. Sum supervised the project and revised the manuscript drafts.
- Dr Q. Zhang, Dr X.F. Liu and I prepared the manuscript drafts.
- I performed all the materials synthesis, collected X-ray diffraction patterns, emission spectrums, temperature-dependent absorption spectrums and conducted data evaluation.
- Dr Q. Zhang and Dr X.F. Liu conducted the lasing experiments and related data evaluation.
- Dr J. Xing performed the atomic force microscopy measurements.

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The contributions of the co-authors are as follows:

- Prof Xiong, Prof. Carole and I conceived the idea and designed the research.
- Prof Xiong, Prof. Diederichs., Prof. T.C.L. and I wrote the manuscript.
- I performed the DBR fabrication, sample growth, and all the optical measurements. J.W. and Prof. Z.C. helped on these experiments.
- Prof. T.C.L. carried out the theoretical calculations.

- S. Liu and W. G. Xu carried out the atomic force microscopy measurements.
- All authors discussed and commented on the manuscript.

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- I conceived the idea, designed the research, and performed the DBR fabrication, sample growth, and all the optical measurements.
- J.Z. and J.X. carried out the atomic force microscopy measurements.
- T.C.H.L. carried out all the theoretical calculations.
- All authors discussed and commented on the manuscript.

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Abstract

All-inorganic cesium lead halide perovskites are emergent semiconductors as excellent light emitters. With the ease of synthesis, high quantum efficiency, large absorption coefficient and seamlessly tunable bandgap, all-inorganic cesium lead halide perovskites are regarded as ideal semiconductor system to compensate traditional semiconductors towards high performance optoelectronic applications. In this thesis, I mainly focus on investigating light-matter interaction properties in cesium lead halide perovskites towards future optoelectronic applications.

The investigation starts from the synthesis of all-inorganic cesium lead halide perovskite crystals with excellent quality. A van der Waals (vdW) epitaxy technique is introduced in synthesizing all-inorganic cesium lead halide perovskite crystals based on a one-step vapor phase synthesis method. High quality cesium lead halide perovskite nanoplatelet crystals and large films can be obtained with excellent crystallinity and strong emissions. The emission of cesium lead halide perovskites can be seamlessly tuned from 1.7 eV to 3.0 eV by composition modulations. Most of the cesium lead halide perovskites are confirmed to possess stable excitons at room temperature by the absorption spectroscopy. Large exciton binding energies of ~ 37 meV for CsPbBr₃ and ~ 70 meV for CsPbCl₃ are extracted from the analysis of temperature-dependent exciton absorption peak linewidth behavior.

With naturally square structure and sharp edges, cesium lead halide perovskite nanoplatelet crystals serve as excellent whisper gallery mode microcavities. These cesium lead halide perovskite microcavities exhibit lasing with low threshold ranging from $2.0 \mu\text{J}/\text{cm}^2$ (peak power density of $2.0 \times 10^7 \text{ W}/\text{cm}^2$) to $10.0 \mu\text{J}/\text{cm}^2$ (peak power density of $1.0 \times 10^8 \text{ W}/\text{cm}^2$) and high quality factor over 3600. Multicolor lasing actions can also be realized by composition engineering in cesium lead halide perovskite crystals, ranging from blue region to red region.

By embedding the cesium lead chloride perovskite crystals into two highly reflective distribute bragg reflectors (DBRs), a strong light-matter interaction regime is realized, which is confirmed by the polariton dispersions. With a two coupled oscillator model, a large Rabi splitting energy of ~ 265 meV can be extracted from the polariton dispersion. Under pulsed laser excitations, the CsPbCl_3 microcavity exhibits polariton condensation and polariton lasing above a threshold of $\sim 12 \mu\text{J}/\text{cm}^2$ (peak power density of $1.2 \times 10^8 \text{ W}/\text{cm}^2$). This conclusion is further strengthened by a superlinear power dependence, macroscopic ground-state occupation, the full wavelength at half maximum (FWHM) narrowing, blueshift of the ground-state emission and the build-up of long-range spatial coherence. A transition from strong coupling to weak coupling regime is also observed in CsPbCl_3 microcavity, which further confirms the appearance of exciton polariton condensation and exciton polariton lasing.

One-dimensional (1D) cesium lead bromide perovskite microcavities are also demonstrated to operate in strong coupling regime. The 1D CsPbBr_3 microcavity exhibits low threshold of $0.8 \mu\text{J}/\text{cm}^2$ (peak power density of $8.0 \times 10^6 \text{ W}/\text{cm}^2$) for polariton condensation. With the unique 1D structure, the propagation properties of polariton condensates are investigated, showing a high propagation velocity of $10 \mu\text{m}/\text{ps}$ and long-range coherent flow of $60 \mu\text{m}$. Through modeling the dynamics of polariton condensate flow, a long lifetime of 3.0 ps is extracted. Our studies on cesium lead halide perovskites expand the semiconductor systems in light matter interactions, which provides considerable promises towards all-optical devices.

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Table of Contents

Abstract.....	1
Acknowledgement.....	3
Table of Contents.....	5
List of Figures.....	8
List of Abbreviations	16
Chapter 1 Introduction.....	17
1.1 Background and Motivations	17
1.2 All-inorganic Cesium Lead Halide Perovskites	22
1.2.1 Crystal Structure of Cesium Lead Halide Perovskites	22
1.2.2 Electronic Structure and Bandgap Engineering.....	23
1.3 Excitons.....	26
1.4 Properties of Microcavities	31
1.4.1 Distribute Bragg Reflectors	31
1.4.2 Fabry-Pérot Semiconductor Microcavity	32
1.4.3 Dispersion of Cavity Photons	33
1.4.3.1 Photon Dispersion in a Two-dimensional Planar Microcavity	33
1.4.3.2 Photon Dispersion in a One-dimensional Planar Microcavity.....	35
1.4.4 Equivalence between Incidence Angles and In-plane Wavevectors	37
1.5 Light-Matter Interactions	38
1.5.1 Weak Coupling Regime.....	39
1.5.2 Strong Coupling Regime	40
1.6 Exciton Polariton Bose-Einstein Condensation	45
1.7 Organization of This Thesis	50
Chapter 2 Experimental Setup	53
2.1 Chemical Vapor Deposition (CVD).....	53
2.2 E-beam Evaporation.....	54
2.3 Atomic Force Microscopy (AFM)	56
2.4 Ultraviolet Visible Near-Infrared Spectroscopy	58

2.5 Photoluminescence Spectroscopy	61
2.6 k -space and real-space Reflectivity and Photoluminescence Spectroscopy.....	63
2.7 Michelson Interferometer	65
2.8 Time-resolved Photoluminescence Spectroscopy	67
2.9 Summary	68

Chapter 3 Synthesis and Optical Properties of All-inorganic Cesium Lead Halide

Perovskites	69
3.1 Introduction	69
3.2 Van der Waals Epitaxy of Semiconductors.....	70
3.3 CVD Synthesis of All-inorganic Cesium Lead Halide Perovskites	72
3.3.1 Synthesis of Perovskite Nanoplatelets.....	72
3.3.2 Characterization of the Perovskite Nanoplatelets.....	74
3.3.3 Synthesis of Perovskite Films.....	76
3.3.4 Transfer Process	78
3.4 Optical Properties of All-inorganic Perovskites.....	79
3.4.1 Room Temperature Absorption and Emission of All-inorganic Cesium Lead Halide Perovskites.....	79
3.4.2 Temperature-dependent Absorption Spectroscopy of All-inorganic Perovskites ...	81
3.5 Summary	87

Chapter 4 Whispering Gallery Mode Photonic Lasing in All-inorganic Cesium Lead

Halide Perovskite Nanoplatelets	89
4.1 Introduction	89
4.2 Photonic Lasing Mechanism	91
4.3 Whispering Gallery Lasing in Perovskite Nanoplatelets	95
4.4 Summary	103

Chapter 5 Room Temperature Polariton Lasing in All-Inorganic Cesium Lead Halide

Perovskites	104
5.1 Introduction	104
5.2 Sample Preparation	109
5.3 Characterization of the Perovskite Microcavity.....	109
5.4 Perovskite Polariton Lasing - Negative Detuning.....	111
5.4.1 Exciton Polariton Dispersion - Negative Detuning	111

5.4.2 Exciton Polariton Lasing - Negative Detuning.....	113
5.4.3 Long-Range Spatial Coherence of Perovskite Polariton Condensates	118
5.5 Perovskite Polariton Lasing - Positive Detuning	120
5.5.1 Exciton Polariton Dispersion - Positive Detuning.....	120
5.5.2 Transition from Strong Coupling to Weak Coupling Regime.....	121
5.6 Summary	127
Chapter 6 Room Temperature Long-Range Polariton Condensate Flow in Cesium Lead Halide Perovskites.....	129
6.1 Introduction	129
6.2 Mechanism of Polariton Condensate Propagation	134
6.3 Fabrication of the Microwire Microcavity	136
6.4 Characterization of the CsPbBr ₃ Perovskite Microwire Microcavity	137
6.5 Polariton Condensation in a CsPbBr ₃ Microwire Microcavity	139
6.5.1 Polariton Dispersion	139
6.5.2 Polariton Condensation in a CsPbBr ₃ Microwire Microcavity	142
6.6 Polariton Condensate Flow in a CsPbBr ₃ Microwire Microcavity	145
6.7 Summary	150
Chapter 7 Conclusion and Future Work	152
7.1 Conclusion.....	152
7.2 Outlook for Future Works	155
7.2.1 Electrically Pumped Polariton Emission and Lasing based on Perovskite Microcavity.....	155
7.2.2 Realization of Room Temperature All-Optical Polariton Switches	156
References	157
Publication List	165

List of Figures

Figure 1-1. Schematic of a typical cubic crystal structure of 3D all-inorganic cesium lead halide perovskites.....	23
Figure 1-2. The calculated electronic band structures for three cesium lead halide perovskites (cubic phase) with density functional theory. Figure is taken from Ref. (65).....	24
Figure 1-3. (a) The colloidal solutions of cesium lead halide perovskites under a UV lamp exhibiting rich colors. (b) Typical PL spectra of cesium lead halide perovskites with different sizes and compositions. (c) Typical absorption and PL spectra of cesium lead halide perovskites with different sizes and compositions, showing the bandgap changes with different halide compositions. Figure is taken from Ref. (65).	25
Figure 1-4. (a) Schematic of a typical Wannier - Mott exciton, showing a large Bohr radius. (b) Schematic of a typical Frenkel exciton, showing a small Bohr radius.	27
Figure 1-5. Schematic of a simple band structure with both conduction and valence bands, showing parabolic behavior with the increase of kinetic energy. Multiple Rydberg excitons with different orders can be observed below the conduction band.....	30
Figure 1-6. (a) Schematic of a typical $\text{HfO}_2/\text{SiO}_2$ DBR. (b) The reflectivity spectrum of a typical 13 pair $\text{HfO}_2/\text{SiO}_2$ DBR showing high reflectivity of 99.5% for perovskite microcavity.	32
Figure 1-7. (a) Schematic of a 2D planar microcavity. (b) The dispersion of typical perovskite cavity photons, showing a parabolic behaviour.	34
Figure 1-8. (a) Schematic of a 1D planar microcavity. (b) The cavity photonic mode dispersion along k_x direction. (c) The cavity photonic mode dispersion along k_y direction. (d) Electric-field distribution of the first four modes. Figure is taken from Ref. (93).	36
Figure 1-9. Energy and in-plane wavevector conservations provide the possibility to probe the cavity photon dispersion by angle-resolved spectroscopy measurements.	38
Figure 1-10. Schematic physical rates of an emitter in a cavity, showing the loss rate of photon κ , the exciton decay rate γ and the light-matter coupling strength g	38
Figure 1-11. (a), (c) and (e) Dispersion of typical perovskite microcavities with detunings of - 80 meV, 0 meV, + 80 meV, respectively, showing the dispersions of the exciton (E_x), the cavity photon (E_c), the lower polariton branch (E_{LP}) and the upper polariton branch (E_{UP}) (b), (d) and (f) The Hopfield coefficients of polaritons as a function of incident angles with detunings of - 80 meV, 0 meV, + 80 meV, respectively, showing the exciton portion ($ X(k) ^2$) and cavity photon portion ($ C(k) ^2$).	44
Figure 1-12. (a) The schematic of a lot of bosons occupying the same quantum state. (b) Schematic of each fermion occupying each state.	45

Figure 1-13. (a) Schematics of the experimental principle for a polariton laser. (b) Schematics of the experimental principle for a photonic laser.	49
Figure 1-14. The two-threshold behaviour for a typical GaAs microcavity with the first threshold corresponding to polariton lasing regime and the second threshold corresponding to the photon lasing regime. Figure is taken from Ref. (108).	50
Figure 2-1. The detailed setup of a home-built CVD system with single-zone furnace. Notes with arrows are shown in the figure for further clarifications.	54
Figure 2-2. The schematic of an e-beam evaporator.	56
Figure 2-3. Schematic of an AFM.	57
Figure 2-4. Schematic of the lambda 950 UV/Vis/NIR spectrometer	59
Figure 2-5. Schematic of the scan process for absolute reflectivity spectroscopy. (a) The reference scan process. (b) The sample scan process. Figure taken from the manual of lambda 950.	60
Figure 2-6. Schematic of a conventional backscattering PL spectroscopy setup.	62
Figure 2-7. Schematic of the angle-resolved spectroscopy setup with Fourier optics.	65
Figure 2-8. Schematic of a Michelson interferometer setup probing the spatial coherence. ...	66
Figure 2-9. Schematic of Streak Camera system (Figure is taken from HAMAMATSU).	68
Figure 3-1. (a) Typical optical and scanning electron microscopy images of as-grown lead halide crystals. (b) The one to one correlation between lead halide crystals and lead halide perovskite crystals before and after conversions. Figure is taken from Ref. (112).	70
Figure 3-2. Schematics demonstrating the influence of lattice mismatch in (a) the conventional epitaxy where covalent bonding leads to strains in epilayers, (b) the unstrained vdW epitaxy of one inert layered material on another, and (c) the unstrained vdW epitaxy of one inert material on a passivated three-dimensional substrate. Figure is taken from Ref. (122).	72
Figure 3-4. (a) Optical microscope images of as-grown CsPbBr₃ nanoplatelets and films. Scale bar, 20 μm. (b) SEM image of CsPbBr₃ nanoplatelets on mica. Scale bar, 10 μm. (c) Optical microscope images of individual nanoplatelets with different thicknesses.	75
Figure 3-5. (a) XRD pattern of as-grown CsPbX₃ nanoplatelets showing cubic phase. (b) The FWHM of the (100) peak is around 0.1° which demonstrates the good crystallinity of as-synthesized perovskite nanoplatelets.	76
Figure 3-6. (a) The comparison of perovskite films on mica substrate and bare mica substrate. The area of perovskite films can be as large as 1.5 × 3 cm². Inset, the perovskite films show intense green emission under a UV lamp. (b) The SEM image of an as-grown continuous perovskite film, showing extremely flat surface. (c) The AFM image of an as-grown continuous	

perovskite film showing a surface roughness of 2 nm. **(d)** The measured XRD patterns of perovskite films after removing the mica substrate, showing excellent crystallinity of perovskite films.....77

Figure 3-7. **(a)** Optical absorption and PL spectra of CsPbCl₃, CsPbBr₃, and CsPbI₃ nanoplatelets. **(b)** Fluorescence images of as-grown CsPbX₃ nanoplatelets. **(c)** PL spectra of as-grown CsPbX₃ nanoplatelets, showing seamless emission wavelength tunability.80

Figure 3-8. **(a)** and **(b)** Temperature-dependent optical absorption spectra of CsPbBr₃ and CsPbCl₃ from 350 K to 77 K. **(c)** Plots of the excitonic absorption peak position as a function of temperature for CsPbCl₃ and CsPbBr₃. **(d)** Plots of the FWHM as a function of temperature for CsPbCl₃ and CsPbBr₃.....83

Figure 3-9. **(a)** Approximate FWHM extraction of the exciton absorption. **(b)** FWHM extraction by fitting the absorption spectrum with Elliot's theory of Wannier excitons.....83

Figure 3-10. The comparison of exciton binding energy of all-inorganic perovskites with traditional semiconductors.....85

Figure 3-11. **(a)** The absorption spectrum of as-grown CsPbBr₃ perovskite nanoplatelets at 12K. **(b)** the absorption spectrum of as-grown CsPbCl₃ perovskite nanoplatelets at 12K.....86

Figure 4-1. **(a)** Schematic of optical measurement principle for perovskite lasing. **(b)** The far-field optical microscopy images of CH₃NH₃PbI₃ nanoplatelets under white light (top panels) and pump laser (bottom panels) excitations. **(c)** and **(d)** Characterization of the lasing action based on individual CH₃NH₃PbI_{3-a} Br_a and CH₃NH₃PbI₃ nanoplatelets. Figure is taken from Ref. (59).90

Figure 4-2. **(a)** Schematic of the stimulated emission process. **(b)** A typical Fabry-Pérot cavity for a laser.....93

Figure 4-3. **(a)** A typical nanowire Fabry-Pérot microcavity. **(b)** WGM microcavity of square nanoplatelet, hexagonal nanoplatelet and nanosphere. **(c)** Photonic crystal microcavity. Figure is taken from Ref. (120).94

Figure 4-4. Schematic of the light propagating in a circular WGM cavity where the dashed lines show the light leakage out of the WGM cavity.....95

Figure 4-5. Lasing Characterization of Cesium Lead Halide Nanoplatelets. **(a)** The schematic of an individual CsPbX₃ (X= Cl, Br or I) nanoplatelet on mica substrate pumped by a 400 nm laser (~100 fs, 1 kHz). The yellow solid line shows the light propagation direction inside the square WGM cavity. **(b)** The measured emission spectra under five different optical pump fluencies, demonstrating the appearance of lasing. Inset: 2D pseudo-color plot of the nanoplatelet emission spectra under different pump fluences. **(c)** A Lorentzian fitting of a lasing mode gives a FWHM of 0.15 nm, which corresponds to a quality factor of 3570. **(d)** Power-dependent lasing output intensity, showing a superlinear increase of the output intensity above a threshold of ~ 2.2 μJ/cm² (peak power density of 2.2× 10⁷ W/cm²). **(e)** TRPL decay kinetics after photoexcitation at a pump fluence below ($P \sim 0.8P_{th}$) and above threshold ($\sim 1.2 P_{th}$),

showing a ~ 3.0 ns SPE decay process below P_{th} and a <30 ps lasing process above P_{th} . A lifetime of ~ 4.2 ns is shown at relatively low pump fluence ($\sim 0.1 P_{th}$).....96

Figure 4-6. Whispering-gallery-mode lasing characterization and numerical calculation.

(a) and (b) Photoluminescence emission image obtained by a CCD below and above the lasing threshold for an individual CsPbBr_3 perovskite nanoplatelet, respectively. Scale bar, $3 \mu\text{m}$. (c) Simulated electric field distribution inside the square perovskite cavity for a TM optical mode. The pattern demonstrates that the cavity supports a WGM lasing. (d) The measured multimode lasing spectra of four perovskite nanoplatelets with different edge lengths ranging from 9 to $29 \mu\text{m}$. The oscillation number of the lasing mode is indicated near the lasing peak in the case of the edge length of $9 \mu\text{m}$. (e) The spacing between two lasing modes is extracted and plotted as a function of the inverse of edge length. Navy dots are the experimental data while the navy line shows the fitting of the experimental data.100

Figure 4-7. Multicolor whispering-gallery-mode microlaser based on inorganic perovskites with high-quality factor.

(a) Lasing spectra and images of individual CsPbX_3 perovskite nanoplatelets with various halide compositions. Left to right: the halide element X in perovskite varies from $\text{Cl}_x\text{Br}_{3-x}$, Br, to $\text{Br}_x\text{I}_{3-x}$. Inset, emission images above the lasing threshold of perovskite with X changing from $\text{Cl}_x\text{Br}_{3-x}$, Br, to $\text{Br}_x\text{I}_{3-x}$. (b) A zoom-in spectrum of a lasing mode of $\text{CsPbBr}_x\text{I}_{3-x}$ perovskite. The blue dots and red line are experimental data and Lorentzian function fitting curve, respectively. The full width at half maximum $\delta\lambda$ of the lasing mode is 0.14 nm102

Figure 5-1. (a) Reflectivity spectrum of a GaAs microcavity at 5K, showing clear energy splitting when the exciton and cavity photon are in resonance. **(b)** The plotted reflectivity peak position as a function of the cavity detuning, showing a clear anticrossing feature. Figure is taken from Ref. (9).....105

Figure 5-2. (a) 3D images of k-space emission as a function of pump power. **(b)** Energy verse in-plane wavevector plot of polaritons as a function of the pump power. Figure is taken from Ref. (30).107

Figure 5-3. (a) The transmission spectra of hybrid perovskite samples at room temperature under different gratings with different pitches under two different polarizations. **(b)** The peak energy in transmission spectra as a function of the cavity detuning. Figure is taken from Ref. (167).108

Figure 5-4. Microcavity structure and emission. (a), Schematic of the perovskite microcavity, which is composed of a CsPbCl_3 rectangular nanoplatelet sandwiched between a top and a bottom $\text{HfO}_2/\text{SiO}_2$ DBR. (b), Schematic of the angle resolved setup with Fourier optics. Two Fourier lenses are shown as f_1 and f_2 . (c) and (d) Optical and fluorescence microscopy images of a rectangular-shaped CsPbCl_3 perovskite microcavity after fabrication. Scale bar, $12 \mu\text{m}$. (e) Room temperature absorption and PL spectra of a CsPbCl_3 perovskite nanoplatelet. The absorption spectrum (Orange trace) of the CsPbCl_3 perovskite nanoplatelet on mica substrate exhibits a strong excitonic peak at $\sim 3.045 \text{ eV}$. The PL emission spectrum (Blue trace) of the CsPbCl_3 perovskite nanoplatelet on mica substrate displays an emission at $\sim 2.99 \text{ eV}$ with a FWHM of 80 meV . The ground state emission (Red trace), along with

Gaussian fitting (black dash line) of a CsPbCl₃ nanoplatelet after microcavity fabrication, demonstrates an emission at ~ 2.90 eV with a FWHM of ~ 9.7 meV. 110

Figure 5-5. Angle-resolved reflectivity and PL mappings of a CsPbCl₃ perovskite microcavity. (a) Angle-resolved reflectivity spectrum measured using a white light lamp. The dashed white lines depict the fitting dispersions of the lower (LP) and upper (UP) polariton branches from a coupled oscillator model. The solid white lines show the dispersions of the cavity photon mode (C) and the uncoupled CsPbCl₃ perovskite exciton (X), extracted from the coupled oscillator model fitting. Another unfitted parabolic-like dispersion corresponding to the bare microcavity mode is observed, caused by the smaller sample size compared with the white light beam diameter. (b) Angle-resolved PL spectrum of the CsPbCl₃ perovskite microcavity. The detuning Δ is indicated inside the figure, which is extracted from the coupled harmonic oscillator model. Note, the slight energy difference between PL and reflectivity spectrum is caused by slightly different sample positions of the excitation spot on the sample. 112

Figure 5-6. Angle-resolved reflectivity dispersion of the bare microcavity without any perovskite inside, showing a resonant mode from SiO₂ spacer. 113

Figure 5-7. Power dependent angle-resolved PL spectrum. (a) Angle-resolved PL spectrum measured at $0.75 P_{th}$, which displays a wide range of distributions at all the emission angles. (b) Angle-resolved PL spectrum measured at $1.0 P_{th}$, which shows predominant emissions at the ground state near $k_{||} = 0$ of the lower polariton branch. (c) Angle-resolved PL spectrum measured at $1.3 P_{th}$. The ground state emission near $k_{||} = 0$ shows a dramatic intensity increase and an energy blueshift. 114

Figure 5-8. Characterizations of CsPbCl₃ microcavity polariton lasing. (a) Ground state emission spectra at $k_{||} = 0$ under different pumping fluences. A sharp increase of emission intensity occurs beyond $1.0 P_{th}$, suggesting the transition to the nonlinear regime. The emission energy is observed to be blue-shifted with the increasing pump fluence. (b) Ground state emission intensity at $k_{||} = 0$ and FWHM as a function of pump fluence. A linewidth narrowing occurs near the threshold of $P_{th} = 12 \mu\text{J}/\text{cm}^2$ (peak power density of $1.2 \times 10^8 \text{ W}/\text{cm}^2$, along with a sharp increase of emission intensity. (c) Energy blueshift with respect to the polariton emission energy at the lowest pump fluence as a function of pump fluence. The experimental blueshift of the ground state emission is shown as blue dots and the red solid line indicates the theoretical calculation of the blueshift. The blueshift trend below the threshold is attributed to polariton - reservoir interaction while the trend above the threshold corresponds to polariton-polariton interaction. 117

Figure 5-9. Demonstration of long-range spatial coherence. (a) Real space photoluminescence image measured above threshold from one arm of the Michelson interferometer. Dashed line, sample edges. Scale bar, $4 \mu\text{m}$. (b) Real space photoluminescence image obtained above threshold from the second arm by using a retroreflector to flip the image in a centrosymmetric way. Dashed line, sample edges. Scale bar, $4 \mu\text{m}$. (c) Interference pattern after superposition of the images above threshold from the two arms of the Michelson interferometer. Clear interferences are readily identified with a distance as large as $15 \mu\text{m}$,

demonstrating the build-up of long-range spatial coherence. Dashed line, sample edges. Scale bar, 4 μm 118

Figure 5-10. (a) Theoretically simulated photoluminescence dispersion below threshold and, (b) above threshold. Note that there is a slight blueshift of the emission with respect to the energy minimum in (a). (c) Simulated real-space distribution of polaritons in a disordered environment, showing condensation at localized points..... 119

Figure 5-11. Angle-resolved dispersion on a 360 nm thick perovskite microcavity. Angle-resolved reflectivity (a) and photoluminescence (b) measured below the polariton lasing threshold, at positive detuning ($\Delta = +70$ meV). The dispersions of the lower polariton (LP) and the Bragg mode (BM) are observed in reflectivity and PL, and the additional bare cavity mode (when no perovskite is embedded in the microcavity) is only observed in PL. The coupled oscillator model fits of the lower polariton (LP) and upper polariton (UP) dispersions are displayed along with the dispersions of the uncoupled exciton (X) and cavity (C) modes. The extracted Rabi splitting is 273 meV..... 121

Figure 5-12. Transition from strong coupling to weak coupling regime in momentum space. (a)-(c), Angle resolved photoluminescence spectrum obtained at 1.0 P_{th} , 1.6 P_{th} and 5.0 P_{th} , showing a transition from the polariton condensate regime to the weak coupling regime with a sharp decrease of the emission intensity at the lower polariton ground state. 122

Figure 5-13. Transition from strong coupling to weak coupling regime in momentum space. (a)-(c), Real space images obtained at 0.9 P_{th} , 1.6 P_{th} and 5.0 P_{th} , showing a broad emission distribution below threshold, while above threshold, a localized polariton condensate shows up in the body of the platelet. By further increasing the pump fluence to 5.0 P_{th} , the polariton condensate vanishes while a two orders of magnitude stronger emission appears at the edges of the platelet..... 124

Figure 5-14. Characterizations of the polariton lasing in a 360 nm thick perovskite microcavity. (a) Ground state emission intensity and FWHM at $k_{||} = 0$ as a function of the pump fluence. A typical S shape power dependent emission relationship suggests the occurrence of polariton lasing with a first threshold P_{th} of 55 $\mu\text{J}/\text{cm}^2$ (peak power density of $5.5 \times 10^8 \text{ W}/\text{cm}^2$), while the emission intensity decreases sharply crossing a pump fluence P_{th2} of 108 $\mu\text{J}/\text{cm}^2$ (peak power density of $1.08 \times 10^9 \text{ W}/\text{cm}^2$). The FWHM first slightly increases (from 10.1 meV to 11.4 meV) below the threshold P_{th} and narrows from 11 meV to 3.5 meV when crossing the threshold P_{th} , and then increases until 19 meV with the further increase of the pump fluence. (b) Ground state emission peak position at $k_{||} = 0$ as a function of the pump fluence. The emission peak position in the strong coupling regime shows continuous blueshift with two different slopes below P_{th2} . When crossing the second threshold P_{th2} of 108 $\mu\text{J}/\text{cm}^2$ to weak coupling regime, the energy position of another arisen peak corresponding to the EHP emission shows redshift with the increase of the pump fluence. (c) Edge emission intensity as a function of the pump fluence, extracted from the real space images of the perovskite microcavity. A clear threshold P_{th2} of 108 $\mu\text{J}/\text{cm}^2$ (peak power density of $1.08 \times 10^9 \text{ W}/\text{cm}^2$) was observed for the emission in the lateral modes. 126

Figure 5-15. The real space emission spectra of the perovskite microcavity at 1.6 P_{th} and 5.0 P_{th} . When the pump fluence is 1.6 P_{th} , the perovskite microcavity exhibits quite broad and weak emission at the EHP emission energy. Multiple narrow and strong peaks with equal mode spacing show up at a pump fluence of 5.0 P_{th} , which is corresponding to the appearance of photonic lasing. 127

Figure 6-1. The operation of an all-optical polariton switch. (a) The polariton density exhibits a transition with the increase of the pump power. At low pump power, the system is at off-state due to the low polariton population. While at high pump power, polariton-polariton interaction gives rise to a significant blueshift which bring the polaritons in resonance with the incident laser to generate high polariton population into on-state. (b) and (c) The experimental real-space images of emission under σ^+ polarization detection with σ^+ pump and σ^+ probe, respectively. (d) The experimental real space image when both the pump and probe with the same σ^+ polarization focus on the sample. (e) The experimental real space images when the pump and probe with opposite circular polarization focus on the sample. Figure is taken from Ref. (178). 131

Figure 6-2. The working principle of a polariton condensate switch. (a) The polariton condensate can freely propagate to the wire end. (b) The polariton condensate is blocked by a barrier caused by the gate beam. Figure is taken from Ref. (180). 133

Figure 6-3. Polariton condensation in microwires. (a) and (c) Momentum space spectra above the condensation threshold of polaritons located at different sides 30 μm away from the pump spot. (b) Momentum space spectra of polaritons at the pump spot. Figure is taken from Ref. (183). 134

Figure 6-4. Simulations of polariton condensation under different pump spot sizes. (a, c) The simulated k-space polariton condensation spectrum for a large pump spot and small pump spot, respectively. (b, d) The polariton population as a function of the in-plane wavevector for a large pump spot and a small pump spot, respectively. Figure is taken from Ref. (184). 136

Figure 6-5. (a) The schematic of the CsPbBr₃ microwire microcavity structure, showing x, y, and z axes. **(b) and (c)** The microscope and fluorescence images of CsPbBr₃ microwire microcavity after the fabrication process. The scale bar is 5 μm . **(d)** Room-temperature absorption and PL spectra of the CsPbBr₃ perovskite. Red trace shows the absorption spectrum of the CsPbBr₃ perovskite on mica substrate with have a strong exciton absorption peak at ~ 2.406 eV. Blue trace displays the PL emission spectrum of the CsPbBr₃ perovskite on mica substrate with a peak at ~ 2.353 eV and a FWHM of 60 meV. Olive trace presents the ground-state emission of the CsPbBr₃ microwire embedded into the microcavity, which shows a peak at ~ 2.297 eV with a FWHM of ~ 2.0 meV. **(e)** The measured emission from normal incidence fitted by a Gaussian function, showing a FWHM of 2.0 meV corresponding to a Q factor of ~ 1150 138

Figure 6-6. Angle-resolved photoluminescence mappings of the CsPbBr₃ perovskite microwire microcavity. (a) The long axis of the CsPbBr₃ microwire is set in parallel to the entrance slit (red arrow). (b) The measured polariton emission dispersion when the long axis x is in parallel to the entrance slit of the spectrometer. The dashed white lines represent the theoretical fitting dispersion of the lower (LP) and upper (UP) polariton branches. The solid

white lines are the dispersions of cavity photon mode (C) and uncoupled CsPbBr₃ perovskite exciton (X) obtained from the two-coupled harmonic oscillator model fitting. (c) The theoretically calculated polariton dispersion when the long axis x is parallel to the entrance slit of the spectrometer. (d) The short axis y of the CsPbBr₃ microwire is in parallel to the entrance slit (red arrow). (e) The measured polariton dispersion when the short axis y is parallel to the entrance slit, showing multiple discrete states. (f) The theoretically calculated polariton dispersion when the short axis y is parallel to the entrance slit. 141

Figure 6-7. Evidence of the strong coupling regime in the perovskite microcavity operating. The polariton dispersion with emission angle up to 64° is shown, when the long axis of the microwire is parallel to the entrance slit. 142

Figure 6-8. Characterization of polariton condensation at room temperature. (a) The polariton dispersion at $0.75 P_{th}$, showing a broad emission distribution at all the angles. (b) The polariton dispersion at $1.30 P_{th}$ showing symmetric dominant emission at around $\pm 20^\circ$. The polariton condensation with non-zero $k_{||}$ inclines the role of polariton propagation. (c) The simulated polariton dispersion mapping at $1.3 P_{th}$. (d) The evolution of emission intensity and linewidth as a function of pumping fluence. (e) The power dependent energy blueshift with respect to the polariton energy at the lowest pump fluence. (f) and (g) Real space image and its inverted image of the perovskite microwire microcavity at $1.3 P_{th}$. The scale bar is $4 \mu m$. (h) The superposition of the real space image and its inverted image of the perovskite microwire microcavity at $1.3 P_{th}$. Clear interferences can be observed within a distance of $25 \mu m$, confirming the build-up of the long-range spatial coherence. 143

Figure 6-9. Real space image of the perovskite microcavity above the threshold. (a) Schematic of the pumping spot (blue) and collection spot (red) on the microwire microcavity. (b) The measured real space image of the microwire microcavity when the pump spot locates at the right end of the wire. (c) The measured real space image of the microwire microcavity when the pump spot locates at the middle of the wire. 146

Figure 6-10. Long-range spatial coherence of propagating polariton condensate. The pump spot (small area of $3 \mu m^2$) was moved to the end of the CsPbBr₃ microwire. 147

Figure 6-11. Polariton condensate propagation at room temperature. (a) and (b) The measured and simulated polariton emission mappings as a function of emission angle respectively when the pump spot locates at the right end of the perovskite wire, showing dominant emission at $\sim -15^\circ$. (c) The measured polariton emission mappings as a function of emission angle respectively when the pump spot locates at the left end of the perovskite wire, showing dominant emission at $\sim 15^\circ$ 148

Figure 6-12. Theoretically calculated time integrated intensity pattern of polaritons generated by pulsed excitation at one end of the microwire. The different plots consider different polariton decay rates. The decay rate must be small enough for a significant fraction of polaritons to traverse the microwire and be reflected for interference fringes to appear as clearly as in the experiment. Parameters: $\hbar r = 0.02 \mu eV$, $gR = 0.082 \mu eV \mu m^2$, $\alpha = 0.5 gR$; the pump spot was taken as a Gaussian with widths $2 \mu m$ and $1.5 \mu m$ along and perpendicular to the microwire axis, respectively. 149

List of Abbreviations

Van der Waals (vdW)
Distribute Bragg Reflectors (DBRs)
Full Wavelength at Half Maximum (FWHM)
One-dimensional (1D)
Three-dimensional (3D)
Two-dimensional (2D)
Photoluminescence (PL)
Bose-Einstein Condensation (BEC)
Chemical Vapor Deposition (CVD)
Atomic Force Microscopy (AFM)
Ultraviolet Visible Near-Infrared (UV-Vis-NIR)
Amplified Spontaneous Emission (ASE)
Whisper Gallery Mode (WGM)
Transverse Magnetic (TM)
Transverse Electric (TE)
Spontaneous Emission (SPE)
Time-resolved Photoluminescence (TRPL)
Finite Domain Time Difference (FDTD)
Electron-hole Plasma (EHP)

Chapter 1 Introduction

1.1 Background and Motivations

The rapid technological advance of cutting-edge tools and techniques to manipulate matter in the nanoscale regime is providing new platforms for efficiently controlling light in semiconductors. Consequently, the interaction between the confined electromagnetic modes and semiconductor active media can be largely tuned (1-4). By integrating semiconductor emitters into microcavities to tailor the dipole emission has given rise to a variety of practical applications, such as laser diodes (5, 6), or to the investigation of interesting phenomena such as emission enhancement due to the coupling with the cavity mode (weak coupling) or exciton-polariton (strong coupling). When the interaction rate between the semiconductor active medium and the confined electromagnetic mode is slower than their losses, the system reaches a ‘weak coupling’ regime (7, 8), leading to the enhancement of emission. In the opposite case in which the interaction rate between the semiconductor active medium and the confined electromagnetic mode becomes faster than their losses, the system turns into a so-called ‘strong coupling’ regime (9, 10).

In 1946, Purcell firstly proposed that the spontaneous emission from a dipole could be greatly enhanced by coupling it to an optical cavity, which is known as *Purcell effect* working in the weak coupling regime (8). In 1983, P. Goy *et al.* reported the first observation of atomic spontaneous emission enhancement by coupling the Rydberg atoms of Na to a niobium superconducting cavity (11). After that, such effect in the weak coupling regime was further extended to quantum dots embedded in microdisks (12), micropillars (13) and photonic crystals (14) to enhance the spontaneous emission. Later, Purcell effect is regarded as an effective way to optimize the performance of optoelectronic applications, such as low threshold lasers (15-18), single photon sources (19, 20), light emitting diodes (21-24).

Strong coupling regime stems from the early work by Kun Huang where coupled states of phonon polaritons were obtained in 1951 (25). Later, Hopfield studied the strong coupling between exciton and photon which can lead to new quasiparticles of exciton polaritons in 1958 (26). Until 1992, C. Weisbuch *et al.* demonstrated the first experimental realization of strong coupling between exciton and photon (9). Four years later, A. Imamoglu *et al.* predicted the low threshold laser without population inversion based on exciton polaritons (27). Thanks to the bosonic nature and low effective mass, exciton polaritons are regarded as promising candidates to investigate exotic quantum phenomena, for example, Bose Einstein condensation (BEC) (28-30), quantum vortices (31-34) and superfluidity (35-42). In 2006, J. Kasprzak *et al.* reported the pioneering work of first exciton polariton BEC in a CdTe microcavity at liquid helium temperature (30), which is regarded as a milestone for polariton research. Since then, it opened the door to study the exotic quantum phenomena of quantum vortices (32) and superfluidity (40), both of which were experimentally observed later. Limited by the small exciton binding energy of CdTe and GaAs, such exotic quantum phenomena can only be observed at liquid helium temperatures. In 2007, S. Christopoulos *et al.* reported the first realization of optically pumped polariton laser at room temperature based on a GaN microcavity (43), which is regarded as a breakthrough. After that, various kinds of semiconductor systems have been adopted to realize BEC at room temperature, including ZnO (44, 45) and organic materials (46-49) with large exciton binding energy. In 2010, S. Kena-Cohen *et al.* firstly realized optically pumped polariton laser at room temperature based on an anthracene crystal (46), followed by several other reports based on organic materials (47-49). In 2013, C. Schneider *et al.* demonstrated the important breakthrough of first electrically pumped polariton laser at room temperature (50), which promotes the practical implementations of polariton devices. Until recently, G. Lerario *et al.* revealed the first room temperature observation of superfluidity based organic polariton condensate (42). Even though

there have been various kinds of breakthroughs on exciton polariton BEC and its related quantum phenomena, significant experimental efforts are still required to push such breakthroughs to room temperature or to be realized in a more accessible way with better performances.

In the recent years, organic-inorganic hybrid lead halide perovskites $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X}=\text{I}$, Br, or Cl, mixed I/ Br, Br/ Cl system) have attracted significant attention in the past decade owing to their remarkable performance as light absorber with large absorption coefficient in solar cells, which have witnessed a remarkable improvement in certified power conversion efficiency surpassing 20% (51-53). In addition to their large absorption coefficient property (54), they also exhibit various advantages, such as direct bandgaps, high quantum efficiency with negligible trapping states, stable excitons at room temperature, seamless wavelength tunability, an ease of material synthesis and abundance. Possessing such a wide range of fascinating properties, organic-inorganic hybrid lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbX}_3$ system have been considered as one of the most promising semiconductor systems towards optoelectronic applications in recent years. In addition to their high performance in photovoltaic technology, organic-inorganic hybrid lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbX}_3$ system also exhibit considerable potential in various light emitting applications, including high efficiency light emitting diodes (55-58), low threshold and high quality factor (Q) nanolasers (59-62). However, the most pronounced disadvantage of organic-inorganic hybrid lead halide perovskite $\text{CH}_3\text{NH}_3\text{PbX}_3$ system is the poor stability under moisture and light, which significantly hinders the possible practical applications. In comparison, their all-inorganic lead halide perovskite counterparts CsPbX_3 ($\text{X}=\text{I}$, Br, or Cl, mixed I/ Br, Br/ Cl system) which possess much better stability (63, 64), similar outstanding optical and electric properties (65), are regarded as ideal alternatives to organic-inorganic lead halide perovskites $\text{CH}_3\text{NH}_3\text{PbX}_3$ to compensate traditional semiconductor systems towards future novel technological advances

(66-72).

As excellent light emitters with large exciton binding energy, all-inorganic cesium lead perovskites are promising candidates to reach different exciton photon coupling regimes, either in weak coupling regime for enhancing the spontaneous emission or in the strong coupling regime for realizing room temperature exciton polariton towards high performance optoelectronic applications. At the early stage of my PhD in 2014, the majority of researchers in the world were focusing on organic-inorganic lead halide perovskites $\text{CH}_3\text{NH}_3\text{PbX}_3$ for various emission applications. The investigations on all-inorganic cesium lead halide perovskites remained largely unexplored, particularly in exploring different light matter interactions. Hence, the major motivation of this thesis is to investigate exciton photon coupling based on all-inorganic cesium lead halide perovskites with the help of microcavities, which is aiming at potential optoelectronic applications with better performance operated at room temperature.

All the possible optoelectronic applications rely on high quality samples. At the time when I began my PhD in 2014, there were few reports on the synthesis of high quality cesium lead halide perovskites, which usually resulted in amorphous or polycrystalline films. Thus, the first motivation of this thesis was to solve the sample preparation issue on cesium lead halide perovskites and aimed to achieve high quality cesium lead halide perovskite nanostructures and films towards nanophotonics and optoelectronic applications.

The second objective of this thesis was to tailor the emission of cesium lead halide perovskites towards optoelectronic applications. Microcavities are useful tools to tailor the emission of active media, while almost no works have been done on cesium lead halide perovskites when I started my PhD. Here I aimed to use active microcavities where the perovskite itself acts as a microcavity, and passive microcavities where the perovskites are embedded in two DBR mirrors, to reach different light-matter coupling regimes. The emission

of perovskites could be significantly increased in a weak coupling regime, giving rise to low threshold lasing. While the emission could also be tailored into new quasiparticles of exciton polaritons in strong coupling regime.

The third objective of this thesis was to achieve room temperature exciton polariton condensation and lasing based on cesium lead halide perovskites in strong coupling regime. As discussed before, exciton polariton condensation and polariton lasing have been achieved in various semiconductor systems. While most of them operates at cryogenic temperatures due to the limitation of small exciton binding energy (30, 73). Until recent years, semiconductors with large exciton binding energy, such as ZnO (45) and GaN (43), have also demonstrated polariton condensation at room temperature with the need of cutting edge epitaxial techniques. Organic semiconductors with stable exciton and solution processability can demonstrate polariton condensation at room temperature (46-48). But limited by the weak polariton-polariton interaction, large polariton condensation threshold is usually observed in organic microcavities. Thus, it is crucial to find a system which can sustain room temperature low threshold operation of polariton condensation and lasing, as well as ease of epitaxy-free fabrications.

Finally, I aimed to achieve room temperature long-range polariton condensate flow based on 1D cesium lead halide perovskite microcavities. Polaritons exhibit great promise in all-optical integrated circuits which is based on the propagation of polaritons. Such basic elements for all-optical integrated polariton circuits, such as optical switches and transistors, can only operate at cryogenic temperatures which is possibly hindered by the limitation of low temperature operation of long-range polariton propagation. Thus, the realization of long-range polariton condensate flow at room temperature could be an important step towards the development of polariton devices in all-optical integrated circuits working at room temperature.

1.2 All-inorganic Cesium Lead Halide Perovskites

1.2.1 Crystal Structure of Cesium Lead Halide Perovskites

A perovskite refers to any material possessing the same crystal structure as calcium titanium oxide (CaTiO_3) crystal which was firstly found by Gustav Rose in the Ural mountain of Russia and is named after a Russian mineralogist L. A. Perovski (74). The typical chemical formula of perovskite compounds can be written as ABX_3 , where A could be a metallic cation or organic cation, B is usually a metallic cation and X is an anion that bonds to both. Figure 1-1 shows the typical cubic crystal structure of the three-dimensional (3D) all-inorganic cesium lead halide perovskites that I am focusing on in this thesis, where A represents the Cs^+ cation, B is the Pb^{2+} cation and X could be Cl^- , Br^- , I^- or their mixture. The Pb^{2+} located at the body center of the perovskite unit cell is surrounded by six halide anions at the face centers to form an $[\text{PbX}_6]^{4-}$ octahedral, constructing a 3D octahedral network. While the Cs^+ cations are sitting at the eight corners of the perovskite unit cell. In order to retain the cubic structure in perovskite, the tolerance factor, which is related to the ionic radii of constituent ions, should be in the range of 0.89–1 (75). If the tolerance factor is smaller than this range, the perovskite will exhibit crystal structure with a lower symmetry, such as orthorhombic phase or tetragonal phase. Inversely, perovskite could exhibit a two-dimensional (2D) layered structure when the tolerance factor is larger than 1. This is usually the case of 2D perovskites by replacing the A cations with long carbon chain ligands, such as $\text{C}_5\text{H}_6\text{CH}_3\text{NH}_2^-$ (BA^-). All-inorganic cesium lead halide perovskite could also exhibit various crystal structures under different temperatures. For example, CsPbBr_3 perovskite possesses a cubic structure at a temperature above 130°C , a tetragonal structure at a temperature between $88\text{--}130^\circ\text{C}$ and an orthorhombic structure at a temperature below 88°C (76). CsPbCl_3 perovskite exhibits the cubic structure at a temperature above 30°C while it changes into a tetragonal phase at a temperature below 30°C (76, 77).

Figure 1-1. Schematic of a typical cubic crystal structure of 3D all-inorganic cesium lead halide perovskites.

1.2.2 Electronic Structure and Bandgap Engineering

In cesium lead halide perovskites, the direct bandgap locates at the R point of the Brillouin zone, as shown in Figure 1-2. Both the electron and hole in all-inorganic cesium lead halide perovskites are associated with the $[\text{PbX}_6]^{4-}$ octahedra. According to density functional theory calculations (65), the $6p$ -orbital electrons in Pb atoms (Pb- $6p$) mainly contribute to the minimum of conduction band in cesium lead halide perovskites, while both the $6s$ -orbitals in Pb atoms (Pb- $6s$) and the p -orbitals in X atoms (X- p) contribute to the maximum of valence band (78). This behavior is opposite to the conventional GaAs system where the valence band is determined by As- p orbital and the conduction band is contributed by Ga- s orbital. Specifically, the maximum of valence band is associated with the I- $5p$ orbital, Br- $4p$ orbital, Cl- $3p$ orbital for CsPbI_3 , CsPbBr_3 and CsPbCl_3 , respectively (65, 78). Due to the atomic orbital increase in binding energy from I to Cl, the bandgap of cesium lead halide perovskite consequently increases from I to Cl (65).

Figure 1-2. The calculated electronic band structures for three cesium lead halide perovskites (cubic phase) with density functional theory. Figure is taken from Ref. (65).

The experimental results are consistent with the theoretical calculations of bandgap behaviour changing from deep blue to red from CsPbCl₃ to CsPbI₃ (65, 78). Consequently, the perovskite bandgap could be readily controlled by changing the perovskite stoichiometry attributing to the ease of halide anion-exchange (79, 80). Taking cesium lead halide perovskite quantum dots as an example, as shown in Figure 1-3 (65), the emission and absorption could be seamlessly tuned by substituting different halide elements. Specifically, by doping I ions into CsPbBr₃ and doping Br ions into CsPbCl₃, the photoluminescence (PL) of cesium lead halide perovskites can be continuously tuned from 400 nm (deep blue region) to 700 nm (red region). In addition, by replacing the lead ions with other metal ions such as Sn, the emission of all-inorganic perovskite could be further extended to near-infrared region (81, 82). The ease of emission wavelength tunability provides all-inorganic cesium lead halide perovskites a promising future in various light emitting devices.

Figure 1-3. (a) The colloidal solutions of cesium lead halide perovskites under a UV lamp exhibiting rich colors. (b) Typical PL spectra of cesium lead halide perovskites with different sizes and compositions. (c) Typical absorption and PL spectra of cesium lead halide perovskites with different sizes and compositions, showing the bandgap changes with different halide compositions. Figure is taken from Ref. (65).

All-inorganic cesium lead halide perovskites are excellent light emitters with direct bandgap and high quantum efficiency (65, 83). High quantum efficiency of 50-90% was reported in the all-inorganic perovskite quantum dots without any surface passivation (65, 83), which is usually much higher than that of conventional semiconductor nanocrystals without any surface passivation. Such high quantum efficiency is crucial towards light harvesting and emitting applications, which could be attributed to a clean bandgap with negligible trapping states in all-inorganic perovskites (84).

In addition to the high PL quantum efficiency, most of cesium lead halide perovskites possess stable excitons at room temperature because the exciton binding energy is larger than that of room temperature thermal energy. It opens the way to novel excitonic applications which significantly favor excitons with large exciton binding energy for room temperature operation. With the effective mass theory, L. Protesescu *et al.* calculated the theoretical exciton binding energies E_b , as well as the Bohr radius a_0 of excitons in cesium lead halide perovskites

(65). As shown in Table1-1, the Bohr radius of excitons in cesium lead halide perovskites increases from 2.5 nm for CsPbCl₃ to 6.0 nm for CsPbI₃, as a result of the increasing effective dielectric constant and the reducing of carrier effective mass. Consequently, the exciton binding energy of cesium lead halide perovskites decreases significantly from 75 meV for CsPbCl₃ to 20 meV for CsPbI₃, which is still dramatically larger than that of traditional semiconductors in the same bandgap region.

Table 1-1. The calculated exciton binding energy and Bohr radius of all-inorganic cesium lead halide perovskites. Data is taken from Ref. (65).

	E_b (meV)	a_0 (nm)
CsPbCl₃	75	2.5
CsPbBr₃	40	3.5
CsPbI₃	20	6.0

Possessing such excellent optical properties of high quantum efficiency and large exciton binding energy, all-inorganic cesium lead halide perovskites are regarded as ideal candidates for tailoring light-matter interactions, as well as novel all-optical applications.

1.3 Excitons

Optical band to band absorption can produce a hole in the valence band and an electron in the conduction band, which could bound together by their attractive Coulomb interaction to generate a hydrogen-like bound state called exciton. Exciton is a fundamental excitation in condensed matter, playing a significant role in the optical properties of semiconductors. Generally, there are two main models to describe excitons in crystals: Wannier-Mott excitons and Frenkel excitons.

Wannier-Mott excitons, also called free excitons, are mainly observed in inorganic materials (85). Figure 1-4a schematically illustrates the formation of Wannier-Mott excitons in crystals. An electron and a hole orbit around each other by their mutual Coulomb attraction within the crystal. This type of excitons usually possess a large Bohr radius, thus encompassing many atoms. For example, the Bohr radius of exciton in GaAs is around 12 nm, as shown in Table 1-2. Wannier-Mott excitons are delocalized states which can move freely in the crystal. Such exciton delocalization gives rise to strong exciton-exciton interactions, which can lead to a large nonlinearity. As a comparison, in Figure 1-4b, Frenkel excitons which are mainly observed in organic materials such as molecules, usually have a relative smaller Bohr radius which is comparable to the lattice constant of around 0.5 nm (86), resulted from a reduced Coulomb screening effect in organic materials. Such feature makes them highly localized and tightly bound to specific atoms, which exhibits less mobility than that of the Wannier-Mott excitons. Frenkel excitons can in fact only move around in the crystal through hopping from one to another atom. Consequently, exciton-exciton interaction is usually weaker in Frenkel excitons than that of Wannier-Mott excitons (87).

Figure 1-4. (a) Schematic of a typical Wannier - Mott exciton, showing a large Bohr radius. (b) Schematic of a typical Frenkel exciton, showing a small Bohr radius.

An exciton could be stable only if the attractive potential between an electron and a hole is larger than the collision energy with phonons. In order to promote excitonic applications, excitons are required to exist at room temperature, which suggests that the exciton binding energy should be larger than that of room temperature thermal excited phonon energy (~25 meV). Due to the large Bohr radius, Wannier-Mott excitons usually possess quite small exciton binding energy which is typically around 0.01 eV, as shown in Table 1-2. In this case, most of the Wannier-Mott excitons cannot exist at room temperature, except in a few wide bandgap inorganic materials, such as ZnO and GaN. On the other hand, due to the tightly bound nature and small Bohr radius, Frenkel excitons usually possess extremely large exciton binding energy up to 1 eV, which provides them high stability at room temperature.

Table 1-2. The calculated bandgap, exciton binding energy and Bohr radius of Wannier-Mott excitons in traditional direct bandgap semiconductors. Data is taken from Ref. (87).

Crystal	Bandgap (eV)	Exciton binding energy (meV)	Bohr radius (nm)
ZnO	3.37	60	2.5
GaN	3.4	26	3.1
ZnSe	2.8	20	4.5
CdS	2.6	28	2.7
ZnTe	2.4	13	5.5
CdSe	1.8	15	5.4
CdTe	1.6	12	6.7
GaAs	1.5	4.2	13
InP	1.4	4.8	12
GaSb	0.8	2.0	23

In Wannier-Mott excitons, the separation of electrons and holes is much wider than the lattice constant of the inorganic material, as shown in Figure 1-4a. Thus, it is reasonable to treat electrons and holes moving in a uniform dielectric material. The internal structure of Wannier excitons can be modelled as a hydrogenic system. This leads to the dispersion of Wannier excitons described by (88):

$$E_{ex}(n_B, k) = E_g - \frac{R_y^*}{n_B^2} + \frac{\hbar^2 k^2}{2(m_e + m_h)}$$

where E_g is the bandgap of the inorganic material, n_B is the principal quantum number, $\hbar$ is the Plank constant, k is the wave vector of exciton, m_e and m_h are the mass of an electron and a hole, respectively. The exciton binding energy R_y^* can be further described by:

$$R_y^* = 13.6eV \frac{\mu}{m_0} \frac{1}{\varepsilon^2}$$

with
$$\mu = \frac{m_e m_h}{m_e + m_h}$$

where ε is the dielectric constant of the inorganic material, μ is the effective exciton mass, and m_0 is the free electron mass. The separation r_n between electron and hole is given by the Bohr Model to be:

$$r_n = \frac{m_0}{\mu} \varepsilon n^2 \alpha_H = n^2 \alpha_X$$

with
$$\alpha_X = \frac{m_0 \varepsilon}{\mu} \alpha_H$$

where α_H is the Bohr radius of the hydrogen atom and α_X is the Bohr radius of the exciton. As one can see, a series of Rydberg excitons with different principal numbers could be formed below the conduction band, as shown in the schematic of band structure in Figure 1-5. The first

order Rydberg exciton ($n=1$) possesses the largest exciton binding energy and the smallest Bohr radius according to the equations. The exciton Bohr radius usually determines the wavefunction overlap between adjacent excitons at a given exciton density. With the increase of exciton density, excitons will dissociate into an electron-hole plasma owing to the screening of the Coulomb interaction. This process is known as a Mott transition process with a critical exciton density known as Mott density n_{Mott} , which can be approximately given by (89):

$$n_{Mott} \approx \frac{1}{\frac{4}{3}\pi r_n^3}$$

Figure 1-5. Schematic of a simple band structure with both conduction and valence bands, showing parabolic behavior with the increase of kinetic energy. Multiple Rydberg excitons with different orders can be observed below the conduction band.

In order to tailor the emission of excitons, microcavities are used as the main technique to explore various exciton photon coupling regimes. In the following sections, I will mainly introduce the properties of microcavities and the interaction between excitons and the confined photons in the cavity.

1.4 Properties of Microcavities

The interaction between excitons and photons is realized by inserting an active medium into a microcavity. The microcavity discussed here is a 2D Fabry-Pérot resonator, which is comprised of the active medium embedded in two Bragg mirrors.

1.4.1 Distribute Bragg Reflectors

A DBR is a kind of highly reflective dielectric mirrors, which is formed by alternating two kinds of dielectric layers with different refractive indices into multiple pairs, as shown in Figure 1-6a. The thickness of each layer is precisely controlled to be $\lambda/4n_i$, where λ is the wavelength of the incoming light and n_i is the refractive index of the dielectric layers. Under these conditions, the reflected light will experience multiple constructive interference processes to yield a high reflectivity of the DBR within a broad spectral range, called stopband. The reflectivity in the stopband is usually affected by the refractive index and number of the pair layers, which can be described by (90):

$$R = 1 - 4 \frac{n_{ext}}{n_c} \left(\frac{n_L}{n_H} \right)^{2N}$$

Where n_H, n_L are the high and low refractive index of dielectric layers, n_{ext} is the refractive index of the external medium and n_c is the refractive index of the cavity. N represents the number of dielectric material pairs. As one can see, n_L / n_H is always smaller than one. The reflectivity of the DBR could then be enhanced by increasing the pair number and also enlarging the refractive index difference between the high and low refractive index dielectric layers. As shown in Figure 1-6b, ultrahigh reflectivity of 99.5% at around 425 nm could be achieved with a typical DBR consisting of 13 pair of $\text{HfO}_2/\text{SiO}_2$ dielectric layers with refractive indices of 2.2 and 1.48 respectively.

In addition to the reflectivity, the spectral width of the stopband Δs is another important parameter for DBR, which is controlled by the refractive index difference between the high and low refractive index layers according to (91):

$$\Delta s = \frac{\lambda(n_H - n_L)n_H n_L}{\pi(n_H + n_L)}$$

Figure 1-6. (a) Schematic of a typical HfO₂/SiO₂ DBR. (b) The reflectivity spectrum of a typical 13 pair HfO₂/SiO₂ DBR showing high reflectivity of 99.5% for perovskite microcavity.

1.4.2 Fabry-Pérot Semiconductor Microcavity

A Fabry-Pérot semiconductor microcavity usually consists of an active medium sandwiched by two highly reflective DBRs. The length between the two highly reflective DBRs is usually designed to be

$$L_c = N \frac{\lambda}{2n_c}$$

Where N is an integer and λ is the wavelength of excitons in our case. However, as the cavity field can penetrate into the DBRs, a penetration length needs to be considered as (90):

$$L_{DBR} = \frac{\lambda}{2n_c} \frac{n_L n_H}{n_H - n_L}$$

In this case, the total cavity length is given by:

$$L_{eff} = L_c + L_{DBR}$$

thus, the resonant optical modes of the Fabry-Pérot microcavity is given by:

$$\lambda_c = \frac{2n_c L_{eff}}{N}$$

The quality of the Fabry-Pérot microcavity is defined by the quality factor (Q), which describes the numbers of round trips of the light travelling in the microcavity and is defined as:

$$Q = \frac{\lambda_c}{\Delta\lambda_c}$$

Where λ_c is the resonance wavelength at normal incidence and $\Delta\lambda_c$ is the FWHM of the resonance peak. Generally, a good microcavity should possess a high Q which can reach values as large as 10^6 (in photonic crystal microcavities for example) and the Q of an ideal microcavity is infinite.

1.4.3 Dispersion of Cavity Photons

1.4.3.1 Photon Dispersion in a Two-dimensional Planar Microcavity

A 2D planar microcavity provides light confinement along the cavity growth direction, while no confinement is induced perpendicularly to the growth direction, as shown in Figure 1-7a. This means that photons are free to propagate in the in-plane direction of the microcavity, which gives rise to the rotational symmetry of cavity photons. Thus, the cavity photon dispersion will not change no matter how the microcavity is rotated with respect to the cavity growth direction. When considering a $\lambda/2$ semiconductor microcavity, the induced confinement

only imposes the light wavevector quantization along the growth direction (z), which can be described by (92):

$$k_z = \frac{\pi}{L_c}$$

thus, the dispersion of cavity photons in 2D planar microcavity can be described by:

$$E_c(k) = \frac{\hbar c}{n_c} \sqrt{k_z^2 + k_{\parallel}^2} = \frac{\hbar c}{n_c} \sqrt{\left(\frac{\pi}{L_c}\right)^2 + k_{\parallel}^2}$$

In the region of $k_{\parallel} \ll k_z$, we have:

$$E_c(k) = \frac{\hbar c}{n_c} \sqrt{k_z^2 + k_{\parallel}^2} \approx \frac{\hbar c}{n_c} \left(k_z + \frac{k_{\parallel}^2}{2k_z}\right) = E_0 + \frac{\hbar^2 k_{\parallel}^2}{2m_{cav}}$$

Where $k_{\parallel}$ is the in-plane wave vector (perpendicular to the growth direction) of photons in the microcavity and E_0 is the energy of light when $k_{\parallel}$ is equal to 0.

Figure 1-7. (a) Schematic of a 2D planar microcavity. **(b)** The dispersion of typical perovskite cavity photons, showing a parabolic behaviour.

The cavity photon dispersion is parabolic as shown in Figure 1-7b. Thus, an effective mass m_{cav} of the cavity photon can be introduced to describe the curvature of the cavity photon dispersion according to:

$$m_{cav} = \frac{n_c \hbar \pi}{L_c c}$$

The effective mass of the cavity photon is usually extremely light, which is usually five orders lower than that of the free electron mass.

1.4.3.2 Photon Dispersion in a One-dimensional Planar Microcavity

Similarly, in a 1D $\lambda/2$ planar microcavity, the wavevector k_z along the cavity growth direction is still quantized:

$$k_z = \frac{\pi}{L_c}$$

While due to the lateral discontinuity of the refractive index in the in-plane direction, an additional quantization along the y direction is introduced, giving rise to a quantized k_y (93):

$$k_y = \frac{(j+1)\pi}{L_y}$$

where L_y is the length of the short axis of the one-dimensional microcavity and $j=0, 1, 2, 3, \dots$

Thus, when taking into account this additional lateral quantization, the cavity photon dispersion is only continuous along the k_x direction, which can be described by:

$$E_c^{1D}(j, k_x) = \frac{\hbar c}{n_c} \sqrt{k_x^2 + k_y^2 + k_z^2} = E_0 \sqrt{1 + \left[\frac{(j+1)\pi}{L_y} \right]^2 \frac{1}{k_z^2} + \frac{k_x^2}{k_z^2}}$$

where $E_0 = \frac{\hbar c k_z}{n_c}$. Consequently, there will be multiple continuous photonic modes along the

k_x direction due to the additional quantized k_y . However, owing to the rotational symmetry breaking, the cavity dispersion along k_y direction is not the same as that of the k_x direction.

Along the k_y direction, the cavity photon dispersion can be described by:

$$E_c^{1D}(j, k_y) = \frac{\hbar c}{n_c} \sqrt{k_x^2 + k_y^2 + k_z^2} = E_0 \sqrt{1 + \left[\frac{(j+1)\pi}{L_y} \right]^2 \frac{1}{k_z^2}}$$

As one can see from the equation, the cavity photon dispersion along k_y direction also exhibits multiple-branch behaviour but with constant energies, as shown in Figure 1-8. Generally, a larger L_y will lead to more cavity photonic branches in the 1D microcavity.

Figure 1-8. (a) Schematic of a 1D planar microcavity. (b) The cavity photonic mode dispersion along k_x direction. (c) The cavity photonic mode dispersion along k_y direction. (d) Electric-field distribution of the first four modes. Figure is taken from Ref. (93).

Due to this additional lateral confinement along y direction, the electric distribution of cavity photonic modes along the k_y direction follows:

$$\cos\left(\frac{(j+1)\pi}{L_y} x\right) \text{ when } j \text{ is even}$$

$$\sin\left(\frac{(j+1)\pi}{L_y} x\right) \text{ when } j \text{ is odd,}$$

Such electric field distribution will give rise to distinct cavity photonic mode behaviours along the k_y direction, changing from continuous dispersion in 2D planar microcavity into discrete states in 1D planar microcavity as shown in Figure 1-8c.

1.4.4 Equivalence between Incidence Angles and In-plane Wavevectors

The energies of cavity photonic modes have a relationship with the in-plane wavevector. To understand the cavity photon behaviour, it is important to directly measure the in-plane wavevector dependent cavity photon dispersions. Such cavity photon dispersions are actually obtained by angle-resolved spectroscopy measurements. Here, I will show how the incidence angle is in equivalence to the in-plane wavevector. As shown in Figure 1-9, When the confined cavity photon travels from cavity (refractive index: n_c) to air (refractive index: n_{ext}), it conserves the in-plane wavevector $k_{\parallel}$ and energy E due to energy and momentum conservation law. Thus, the k_z component of the emitted photons can be written as:

$$k_z = \sqrt{\left(\frac{E}{\hbar c}\right)^2 - k_{\parallel}^2}$$

As shown in Figure 1-9, we can have

$$\tan(\theta_{ext}) = \frac{k_{\parallel}}{k_z} = \frac{k_{\parallel}}{\sqrt{\left(\frac{E}{\hbar c}\right)^2 - k_{\parallel}^2}}$$

$$k_{\parallel} = \frac{E}{\hbar c} \sin(\theta_{ext})$$

As one can see from the equation, the in-plane wavevector of cavity photon is indeed equivalent to the in-plane wavevector.

Figure 1-9. Energy and in-plane wavevector conservations provide the possibility to probe the cavity photon dispersion by angle-resolved spectroscopy measurements.

1.5 Light-Matter Interactions

This section introduces different light-matter interaction regimes in 2D planar semiconductor microcavities. Generally, as shown in Figure 1-10, the regime of light-matter interaction is determined by three parameters:

- The loss rate of photon leaving the microcavity κ ;
- The exciton decay rate γ ;
- The light-matter coupling strength g .

Figure 1-10. Schematic physical rates of an emitter in a cavity, showing the loss rate of photon κ , the exciton decay rate γ and the light-matter coupling strength g .

1.5.1 Weak Coupling Regime

When the light-matter coupling strength g between the exciton in the active medium and the cavity photon is smaller than the losses either induced by the loss of the cavity photon (κ) or the exciton (γ), the system operates in the weak light-matter interaction regime. The microcavity here can be treated as a perturbation on the spontaneous emission of the excited states. In more details, when the frequency of the exciton transition is out of resonance with the cavity photon mode, the density of excited states will be significantly reduced, thus the emission rate will be dramatically slower. In contrast, when the frequency of the exciton transition is in resonance with the cavity photon mode, the density of state will be greatly enhanced, thus having a much faster emission rate. Generally, the spontaneous emission rate of an excited state is characterized by the Fermi's golden rule:

$$\Gamma_{sp} = \frac{2\pi}{\hbar} |\langle i | H_{int} | f \rangle|^2 \rho(\hbar\omega)$$

Where $|\langle i | H_{int} | f \rangle|^2$ is the matrix elements for interaction and $\rho(\hbar\omega)$ is the density of excited states. In free space, the density of excited states is given by:

$$\rho_{free}(\hbar\omega) = \frac{V\omega^2 n^3}{\pi^2 c^3}$$

While in microcavities, the density of excited states of an emitter is largely altered and the density of states can be described by:

$$\rho_c(\hbar\omega) = \frac{\delta\omega_c}{2\pi} \frac{1}{(\omega - \omega_c)^2 + \delta\omega_c^2}$$

where ω_c is the cavity resonance frequency and $\delta\omega_c$ is the FWHM of the cavity resonance frequency. Compared with that of in free space, the emission rate in a microcavity is enhanced by a factor, known as Purcell factor F_p given by (94):

$$F_p = \frac{\Gamma_c}{\Gamma_{free}} = \frac{3Q(\lambda/n)^3}{4\pi^2 V_{eff}}$$

Where Q is the quality factor of the microcavity, λ illustrates the cavity photon wavelength and V_{eff} represents the effective mode volume. In order to maximize the emission rate of exciton transition, the microcavity should possess a large quality factor and a small mode volume, which is usually the case of photonic crystal microcavities and micropillar microcavities.

1.5.2 Strong Coupling Regime

Taking exciton polariton for example, when the coupling strength g between the cavity photon and the exciton in the active medium is larger than the loss caused by the cavity photon (κ) and the exciton (γ), the system comes into a strong light-matter coupling regime. In this case, the interaction between excitons and cavity photons is reversible and the system coherently oscillates between excitons and cavity photons, leading to two new eigenstates which are referred as lower exciton polariton and upper exciton polariton (27). When the cavity photon mode and the exciton are close to resonance, this reversible energy transfer between exciton and cavity photon will lead to an energy splitting which is named the vacuum Rabi splitting ($\hbar\Omega$), thus the dispersion of exciton polaritons will exhibit an anticrossing feature. Experimentally, the appearance of strong coupling regime is usually evidenced by the observation of such anticrossing feature in angle-resolved reflectivity and PL spectroscopy.

Generally, the interaction between the cavity photon and the exciton can be regarded as the interaction between two oscillators and can be described by a quantum mechanical two coupled-oscillator model. The total Hamiltonian of the hybridized system can be described as (92):

$$\hat{H} = \hat{H}_{cav} + \hat{H}_x + \hat{H}_{int} = \sum_{k_{||}} E_c(k_{||}) \alpha_{k_{||}}^\dagger \alpha_{k_{||}} + \sum_{k_{||}} E_x(k_{||}) b_{k_{||}}^\dagger b_{k_{||}} + \sum_{k_{||}} g (\alpha_{k_{||}}^\dagger b_{k_{||}} + \alpha_{k_{||}} b_{k_{||}}^\dagger)$$

Where $\alpha_{k_{\parallel}}^{\dagger}, \alpha_{k_{\parallel}}$ represent the creation and annihilation operators for photons with in-plane wavevector $k_{\parallel}$, respectively. $b_{k_{\parallel}}^{\dagger}, b_{k_{\parallel}}$ are the creation and annihilation operators for excitons with in-plane wavevector $k_{\parallel}$, respectively. g is the coupling strength between the cavity photon and the exciton. $E_c(k_{\parallel})$ and $E_x(k_{\parallel})$ are the energies of cavity photon and exciton at a given in-plane wavevector, respectively. The above Hamiltonian can be written by unitary transformation as:

$$\begin{pmatrix} p_k \\ q_k \end{pmatrix} = \begin{pmatrix} X_k & C_k \\ -C_k & X_k \end{pmatrix} \begin{pmatrix} b_k \\ a_k \end{pmatrix}$$

Where p_k and q_k are the lower polariton and upper polariton annihilation operators, respectively. C_k and X_k represent the Hopfield coefficients to demonstrate the contribution of exciton polaritons from cavity photons and excitons, which satisfy the following relationship (26):

$$|X_k|^2 + |C_k|^2 = 1$$

Thus, the Hamiltonian for the polaritons can be written as:

$$\hat{H}_{pol} = \sum_{k_{\parallel}} (E_{LP}(k_{\parallel}) p_{k_{\parallel}}^{\dagger} p_{k_{\parallel}} + E_{UP}(k_{\parallel}) q_{k_{\parallel}}^{\dagger} q_{k_{\parallel}})$$

Taking into account the finite linewidths of both the exciton and cavity photon, the solution of the polariton Hamiltonian at each wavevector can be written as:

$$\begin{vmatrix} E_{x,k_{\parallel}} - i\gamma_{x,k_{\parallel}} & g \\ g & E_{c,k_{\parallel}} - i\gamma_{c,k_{\parallel}} \end{vmatrix} = 0$$

Thus the eigenvalues can be written as (92):

$$E_{UP,LP}^{k_{\parallel}} = \frac{E_{c,k_{\parallel}} + E_{x,k_{\parallel}}}{2} - i \frac{\gamma_{c,k_{\parallel}} + \gamma_{x,k_{\parallel}}}{2} \pm \frac{1}{2} \sqrt{(2g)^2 + [(E_{c,k_{\parallel}} - E_{x,k_{\parallel}}) - i(\gamma_{c,k_{\parallel}} - \gamma_{x,k_{\parallel}})]^2}$$

Where $\gamma_{c,k_{\parallel}}$ and $\gamma_{x,k_{\parallel}}$ are the dissipation rate of cavity photons and excitons at a given in-plane wavevector, respectively. As one can see from the polariton eigenvalue equation, strong coupling can be obtained when the coupling strength follows $(2g)^2 > (\gamma_c - \gamma_x)^2$. In contrast, when the coupling strength follows $(2g)^2 < (\gamma_c - \gamma_x)^2$, the system operates in the weak coupling regime (92). However, the Rabi splitting energy derived from above equations does not guarantee the observation of the energy splitting in the absorption spectrum. In order to observe it, Savona *et al.* calculated more stringent conditions on the ratio between the Rabi splitting energy and the exciton/photon broadenings (90). The system is in strong coupling regime when the coupling strength follows $2g^2 > (\gamma_c^2 + \gamma_x^2)$, while the system keeps in weak coupling regime when the coupling strength follows $(2g)^2 < (\gamma_c - \gamma_x)^2$. There is an intermediate regime when the coupling strength follows $\frac{(\gamma_c^2 + \gamma_x^2)}{2} > g^2 > \frac{(\gamma_c - \gamma_x)^2}{4}$. In this case, the energy splitting exists in the two coupled oscillator model but cannot be observed in the absorption spectrum (95).

When the system operates in strong coupling regime, the new eigenstates of the system is described by the real parts of the above eigenvalues, which can be written as (92):

$$E_{UP,LP}^{k_{\parallel}} = \frac{E_{c,k_{\parallel}} + E_{x,k_{\parallel}}}{2} \pm \frac{1}{2} \sqrt{(2g)^2 + (E_{c,k_{\parallel}} - E_{x,k_{\parallel}})^2}$$

The cavity detuning is defined as the energy difference between the cavity mode and the exciton, which can be written as : $\Delta_{k_{\parallel}} = E_{c,k_{\parallel}} - E_{x,k_{\parallel}}$. When the cavity photon mode is in resonance with the exciton ($\Delta_k = 0$), the energy splitting between the upper polariton branch

and the lower polariton branch is defined as vacuum Rabi splitting energy $\hbar\Omega$ which is equal to $2g$. The Hopfield coefficients can be further written as (26):

$$|X_k|^2 = \frac{1}{2} \left(1 + \frac{\Delta_k}{\sqrt{\Delta_k^2 + (\hbar\Omega)^2}} \right)$$

$$|C_k|^2 = \frac{1}{2} \left(1 - \frac{\Delta_k}{\sqrt{\Delta_k^2 + (\hbar\Omega)^2}} \right)$$

As one can see from the Figure 1-11, the Hopfield coefficients, which illustrate the exciton and photon portions, directly depend on the cavity detuning. As the exciton energy keeps constant in a limited in-plane wavevector region and the energy of the cavity photon exhibits a parabolic increase trend with the increase of the in-plane wavevector, the cavity detuning is larger and larger and the exciton portion in the lower polariton state is therefore larger and larger as well. Consequently, the lower polariton branch exhibits a photonic like dispersion at small angles and finally becomes a more exciton-like dispersion at large angles. As shown in Figure 1-11, depending on the exciton and photon portions, exciton polariton dispersions with different detuning at normal incidence exhibit totally distinct curvatures. Such part-exciton, part-photon nature of polaritons gives rise to the peculiar dispersions of polaritons, which lays the foundation towards various crucial applications based on polaritons.

Figure 1-11. (a), (c) and (e) Dispersion of typical perovskite microcavities with detunings of -80 meV, 0 meV, +80 meV, respectively, showing the dispersions of the exciton (E_x), the cavity photon (E_c), the lower polariton branch (E_{LP}) and the upper polariton branch (E_{UP}) (b), (d) and (f) The Hopfield coefficients of polaritons as a function of incident angles with detunings of -80 meV, 0 meV, +80 meV, respectively, showing the exciton portion ($|X(k)|^2$) and cavity photon portion ($|C(k)|^2$).

In the next section, I will mainly introduce the properties and origin of exciton polariton condensation.

1.6 Exciton Polariton Bose-Einstein Condensation

Bosons and fermions are two classes of fundamental particles in nature. Due to the Pauli exclusion principle, two or more fermions cannot occupy the same quantum state, as shown in Figure 1-12. While unlike fermions, bosons do not follow such Pauli exclusion principle, which means that bosons can massively occupy a single quantum state. Meanwhile, the scattering rate towards a bosonic state can be enhanced by other bosons in the same quantum state, which will lead to an avalanche process to achieve higher occupancy in the same quantum state. This feature is known as bosonic final state stimulation (27, 96). These two combined features are regarded as the origin and basis of BEC.

Figure 1-12. (a) The schematic of a lot of bosons occupying the same quantum state. (b) Schematic of each fermion occupying each state.

BEC is one of the most striking quantum phenomenon, which has been firstly predicted by Satyendra Nath Bose and Albert Einstein in 1924 and experimentally demonstrated in a gas

of rubidium atoms by Eric Cornell and Carl Wieman in 1995 (28, 29, 97). Upon reaching a critical transition temperature which is close to the absolute temperature, a large fraction of bosons will massively occupy the single ground state, leading to the appearance of BEC. The energy distribution of non-interacting bosons in thermal equilibrium at temperature T will follow the Bose-Einstein distribution (98):

$$f(k, T, \mu) = \frac{1}{e^{\frac{E(k) - \mu}{k_B T}} - 1}$$

Where μ is the chemical potential, k_B is the Boltzmann constant and T is the effective temperature. BEC is not only important for fundamental studies in Physics but also promising for future quantum technological applications, such as quantum communications and quantum computing (99). However, the development of BEC is hindered due to the requirement of ultralow critical temperature. This critical transition temperature T_c to observe BEC is actually given by (98):

$$T_c = \left(\frac{n}{\zeta(3/2)} \right)^{\frac{2}{3}} \frac{2\pi\hbar^2}{mk_B} \approx 3.3125 \frac{\hbar^2 n^{2/3}}{mk_B}$$

Where n is the particle density, m is the mass of a boson, ζ is the Riemann zeta function and k_B is the Boltzmann constant. As one can see from the equation, this critical transition temperature is determined by the particle density and the mass of the boson. If one can largely reduce the mass of the boson, the critical transition temperature can be dramatically increased even to room temperature.

Exciton polaritons are such ideal bosons to realize polariton BEC at high temperatures (30, 43, 45-50, 73, 100-104). As half-light, half-matter quasiparticles, exciton polaritons combine the excellent properties of excitons and photons (105). Compared with the uncoupled exciton, an exciton polariton possesses a four orders of magnitude lower effective mass, which

is also eight orders of magnitude lower than that of the atom. Meanwhile, the exciton polariton conserves the high nonlinearity from their exciton component (105). These two features, combined with their bosonic nature which can lead to the bosonic final state stimulation, provide the foundation to realize polariton BEC at high temperatures.

BEC of exciton polaritons was firstly demonstrated in a CdTe microcavity at low temperature by J. Kasprzak *et al.* in 2006 (30). After that, the realization of BEC of exciton polaritons have been achieved at room temperature in different material systems, including GaN (43), ZnO (45) and organic systems (46-49). From the experimental point of view, the semiconductor microcavity is usually optically excited to generate excitons to form polaritons, which will then relax along the lower polariton branch mainly by polariton-phonon interactions at low polariton density, as shown in Figure 1-13a. However, due to the peculiar shape of the lower polariton branch, polaritons are difficult to relax to the ground state by dissipating a lot of energy with little simultaneous consumption in wavevector (106, 107). Meanwhile, due to the finite lifetime, polaritons usually cannot successfully reach the ground state before escaping outside the microcavity, thus congesting at high k states. This phenomenon is the so-called *bottleneck effect*, which is detrimental to the realization of polariton condensation (107). In order to achieve polariton BEC, such bottleneck effect has to be overcome to allow polaritons to efficiently relax to the ground state of lower polariton branch. This can be achieved by a stimulated scattering process (27). Due to the excitonic component of polaritons, polaritons inherit the strong Coulomb interaction from the exciton component, giving rise to a strong polariton-polariton repulsive interaction which can greatly accelerate the polariton thermalization process, as shown in Figure 1-13a. With the increase of polariton density, polariton-polariton scattering becomes prominent and the stimulated scattering process can be triggered when the polariton density crosses the critical density. Above a threshold, the bottleneck effect can be suppressed and polaritons can smoothly relax to the ground state.

Thanks to the bosonic nature of polaritons, this polariton-polariton scattering process is actually enhanced by a factor of $N_0 + 1$, where N_0 is the polariton population in the ground state. This suggests that the more ground state population will result in a faster polariton relaxation process, which can lead to an avalanche-like process to achieve polariton BEC. As one can see, polariton-polariton scattering is the key to achieve efficient polariton relaxation and thus polariton condensation.

As proposed by A. Imamoglu *et al.* (27), the stimulated scattering process in polaritons directly gives rise to nonlinear emission and the single quantum state nature of polariton condensate gives rise to striking coherence properties of the emission, which makes the emission from polariton condensate acting as a laser. The major difference between a polariton laser and a photonic laser is that no population inversion is needed between the conduction band and valence band for the former system. A photonic laser is achieved by population inversion and stimulated emission of photon into the ground state of the cavity photon mode, as shown in Figure 1-13b. While a polariton laser is achieved by stimulated scattering of massive polaritons occupying the polariton ground state in the lower branch. The main advantage for a polariton laser over a photonic laser is the significant lower threshold thanks to the unnecessary population inversion process. The difference of operating mechanism is schematically shown in Figure 1-13.

Figure 1-13. (a) Schematics of the experimental principle for a polariton laser. (b) Schematics of the experimental principle for a photonic laser.

An unambiguous evidence to demonstrate polariton lasing is the observation of a second threshold (108), which corresponds to the transition from strong coupling regime (polariton lasing) to weak coupling regime (photonic lasing). The semiconductor microcavity usually exhibits the first threshold at lower pump powers, which corresponds to the polariton laser threshold. At higher pump powers, due to the screening of excitons, the microcavity will lose the strong coupling regime and transit into a weak coupling regime with excitons changing into electro-hole plasma. Population inversion could be achieved at this weak coupling regime and leads to the conventional photonic lasing. This evolution of lasing in a microcavity is schematically shown in Figure 1-14. However, such two-threshold behaviour is usually observed in III-V microcavity system and it is not clear yet why such two-threshold behaviour does not show up in other systems (30, 45). Another important evidence for polariton lasing is the spontaneous build-up of long-range order (30), which is one of the signatures of condensate formation. In the linear regime, polaritons are expected to possess a characteristic coherence length in the order of the thermal de Broglie wavelength $\lambda_{dB} = 760$ nm (47). While in the

nonlinear regime, condensed polaritons will exhibit much longer coherence length than the thermal de Broglie wavelength λ_{dB} .

Figure 1-14. The two-threshold behaviour for a typical GaAs microcavity with the first threshold corresponding to polariton lasing regime and the second threshold corresponding to the photon lasing regime. Figure is taken from Ref. (108).

1.7 Organization of This Thesis

In Chapter 1, I have introduced the motivations and related fundamental physics in this thesis. It can be divided into several parts: (1) I introduced the background and motivations of this thesis. (2) I introduced the fundamental properties of all-inorganic cesium lead halide perovskites, including the crystal structure, the electronic structure, bandgap engineering and optical properties. (2) The fundamental theory of Wannier-Mott exciton and Frenkel exciton is reviewed. (3) The fundamental physics of a Fabry-Pérot microcavity is reviewed, including DBR mirrors and the cavity photon dispersions in 2D and 1D microcavities. (4) The fundamental physics of different light-matter interaction regimes is introduced, including weak coupling regime and strong coupling regime. (5) The basic properties of exciton polariton in

strong coupling regime have been demonstrated in detail. (6) The mechanism of exciton polariton condensation and lasing is also discussed in detail.

In chapter 2, I will describe the related equipment in this thesis, including the homebuilt chemical vapor deposition system for the synthesis, the e-beam evaporation system for the fabrication of microcavities, the angle-resolved spectroscopy system for measuring the dispersion of cavity photons and exciton polaritons and also the setup of Michelson interferometer for probing the spatial coherence of exciton polariton condensate.

In chapter 3, I will first introduce the synthesis of high quality all-inorganic cesium lead halide perovskites which includes the growth of well-defined square and rectangular perovskite crystals, as well as the synthesis of large area high quality perovskite films. The room temperature absorption and photoluminescence spectroscopy of cesium lead halide system will be introduced. Furthermore, we will introduce the exciton behaviours in the absorption spectroscopy as a function of temperature. The exciton binding energy of CsPbCl_3 and CsPbBr_3 can be extracted from the temperature dependent absorption spectroscopy. In addition, Rydberg excitons up to $n=2$ will be demonstrated, which will further confirm the exciton binding energy of cesium lead halide perovskites.

In chapter 4, I will present my PhD work on low threshold lasing based on square perovskite crystals with themselves acting as cavities. The cesium lead halide perovskite are naturally active whisper gallery mode microcavities thanks to the well-defined square and rectangular shapes. Low threshold and high quality factor lasing will be demonstrated in CsPbBr_3 nanoplatelets. Furthermore, lasing with tunable wavelength and low threshold will be shown by bandgap engineering of cesium lead halide perovskites.

In chapter 5, I will introduce my PhD work on room temperature exciton polariton lasing based on CsPbCl_3 perovskite. In this section, I will show the capability to fabricate epitaxy-free perovskite microcavities which operate in strong coupling regime. Meanwhile, the detailed

evidences of room temperature polariton lasing will be demonstrated as well, including the superlinear increase of ground state emission intensity, massive occupation of the polariton ground state, build-up of long-range spatial coherence as well as the transition from strong coupling regime into weak coupling regime.

In chapter 6, I will demonstrate my PhD work on room temperature long-range coherent exciton polariton condensate flow. Here, I will show the realization of 1D CsPbBr₃ perovskite microcavity by an etching-free method. In addition, the realization of room temperature epitaxy-free polariton condensation could be extended to green region in 1D CsPbBr₃ perovskite microcavity, which is unique from previous inorganic wide bandgap semiconductor systems. The long-range polariton condensate propagation will also be discussed.

In chapter 7, I will give a conclusion on my thesis and provide possible perspectives on future works.

Chapter 2 Experimental Setup

In this chapter, I will mainly introduce all the experimental setups used in the thesis for sample synthesis, fabrication techniques and optical spectroscopy measurements.

2.1 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is a chemical process which is widely used as a material synthesis technique for thin-film coating, fabricating some composite materials, as well as producing high-purity bulk materials and powders. In semiconductor industry, CVD plays an important role in thin-film coatings for various materials including polysilicon, silicon dioxide, metals, diamonds and so on. Particularly, with the development of nanomaterials, CVD is regarded as an effective technique in research labs to synthesize various high-quality nanomaterials with various structures, including nanowires (*109, 110*), nanobelts (*111*), nanoplatelets (*69, 112*), atomic thin layers (*113, 114*) and so on.

The homebuilt CVD system used in this thesis consists of three basic elements: transporting gas (upstream), heating furnace with quartz tube, and pump/exhaust (downstream). As shown in Figure 2-1, the transporting gas, either used only for transporting compounds or also for reacting with the compounds, flows from the upstream through a gas-line into the quartz tube. Various gas could be used in our lab, including H₂, O₂, N₂ and Ar, which depends on the compound we want to synthesize. The flow rate of the gas can be continuously tuned with a gas flow controller. The quartz tube is located in the middle of the system, held by two supports and going through the heating furnace with heating wires. A thermocouple sits in the middle of the heating furnace for temperature detection so that the temperature in the furnace can be effectively tuned. On the downstream side, several basic elements are located after the exhaust outlet of the quartz tube, including a baratron gauge, a filter, a control valve, a mechanical pump, etc. The baratron gauge is used for monitoring the pressure inside the system

and the filter protects the mechanical pump from those condensed compounds during the synthesis process. The control valve is used for controlling and stabilizing the pressure inside the chamber, which is crucial for the synthesis of various nanomaterials. The mechanical pump in the end is not only used for pumping the chamber into vacuum at early stage so that the synthesis process will not be influenced by the air, but also for pumping the transporting gas to keep it effectively flowing.

Figure 2-1. The detailed setup of a home-built CVD system with single-zone furnace. Notes with arrows are shown in the figure for further clarifications.

In order to synthesize a compound, a quartz boat with sources will be put in the center of the quartz tube, where it is the closest to the thermocouple. The suitable substrates will be put in the downstream region at low temperatures so that the compounds can condense onto the substrate. By changing the temperature, pressure and gas flow inside the chamber, various kinds of high-quality nanomaterials can be obtained, including ZnO (115), CdS (110), ZnTe (116) and perovskites (112).

2.2 E-beam Evaporation

E-beam evaporation is a technique using a physical vapor deposition process for the deposition of high quality thin-films of metals and dielectric materials under high vacuum

environment. Unlike the conventional thermal evaporation technique which will totally melt the source materials, e-beam evaporation is performed using an electron beam which can scan at the surface of the source materials and then evaporate or sublimate the materials from its surface without totally melting the source materials. The detailed evaporation process of e-beam evaporation is schematically shown in Figure 2-2. In general, a current is firstly engaged to pass through a tungsten filament which will give rise to electron emission and heating. The emitted electrons will be accelerated to the crucible containing the deposition material by a high voltage which is applied between the hearth and the filament. Then a strong magnetic field is utilized to focus the electrons into a unified beam. Upon reaching the deposition material, the energy of this electron beam is transferred to the deposition material, inducing its evaporation and deposition onto the substrate. During the deposition process, the crucible containing the evaporation materials needs to be cooled down as lots of heat will be produced at the crucible. In such case, high purity crucible with high melting point is crucial to avoid contaminations during the deposition process. E-beam evaporation have many advantages over conventional thermal deposition and magnetic sputtering. For example, thermal evaporation can only deposit materials with lower melting points, such as Au, Ag and Cr. While e-beam evaporation can deposit both materials with low and high melting points, especially dielectric materials with high melting point, such as Ta_2O_5 , HfO_2 , TiO_2 and so on. Another important advantage is the fast deposition rate with e-beam evaporation. As e-beam evaporation is able to heat materials to much higher temperatures, it leads to much higher evaporation and deposition rates of high melting point materials, compared with thermal evaporation and magnetic sputtering. Moreover, films obtained by electron beam evaporation usually possess better purity of the source material as the water cooling of crucible can precisely control the electron beam to evaporate specific area of the deposition material, which eliminates contamination from any unwanted components.

These advantages make e-beam evaporation an excellent candidate for fabricating high quality DBR mirrors, which is the foundation of the research done in this thesis as tens of dielectric layers must be deposited continuously. The thickness of each thin film is monitored in real time using a quartz crystal-based thickness monitor. The deposition rate of thin films can be tuned by changing the current in the filament, ranging from 10^{-2} nm/s to 10 nm/s. The quality of thin films deposited by the e-beam evaporator is highly dependent on the deposition rate and chamber vacuum. In addition, the substrate holder is usually rotated during the deposition process in order to achieve a uniform thin film. Specifically, all the dielectric layers in this thesis, including HfO_2 , SiO_2 , Ta_2O_5 , are deposited by e-beam evaporation.

Figure 2-2. The schematic of an e-beam evaporator.

2.3 Atomic Force Microscopy (AFM)

An atomic force microscope is a type of high resolution scanning probe microscope which is commonly used in nanotechnology. It was pioneered in 1986 by Nobel Prize Winner Gerd Binnig along with Calvin Quate and Christoph Gerber. Due to its flexibility, the AFM has served as a crucial technique for material characterization along with optical and electron

microscopies, which can possess high resolutions down to nanometer scale and beyond. AFM is suitable in various environments ranging from fluids to ultra-high vacuum environment, thus serving for various fields in science. The basic mechanism of AFM lies with the measurements of weak atomic forces, as shown in Figure 2-3. A cantilever/tip assembly, which is regarded as a probe, interacts with the samples through a raster scanning motion. The motion of the tip during the scanning process along the sample surface will be monitored through the beam deflection method. When the tip is moved close to the sample surface, the atomic force between the sample surface and the tip will lead to a deflection of the cantilever. This deflection is usually measured based on the reflected laser beam from the top surface of the cantilever which is sent to a position sensitive detector tracking the lateral and vertical motions of the probe. In order to be precise, the relationship between a unit of voltage measured on the detector and nanometers of motion, which defines the deflection sensitivity, is required to be calibrated carefully. Generally, the vertical resolution of AFM could be as small as 0.1 nm while the lateral resolution is around ~5 nm.

Figure 2-3. Schematic of an AFM.

Compared with conventional electronic microscopy such as scanning electron microscopy and scanning tunnelling microscopy, AFM could be utilized to investigate those electrically non-conductive materials, which is usually difficult to be done in electronic microscopy. Moreover, the vertical dimension of the sample could be precisely measured with AFM, which is usually not the case for conventional electronic microscopy. However, AFM also have some disadvantages such as thermal shift due to slow scanning rate, possibility to destroy sample surfaces and extreme sensitivity to surface conditions. Specifically, all the thicknesses of the samples in this thesis are measured through AFM.

2.4 Ultraviolet Visible Near-Infrared Spectroscopy

Ultraviolet Visible Near-Infrared (UV-Vis-NIR) spectroscopy is a powerful technique to characterize the transmission, absorption and reflection of a variety of materials. Absorbance spectroscopy is an analytical technique based on measuring how much amount of light is absorbed by the material at a given wavelength which can be extended from ultraviolet to near-infrared region. In this thesis, absorbance spectroscopy is widely used to study the exciton properties in lead halide perovskites. Here, we use a lambda 950 UV/Vis/NIR spectrometer (PerkinElmer) to perform absorption spectroscopy either at room temperature or at cryogenic temperatures by using a liquid helium cryostat. Figure 2-4 shows the schematic of our UV-Vis-NIR spectroscopy system. Two radiant sources are used in this system including a deuterium lamp for light in the UV region and the tungsten lamp for light in the visible-near infrared range. High purity light with resolution down to 0.02 nm can be obtained after passing through two monochromators. Subsequently, the high purity beam is separated with identical intensity into a reference beam and a signal beam going through the measured sample. The reference beam and the signal beam will be collected by either a photomultiplier tube (PMT) for light in the ultraviolet-visible range or by a lead sulfide (PbS) detector for light in the near-infrared region.

Figure 2-4. Schematic of the lambda 950 UV/Vis/NIR spectrometer

In addition to absorbance spectroscopy, absolute reflection spectroscopy of thin films can be also probed in our lambda 950 UV/Vis/NIR spectrometer system, which is widely used in the thesis for the measurement of absolute reflectivity of DBRs. In order to obtain absolute reflection spectroscopy, a universal reflectance accessory needs to be installed in our lambda 950 UV/Vis/NIR spectrometer system. The detailed measurement process is depicted in Figure 2-5. During the reference scan process, the reference beam is directly guided to the detector without going to the measured sample and the obtained spectrum is regarded as a reference. While during the sample scan process, the signal beam is tuned by the input mirror, passing to the surface of the measured sample with an angle. Meanwhile, the position of the detector needs to be properly adjusted in order to collect the reflected signal from the measured sample. In such case, the angle between the signal beam and sample can be continuously tuned between 8° - 65° with the accuracy of 1° by the input mirror so that angle-resolved reflectivity

spectroscopy could be carried out. Generally, the size of the radiant beam can be well-controlled by the width of the slit. The beam size is around 4.5 mm×4.5 mm before passing through the slit and can narrow to 1mm×1mm after going through the slit and a common beam mask.

Figure 2-5. Schematic of the scan process for absolute reflectivity spectroscopy. (a) The reference scan process. **(b)** The sample scan process. Figure taken from the manual of lambda 950.

2.5 Photoluminescence Spectroscopy

PL spectroscopy is a widely used technique for probing the optical and electronic properties of semiconductors. Generally, the steady-state PL is measured through a combination of excitation sources and detecting elements, as shown in Figure 2-6. The system normally consists of a laser source, a white light source, a sample stage, filters, gratings and detectors. The first step when doing the measurement of PL spectroscopy is to image the sample surface in order to localize the sample to be measured. As shown in Figure 2-6, a white light source is guided by a beamsplitter 1 to illuminate the sample we need. The reflected white light from the sample is guided by beamsplitters 2 and 3 and then collected by a CMOS camera to image the sample surface. After having identified the sample we want to study, a laser source goes through beamsplitter 3 and is directed by beamsplitter 2, focusing onto the sample by a microscope objective. Various objectives are available in our lab including 5×, 10×, 50×, 100×, depending on the sizes of the sample and also the needed laser spot size. In order to have better collection efficiency, the beamsplitter 1 is removed when measuring the spectrum. Under the backscattering configuration, the scattered signal from the sample is collected by the same objective and goes through beamsplitter 2. The scattered signal mainly consists of the strong incident laser light and the PL signal from the sample we measured. In this case, a laserline filter is needed to put in front of the entrance slit of the spectrometer to prevent the detector from the damage of the intense laser. The filter could be either a long-pass filter or a notch-filter, depending on what we need. After passing through the filter, the backscattered signal mainly consists of the PL signal from the sample, which is focused by a lens to the entrance slit of the spectrometer. Then, it is directed to a dispersive grating which is used for separating lights of different wavelengths. Several gratings of 150 grooves/mm, 600 grooves/mm and 1800 grooves/mm are available, depending on the wavelength resolution that is needed. (the larger number will have a better wavelength resolution). The grating with 1800 grooves/mm

has a resolution of 0.03 nm while the grating of 150 grooves/mm only has a resolution of 0.46 nm. However, the collection efficiency is relatively lower in gratings with larger numbers of grooves/mm if we do not take the blazing wavelength of gratings into account. Therefore, it is a compromise between collection efficiency and wavelength resolution when choosing a suitable grating.

After the PL signal is dispersed by the grating, it is reflected by a mirror into the slit before a CCD detector. The CCD detector here is cooled by liquid nitrogen and composed of 1024×256 pixels. Compared with the thermoelectric cooled CCDs, this CCD detector has lower dark currents and thus a lower noise signal as it can reach lower temperatures.

Figure 2-6. Schematic of a conventional backscattering PL spectroscopy setup.

2.6 *k*-space and real-space Reflectivity and Photoluminescence Spectroscopy

In the previous section, the steady-state PL is actually measured in the real space which means that the CCD detector collects PL signals from the sample by mixing PL signals from different emission angles. However, in order to study the properties of polaritons, it is crucial to perform the *k*-space spectroscopy of polaritons. Owing to the conservation of the in-plane wavevector and the energy, the polariton properties in *k*-space can be studied by detecting their photonic part or in other words by detecting the photons leaking out of the microcavity as a result of the finite reflectivity of the mirrors. As presented in Chapter 1 (see Figure 1- 9), the in-plane wavevector is directly related to the emission angle of photons according to $k_{\parallel} = E \sin(\theta)/\hbar c$, where E is the energy of photon, θ is the emission angle, c is the speed of light and $\hbar$ is the reduced Planck constant. The way to obtain the *k*-space spectroscopy is actually based on separating signals into different angles that can be directly measured by a spectrometer, as shown in Figure 2-7. The angle-resolved spectroscopy can be obtained through a home-built setup by imaging the Fourier plane at the entrance of the spectrometer. Generally, the setup consists of three lenses, a sample stage and a spectrometer. For the measurements of angle-resolved reflectivity spectroscopy, a collimated Tungsten Halogen white light source, which is guided by beamsplitter 1, is used for the reflectivity measurements as well as for imaging the sample. A pinhole is put in front of the output of the collimated white light source to tune the size of the beam. After being reflected by the beamsplitter 1, the collimated white light source will go through a microscope objective (Lens 1) and focus onto the sample. For angle-resolved spectroscopy, we usually use a 100× microscope objective with a large numerical aperture (NA) of 0.9 giving access to large angles up to $\pm 64.1^\circ$. The white light reflected by the sample with different angles will be collected by the same objective and transform into a collimated beam at the first Fourier plane. Another lens 2 will be put at a distance of its focal length f_2 away

from the Fourier plane. The collimated beam will go through the lens 2 and focus at the real plane. A spatial filter of pinhole will be put exactly at the real plane to block the reflected signal from the environment and another lens 3 will be put exactly at a distance of its focal length f_3 away from the real plane. After passing through the spatial filter, the real space signal from the sample will go through the lens 3 and transform into a circular collimated beam again. The entrance slit is put exactly at a distance of f_3 away from the lens 3. Consequently, the circular signal beam is cut by the entrance slit of the spectrometer and collected by the CCD detector. In this case, the signal after the entrance slit actually has a line shape and is angle resolved with angles ranging from -64.1° to $+64.1^\circ$ from bottom to top of the line signal. As the entrance slit of the spectrometer is conjugated with the CCD detector, the signal before the CCD detector actually preserves the angle information from top to bottom after being dispersed by the grating. In this case, a CCD detector with pixel arrays is compulsory for performing angle-resolved spectroscopy where a 2D mapping is measured with one dimension corresponding to wavelengths and another dimension corresponding to angles.

Angle-resolved PL spectroscopy can be also done with the same setup by replacing the incident collimated white light beam by a laser source. A laser filter must then be put in front of the entrance slit of the spectrometer to prevent the CCD detector from the damage of the intense laser source. Linear polarizers or waveplates could also be put in front of the entrance slit to perform angle-resolved spectroscopy under different polarizations. In addition to the angle-resolved spectroscopy in k -space, the real space image could also be measured within this home-built setup. By simply removing the lens 2 and placing the grating at zero order, the CCD detector will directly image the real space information of the samples. The magnification of the real space image of the sample on the CCD is then determined by the ratio between the focal lengths f_3 and f_1 .

In order to probe the k -space spectroscopy and real space spectroscopy at low temperatures, the sample holder could be replaced by a liquid helium cryostat with sample inside. This setup can thus be used for both the k -space spectroscopy and real space spectroscopy at low temperatures as low as 10 K.

Figure 2-7. Schematic of the angle-resolved spectroscopy setup with Fourier optics.

2.7 Michelson Interferometer

The appearance of polariton condensation is accompanied with spontaneous coherence. The build-up of off-diagonal long-range spatial coherence is one of the signatures for polariton condensate formation. In the linear regime, polaritons are expected to possess a characteristic coherence length in the order of the thermal de Broglie wavelength $\lambda_{dB} = 760$ nm (47). While in the nonlinear regime, condensed polaritons will exhibit much longer coherence length (tens of μm) than the thermal de Broglie wavelength λ_{dB} . The appearance of this long-range order can be probed by investigating the first order spatial coherence function $g^{(1)}(\mathbf{r}, \mathbf{r}')$, which quantifies the phase coherence between points at $\mathbf{r}$ and $\mathbf{r}'$.

Figure 2-8. Schematic of a Michelson interferometer setup probing the spatial coherence.

In this case, a Michelson interferometer is used to study the first order coherence by measuring the interference fringe contrast $C(r)$ (117):

$$C(r) = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = \frac{2\sqrt{I(r)I(-r)}}{I(r) + I(-r)} g^{(1)}(r, -r)$$

Where I is the light intensity, I_{max} and I_{min} are the maximum and minimum intensities measured in the interference fringes respectively. As one can see, the first order spatial coherence function is directly related to the contrast $C(r)$ of interference fringes. The emission collected by the microscope objective is sent to a beamsplitter cube with splitting ratio of 50:50 and split into two identical beams. One of the beams is sent to a mirror mounted on a piezo-electric stage which can be controlled by the computer to tune the delay. Another beam is sent to another arm of the Michelson interferometer, which is replaced by a retroreflector that inverts the image in a centro-symmetrical way, as shown in Figure 2-8. The use of the retroreflector enables the characterization of phase coherence between points $\mathbf{r}$ and $-\mathbf{r}$ with respect to the spot center, which can be deduced from the measurements of the fringe contrast as a function of the interferometer delay. After being reflected by the two arms of the Michelson interferometer, these two beams will be collimated and go through a lens to superimpose at the focal plane of lens 2. A CMOS camera is put exactly at the focal plane of the lens to image the interference

patterns at the zero-delay point between both arms. By changing the delay line, one can obtain the evolution of first order coherence as a function of delay. Care has to be taken that the interference fringes image should be large enough to be resolved by the CMOS camera with typical pixel sizes of $3 \times 3 \mu\text{m}^2$. The width of the fringe is determined by the wavelength of the emission and the angle between two incident beams. One can shrink the angle between two incident beams by either increase the focal length of lens 2 or reduce the space of the two collimated beams before the lens 2.

2.8 Time-resolved Photoluminescence Spectroscopy

In order to probe the time-resolved photoluminescence spectroscopy, we use a streak camera system to carry out such measurements. The basic principle of a streak camera is shown in Figure 2-9, optical pulses with different time and space (corresponding to wavelength) go through a slit and image on the photocathode, which is converted into electrons with numbers proportional to the intensity of the original optical pulses. The electrons will then go through a pair of sweep electrodes with high voltages which is synchronized to the trigger signal of the laser pulse. Consequently, the electrons arriving at different time will be deflected at different angles in the vertical direction and enter into the micro-channel plate. After that, the electrons will be multiplied by thousands of times to impact against the phosphor screen and then converted into light.

In a typical phosphor image obtained by the streak camera system, the signal from top to bottom defines the time sequence of the optical pulses with different time. The brightness of the phosphor image illustrates the intensity of the different optical pulses while the horizontal direction of the phosphor image demonstrates the wavelength of the optical pulses.

Figure 2-9. Schematic of Streak Camera system (Figure is taken from HAMAMATSU).

2.9 Summary

In summary, I have introduced the working mechanism of experimental techniques including CVD for sample synthesis, E-beam evaporation for DBR fabrication and microcavity fabrication, AFM for sample thickness characterization, UV-Vis-NIR for optical absorption measurements, microphotoluminescence setup for PL characterization, streak camera system for time-resolved spectroscopy, home-built angle-resolved spectroscopy setup for angle-resolved spectroscopy characterization and Michelson interferometer for probing the spatial coherence.

Chapter 3 Synthesis and Optical Properties of All-inorganic Cesium Lead Halide Perovskites

3.1 Introduction

Adopting all-inorganic cesium lead halide perovskites into various optoelectronic applications start from the synthesis of high quality all-inorganic perovskites. At the time I enrolled in my PhD study in 2014, several methods have been reported to synthesize all-inorganic perovskites. A quench deposition method was firstly used by S. Kondo *et al.* to prepare all-inorganic perovskite large films (118). The obtained films are amorphous and can be transformed into microcrystalline state with an annealing process at 500 K. After that, several groups have utilized solution chemistry to synthesize all-inorganic perovskite crystalline nanostructures such as zero-dimensional quantum dots (65) and one-dimensional nanowires (119, 120), which exhibit excellent performance in various light emitting applications (67, 70). The simplest way to obtain perovskite films is by spin-coating a solution containing all-inorganic perovskite precursors. This method is quite simple and fast but usually leading to inhomogeneous, polycrystalline films with large surface roughness and poor emission properties (64, 121). However, novel applications based on perovskites significantly rely on high quality crystals. Particularly, for the purpose of tailoring the emission based on perovskites in the thesis, high quality, single crystalline all-inorganic perovskite crystals with a naturally formed cavity are highly desirable. Previously, a vapor phase CVD synthesis method has ever been reported by S.T. Ha *et al.* for organic-inorganic hybrid perovskite nanoplatelets based on a two-step process (112). The perovskite precursors of lead halides PbX_2 ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) are firstly synthesized (Figure 3-1a) and followed by an intercalating reaction of gas-phase methyl ammonium halides. The thicknesses of perovskites exhibit a linear relationship with the thickness of lead halides after the intercalating reaction, as shown

in Figure 3-1b. However, this two-step vapor phase method is difficult to be controlled and may result in insufficient conversion or over conversion from lead halide crystals to lead halide perovskites. Thus, the quality of the obtained perovskite crystals based on this two-step method may not be good enough.

In this chapter, I will introduce a one-step method to synthesize high quality, single crystalline all-inorganic perovskite crystals based on van der Waals (vdW) epitaxy. In addition, I will demonstrate the exciton properties of as-synthesized perovskite crystals.

Figure 3-1. (a) Typical optical and scanning electron microscopy images of as-grown lead halide crystals. (b) The one to one correlation between lead halide crystals and lead halide perovskite crystals before and after conversions. Figure is taken from Ref. (112).

3.2 Van der Waals Epitaxy of Semiconductors

Epitaxial growth has been a footstone in semiconductor industry as it allows the commensurate growth of semiconductor heterostructures, which enables the best crystal quality of semiconductors towards their optoelectronic applications. However, good epitaxial

growth is only limited within a few combinations of materials due to the issue of lattice mismatching between the substrates and epitaxial layers. In conventional 3D semiconductor systems, lattice mismatch is such a detrimental issue for semiconductor growth due to the existence of dangling bonds at the surface of 3D materials. The dangling bonds can only well connect to the atoms of a well-lattice-matched material as the angle and length of the dangling bonds are difficult to be changed. During the deposition process, the epitaxial layer atoms firstly interact with the dangling bonds in a covalent way and follows the lattice constant of the substrate, as shown in Figure 3-2, which will lead to strains as the in-plane bonds are compressed or stretched. The strains near the surface of the substrate can only be stable within a critical thickness and will result in the formation of misfit dislocations at the heterostructure interface, which will do harm to the optical and electrical properties of the as-grown materials.

As a comparison, the discovery of vdW epitaxy by A. Koma *et al.* in University of Tokyo greatly relieves the lattice mismatching situation for semiconductor epitaxial growth by taking advantage of substrates and/or epitaxial materials which have an inert van der Waals surface possessing no dangling bonds (122). This can be achieved by using a substrate with a 2D layered structure such as transition metal dichalcogenides and graphene, or by removing the dangling bonds at the surface of a 3D substrate. Without the dangling bonds at the surface, epitaxial material does not necessarily interact with the substrate to form covalent bonds. Only vdW forces exist at the interface to form a vdW gap as shown in Figure 3-2. Comparing with the covalent bonds, these vdW forces, which originate from the dipole interactions between atoms from the substrate and epitaxial materials, are much weaker. In this case, the epitaxial material can be grown unstrained even on a lattice-mismatched substrate. Up to now, vdW epitaxy has been adopted to synthesize various high quality materials with different dimensions including Se films (123), ZnO (124), transition metal dichalcogenides (125), CdS (110) and so on. In the following sections, I will demonstrate the capability of vdW epitaxy to synthesize

high quality, single crystalline all-inorganic cesium lead halide perovskite crystals in a homebuilt CVD system.

Figure 3-2. Schematics demonstrating the influence of lattice mismatch in **(a)** the conventional epitaxy where covalent bonding leads to strains in epilayers, **(b)** the unstrained vdW epitaxy of one inert layered material on another, and **(c)** the unstrained vdW epitaxy of one inert material on a passivated three-dimensional substrate. Figure is taken from Ref. (122).

3.3 CVD Synthesis of All-inorganic Cesium Lead Halide Perovskites

3.3.1 Synthesis of Perovskite Nanoplatelets

The CsPbX_3 perovskite compounds are grown by a vapor transport method using a home-built CVD system as shown in the schematic of Figure 3-3. The muscovite mica substrate ($1.5 \times 5 \text{ cm}^2$) is freshly cleaved and put inside the downstream of a quartz tube mounted in a single zone furnace (Lindberg/Blue MTF55035C-1). The source is a mixed powder of lead halide PbX_2 and CsX with molar ratio 1:1. After the substrate and sources are placed inside the quartz tube, the latter is pumped down with a setting base pressure of 50 mTorr and is followed by a 30 sccm flow of high purity N_2 (99.999%). The temperature and pressure inside the quartz tube

are then set and stabilized for 20 min. For CsPbCl₃, CsPbBr₃, and CsPbI₃, the temperature and pressure are 625 °C and 100 Torr, 575 °C and 50 Torr, and 550 °C and 100 Torr, respectively. Detailed synthesis parameters for different perovskite compounds can be found in Table 3-1. After the synthesis, the tube is cooled down naturally.

Figure 3-3. Schematic of the one-step growth procedure of all-inorganic perovskite in a home-built CVD system.

It is noted that the temperature in a vapor phase synthesis is usually set below the melting point of the compounds at ambient pressure as it will ensure the suitable evaporation rates to obtain well-defined nanostructures. The use of muscovite mica substrate, which is a 2D layered structure with no dangling bonds at its surface, lies at the heart of the vdW epitaxy growth mechanism. There are several additional advantages for the use of such substrate. Firstly, muscovite mica can be easily cleaved and it saves the cleaning process of a substrate. Secondly, muscovite mica can provide atomic flat surface which further facilitates the achievement of unstrained high-quality crystals. Finally, muscovite mica is highly transparent, which provides a good platform to characterize in a transmission configuration the optical properties of perovskite crystals. It saves the transfer process that is usually needed for semiconductors grown on conventional non-transparent substrate and it therefore conserves the intrinsic properties of as-grown semiconductors.

Table 2-1. The detailed synthesis parameters for all-inorganic perovskite compounds

Material	Temperature (degree)	Flow gas	Flow rate (sccm)	Pressure (Torr)	Reaction Time (min)
CsPbCl ₃	625	N ₂	30	100	15
CsPbBr ₃	575	N ₂	30	40	15
CsPbI ₃	550	N ₂	30	100	15

3.3.2 Characterization of the Perovskite Nanoplatelets

The as-synthesized all-inorganic cesium lead halides on transparent mica substrates are characterized by their optical contrast in the optical microscope. Figure 3-4a shows a typical optical microscopy image of CsPbBr₃ nanoplatelets grown on a mica substrate. The as-synthesized nanoplatelets display well-defined rectangular or square shapes which are determined by their crystalline structure. The intrinsic high temperature cubic phase gives rise to the dominant square or rectangular shapes through epitaxial growth. The lateral dimension of as-synthesized nanoplatelets ranges from 1 μm to 50 μm . Similar well-defined structures can also be obtained on CsPbX₃ (X= Cl, Br, or I, mixed Cl/ Br and Br/ I system) by modulating the halide compositions in the perovskite compounds with different synthesis parameters. As seen in Figure 3-4a, the CsPbBr₃ nanoplatelets' edges on mica are oriented predominantly at multiples of 90°. This orientation-controlled nanoplatelet alignment strongly suggests the van der Waals epitaxial nature of CsPbBr₃ crystals on mica (126). Figure 3-4b displays the SEM images. We can observe that the nanoplatelets on mica possess a highly smooth and flat surface, which is of great importance to achieve good optical confinement. In addition, due to a diffraction effect, the perovskite nanoplatelets exhibit rich colors corresponding to different thicknesses ranging from 50 to 250 nm, as shown in Figure 3-4c.

Figure 3-4. (a) Optical microscope images of as-grown CsPbBr₃ nanoplatelets and films. Scale bar, 20 μm . (b) SEM image of CsPbBr₃ nanoplatelets on mica. Scale bar, 10 μm . (c) Optical microscope images of individual nanoplatelets with different thicknesses.

The as-grown perovskite nanoplatelets are further characterized by powder X-ray diffraction (XRD) analysis in a $\theta-\theta$ geometry, which suggests that only planes parallel to the substrate surface will contribute to the measured XRD patterns. As shown in Figure 3-5, three peaks, corresponding to the (100), (110), and (200) planes, can be well attributed to the cubic phase of CsPbX₃ perovskites, while the other peaks come from the mica substrate and the source materials. It is important to be noted that the FWHM of the dominant (100) peak is only 0.1° which is comparable to the FWHM of natural muscovite mica. This feature strongly confirms the excellent quality of as-synthesized perovskite nanoplatelets. Furthermore, these three peaks exhibit a redshift trend from CsPbI₃ to CsPbCl₃, which is due to the decreasing lattice constant from CsPbI₃ to CsPbCl₃. Generally, there are three types of crystalline structures in CsPbX₃ perovskites, including orthorhombic (*i.e.*, below 88 °C for CsPbBr₃), tetragonal (*i.e.*, 88 °C for CsPbBr₃), and cubic polymorphs (*i.e.*, 130 °C for CsPbBr₃). While cubic phase which is expected to exist above 130 °C, is observed for all the samples even at room temperature, which could be attributed to the high temperature synthesis (65).

Figure 3-5. (a) XRD pattern of as-grown CsPbX₃ nanoplalelets showing cubic phase. **(b)** The FWHM of the (100) peak is around 0.1° which demonstrates the good crystallinity of as-synthesized perovskite nanoplalelets.

3.3.3 Synthesis of Perovskite Films

In addition to the successful synthesis of all-inorganic perovskite individual nanoplalelets, large area continuous perovskite films can also be synthesized by changing the synthesis parameters. Specifically, by increasing the synthesis temperature and lowering the synthesis pressure, the evaporation rates of perovskite precursors can be accelerated to form large area perovskite films.

Figure 3-6a shows a clear comparison of as-synthesized CsPbBr₃ perovskite films on muscovite mica and the bare muscovite mica. Large area CsPbBr₃ perovskite films with a size around $1.5 \times 3 \text{ cm}^2$, showing a deep yellow color as compared with the near transparent bare muscovite mica, were successfully obtained. It exhibits an intense green emission under a UV lamp excitation, demonstrating its excellent light emitting properties. Furthermore, the film morphology is investigated by SEM, as shown in Figure 3-6b. A highly smooth surface is observed in our CVD grown CsPbBr₃ perovskite films along with the grain boundary which acts as a reference. This is in sharp contrast to the solution processed CsPbBr₃ perovskite films

presented in the literature (64, 121). A surface roughness of 2 nm is measured by AFM (see Figure 3-6c). Such highly smooth film could potentially meet the requirements and promote the development of high quality optoelectronic applications. In addition, the XRD pattern of as-synthesized CsPbBr₃ perovskite films on mica reveals signature peaks at 15.2° and 30.7°, which correspond respectively to the reflections from the (100) and (200) planes of a cubic phase CsPbBr₃ perovskite crystal. The dominance of the (100) and (200) peaks in the XRD pattern suggests that the CVD grown perovskite films are highly oriented, with the a-axis perpendicular to the mica substrate plane. Similarly, the narrow FWHM of 0.1° and the strong peak intensity indicate the excellent crystallinity of our CVD grown CsPbBr₃ perovskite films, which is much better than that of solution processed polycrystalline perovskite films.

Figure 3-6. (a) The comparison of perovskite films on mica substrate and bare mica substrate. The area of perovskite films can be as large as $1.5 \times 3 \text{ cm}^2$. Inset, the perovskite films show intense green emission under a UV lamp. (b) The SEM image of an as-grown continuous perovskite film, showing extremely flat surface. (c) The AFM image of an as-grown continuous

perovskite film showing a surface roughness of 2 nm. **(d)** The measured XRD patterns of perovskite films after removing the mica substrate, showing excellent crystallinity of perovskite films.

3.3.4 Transfer Process

The successful realization of large area perovskite single crystalline films could potentially pave the way towards high performance optoelectronic devices based on all-inorganic perovskites. However, for device applications requiring an electric conducting substrate, our perovskite films on mica substrate is not suitable as the mica substrate is totally insulating. In this case, a successful transfer process of perovskite films is highly demanded. Here, we adopted a “printing” process to transfer as-synthesized CsPbBr₃ perovskite films onto other substrates (127). As a 2D layered material, the muscovite mica substrate hosting perovskite films can be indeed easily removed by mechanical exfoliation. More specifically, the perovskite films are firstly attached to a tape with the mica substrate facing up. Then the mica substrate is removed with a scotch tape by a layer-by-layer mechanical exfoliation process, leaving the perovskite crystals on the original tape. Consequently, other substrates, such as silicon substrates, ITO substrates and sapphire substrates could be used as the hosting substrate for accepting perovskite films by simply placing the original tape with CsPbBr₃ perovskite crystals down to the host substrate and adding some pressure on the back side of the original tape to eliminate the air gap.

3.4 Optical Properties of All-inorganic Perovskites

3.4.1 Room Temperature Absorption and Emission of All-inorganic Cesium Lead Halide Perovskites

Room temperature optical absorption and PL spectroscopy are performed on the individual nanoplatelets to probe the changes of bandgap energy from CsPbCl₃ to CsPbI₃, as shown in Figure 3-7. All the cesium lead halide perovskites are direct bandgap semiconductors. As discussed in Chapter 1, in CsPbX₃ perovskites, band edge states are mainly determined by inorganic PbX₆²⁻ octahedron. The hybridization states between cation Pb and anion X orbital leads to the formation of conduction and valence band in CsPbX₃ perovskite. The bond strength between Pb and X tends to increase when the halide elemental weight decreases from I to Cl, giving rise to the increase of the band gap between the valence and conduction band. The room temperature PL spectra demonstrate that CsPbCl₃, CsPbBr₃, and CsPbI₃ emit light at 3.00 eV (412 nm), 2.35 eV (527 nm), and 1.77 eV (700 nm), respectively. The PL FWHM of CsPbX₃ nanoplatelets (8.0 -30.0 nm) is smaller than that of highly luminescent CsPbX₃ QDs (12.0–42.0 nm) at room temperature (65), which suggests the high quality and good optical/excitonic properties of as-grown nanoplatelets. Both CsPbCl₃ and CsPbBr₃ are PL active at room temperature, showing strong band edge emission in the blue and green regions, respectively. However, it should be noted that the CsPbI₃ nanoplatelets exhibit a strong red PL emission after the synthesis which tends to disappear quickly. This effect can be attributed to a phase transition from a black phase (cubic, PL active) to a yellow phase (orthorhombic, PL inactive), which is in good agreement with previous reports (65, 76, 128, 129). As shown in the optical absorption spectra in Figure 3-7a, the as-synthesized CsPbBr₃ and CsPbCl₃ nanoplatelets show a strong excitonic absorption peak at 505 nm and 399 nm, respectively, which implies a large exciton binding energy in the as-grown CsPbBr₃ and CsPbCl₃ nanoplatelets. Further investigations will be discussed later.

Figure 3-7. (a) Optical absorption and PL spectra of CsPbCl₃, CsPbBr₃, and CsPbI₃ nanoplatelets. (b) Fluorescence images of as-grown CsPbX₃ nanoplatelets. (c) PL spectra of as-grown CsPbX₃ nanoplatelets, showing seamless emission wavelength tunability.

By tuning the ratio between different halogens (Cl, Br, and I), we have successfully obtained CsPbX₃ nanoplatelets with tunable bandgap. For all the ratio, the CsPbX₃ nanoplatelets show well-defined morphology and flat surface. Figure 3-7b shows the fluorescence microscopy images of single CsPbX₃ nanoplatelets. Under UV light illumination, all the nanoplatelets show strong light emission, displaying different colors from blue to red. Moreover, the light emission along the edges is stronger than the body center, indicating a 2D optical confinement within the square nanoplatelets. Specifically, bandgap engineering is achieved by doping different percentages of bromine into CsPbCl₃ to form CsPbCl_xBr_{3-x} ($0 \leq x \leq 3$) and doping iodine into CsPbBr₃ to form CsPbBr_xI_{3-x} ($0 \leq x \leq 3$). As a result, the PL emission of CsPbX₃ nanoplatelets can be seamlessly tuned from 410 nm to 700 nm, as shown in Figure 3-7c.

3.4.2 Temperature-dependent Absorption Spectroscopy of All-inorganic Perovskites

To probe the exciton properties of all-inorganic perovskites, we carried out temperature-dependent absorption spectroscopy on perovskite nanoplatelets. We mainly focus on the CsPbBr₃ and CsPbCl₃ perovskites, as the CsPbI₃ perovskite is PL-inactive at room temperature.

Temperature-dependent optical absorption spectroscopy is conducted on CsPbBr₃ and CsPbCl₃ within a broad temperature range from 350 K to 77 K and to focus on the exciton properties, we only present the spectra near the excitonic absorption peak. As shown in Figure 3-8a, a strong excitonic peak at ~513nm can be observed at 350 K in CsPbBr₃ perovskite crystals. With the decrease of temperature, the excitonic peak in the optical absorption spectra continuously shifts to longer wavelengths. To analyze the exciton behavior of CsPbBr₃ perovskite in more details, we plot the excitonic peak position in absorption spectra as a function of temperature. Figure 3-8c displays the excitonic peak position along with a fit to the Varshni equation which is given by (130):

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

The best fit is given by $\alpha_3 = 1.56 \times 10^{-4}$ eV/K and $\beta = 13.5$ K. The continuous redshift trend with the decrease of temperature suggests that no phase transition exists within the temperature range (76, 131), whereas a phase transition at around 160 K is usually found in MAPbI₃ perovskite (132). In most inorganic semiconductors, for instance, ZnO and CdS, a blueshift trend is usually observed with the decrease of temperature. However, CsPbBr₃ perovskite exhibits a totally opposite trend as it is widely seen in lead halide perovskites. With the temperature decreasing, the lattice of all-inorganic perovskites tends to contract, strengthening the interaction between the *p* orbit of Br and the *s* orbit of Pb (82, 131, 133, 134). Consequently,

the valence band maximum which is derived by the p orbit of Br and the s orbit of Pb, tends to increase in energy, leading to the decrease of the bandgap in all-inorganic perovskites (134).

Similarly, Figure 3-8b depicts the excitonic peak transition in the optical absorption spectra of as-grown CsPbCl₃ nanoplatelets as a function of temperature from 350 K to 77 K. As shown in Figure 3-8b, the optical absorption spectra of as-grown CsPbCl₃ nanoplatelets exhibit a sharp excitonic peak even at 350 K, which indicates that the excitons are stable even above room temperature. With the temperature decreasing, the excitonic peak in the optical absorption spectra exhibit two distinct redshift trends. To gain more insights, we plotted the excitonic peak position of CsPbCl₃ perovskite as a function of temperature as shown in Figure 3-8c where two distinct regions can be observed with different peak transition slopes. The excitonic peak firstly shows a fast redshift trend until 320 K, followed by a slower redshift trend below 320 K. This phenomenon is attributed to a phase transition from cubic phase to tetragonal phase which occurs at around 320 K during the cooling process. The excitonic peak position is well fitted by using the Varshni equation with $\alpha_1 = 3.382 \times 10^{-4}$ eV/K for the cubic phase and $\alpha_2 = 2.376 \times 10^{-5}$ eV/K for the tetragonal phase, which is in good agreement with previous reports (77).

Figure 3-8. (a) and (b) Temperature-dependent optical absorption spectra of CsPbBr₃ and CsPbCl₃ from 350 K to 77 K. (c) Plots of the excitonic absorption peak position as a function of temperature for CsPbCl₃ and CsPbBr₃. (d) Plots of the FWHM as a function of temperature for CsPbCl₃ and CsPbBr₃.

Figure 3-9. (a) Approximate FWHM extraction of the exciton absorption. (b) FWHM extraction by fitting the absorption spectrum with Elliot's theory of Wannier excitons.

Furthermore, we carried out detailed analysis on the FWHM behaviors of the excitonic absorption peak. The FWHM is approximately extracted by the method as shown in Figure 3-9a, which is similar to the extracted FWHM by fitting the absorption spectrum with Elliot's theory of Wannier excitons (87), as shown in Figure 3-9b. Generally speaking, the linewidths of the exciton absorption are largely determined by inhomogeneous and homogenous broadenings. The inhomogeneous broadening, mostly caused by disorders, is temperature-independent and will not be considered here. On the other hand, two contributions to the homogenous broadening of the exciton linewidth can be considered: (1) the natural population relaxation of the excited states, including both of radiative and nonradiative recombination processes; (2) the elastic scattering events due to exciton–exciton or exciton–phonon interactions. As shown in Figure 3-8b, the exciton absorption peak exhibits a strong narrowing when the temperature is decreased from 350 K to 77 K along with an increase of the peak intensity. This behavior suggests that the exciton broadening is dominated by the exciton–phonon scattering processes. Based on the model from ref. (135), the linewidth of the exciton absorption peak depends on the temperature as (135):

$$\Delta\nu = \Delta\nu_0 + V_T e^{-\frac{E_B}{k_B T}}$$

Where ν , ν_0 , V_T is the bandwidth of exciton peak, temperature-independent broadening, temperature dependent broadening, respectively. T , E_B , k_B is the temperature, exciton binding energy, and Boltzmann constant, respectively. As shown in Figure 3-8d, the FWHM of the excitonic absorption peaks of CsPbCl₃ and CsPbBr₃ as a function of temperature can be well fitted by the above equation with an exciton binding energy of 38 ± 3 meV and 72 ± 3 meV for CsPbBr₃ and CsPbCl₃, respectively. The obtained values agree well with previous theoretical calculation results (65). Concerning CsPbI₃, previous studies have shown that this compound possesses a relatively smaller exciton binding energy of 20 meV which agrees well with our

absorption spectra where no clear excitonic peak can be observed. The large exciton binding energy ($E_b > 25$ meV) for CsPbCl_3 and CsPbBr_3 perovskite confirms that excitons in most of the as-grown all-inorganic lead halide perovskites are stable and will not ionize into free carriers at room temperature. It then well explains the observations of a sharp exciton absorption peak and narrow band emission in absorption and emission spectroscopy (Figure 3-7a). As shown in Figure 3-10, the exciton binding energy of CsPbX_3 perovskite are relatively higher than that of II-VI and III-V semiconductors in the same spectral range, which promises CsPbX_3 perovskite an exceptional future for excitonic applications such as excitonic lasing and exciton polariton condensation at room temperature.

Figure 3-10. The comparison of exciton binding energy of all-inorganic perovskites with traditional semiconductors.

In addition, we further carried out the absorption spectroscopy measurements on the as-grown CsPbBr_3 and CsPbCl_3 nanoplatelets near the liquid helium temperature at 12 K. As shown in Figure 3-11a, two distinct peaks at 2.3517 eV and 2.3794 eV appear near the band edge of CsPbBr_3 perovskite. We attribute these two peaks to the Rydberg excitons in CsPbBr_3 perovskite. As discussed in Chapter 1, the Rydberg exciton dispersion can be described by (87, 136):

$$E_{ex}(n_B, k) = E_g - \frac{Ry^*}{n_B^2} + \frac{\hbar^2 k^2}{2(m_e + m_h)}$$

where E_g is the bandgap of the inorganic material, Ry^* is the exciton binding energy, n_B is the principal quantum number, $\hbar$ is the Planck constant, k is the wave vector of exciton, m_e and m_h are the mass of an electron and a hole, respectively. In our case, the excitonic peak at 2.3517 eV can be attributed to the first order ($n=1$) Rydberg exciton while the excitonic peak at 2.3794 eV can be attributed to the second order ($n=2$) Rydberg exciton. The energy difference between these two peaks is ~ 28 meV, which is approximately three-quarters of the measured exciton binding energy of CsPbBr₃. This finding agrees well with the theoretical dispersion relation of the hydrogenic Rydberg excitons, which further confirms the Rydberg exciton origin of the observed peaks in the absorption spectrum of the CsPbBr₃ perovskite. Similarly, we also carried out the absorption spectroscopy measurements on the as-grown CsPbCl₃ nanoplatelets at 12 K. We also observed two peaks at around 3.0129 eV and 3.0633 eV which correspond to the first order ($n=1$) and second order ($n=2$) Rydberg excitons in CsPbCl₃ perovskite. The observation of Rydberg excitons further suggests the high quality of as-grown CsPbX₃ perovskites, which can provide a good platform to study quantum coherent many-body physics.

Figure 3-11. (a) The absorption spectrum of as-grown CsPbBr₃ perovskite nanoplatelets at 12K. (b) the absorption spectrum of as-grown CsPbCl₃ perovskite nanoplatelets at 12K.

3.5 Summary

In this chapter, I have introduced the mechanism of van der Waals epitaxy and utilized this epitaxy technique to synthesize high quality all-inorganic cesium lead halide perovskites on mica substrates. The as-synthesized CsPbX₃ perovskites exhibit well-defined square or rectangular shapes with lateral dimensions ranging from 1 μm to 50 μm and thickness ranging from 50 nm to several hundreds of nanometers. The XRD patterns of these CsPbX₃ perovskite nanoplatelets show strong and narrow peaks with FWHM of 0.1°, which suggests the cubic phase and superior crystallinity of CsPbX₃ perovskite nanoplatelets. Furthermore, by changing the synthesis parameters, perovskite films of large and continuous area as large as 1.5 × 3 cm² can also be obtained. The as-grown perovskite nanoplatelets and films exhibit smooth surface with a surface roughness of ~2 nm, which may find important applications in light emitting devices.

The as-grown CsPbX₃ crystals exhibit intense emission at room temperature, which can be seamlessly tuned throughout the whole visible range by simply changing the halide composition. The perovskite exciton behaviors, and more particularly the structural phase transitions, are studied by absorption spectroscopy as a function of temperature. No structural phase transition is found in CsPbBr₃ perovskite while a transition between cubic phase and tetragonal phase was found in CsPbCl₃ by changing the temperature from 350 K to 77 K. Moreover, by analyzing the exciton behaviors as a function of temperature, we extract a large exciton binding energy of 38 meV and 72 meV for CsPbBr₃ and CsPbCl₃ perovskites, respectively, which is larger than that of traditional semiconductors with bandgaps in the same energy region. This excellent property enables CsPbX₃ perovskites a bright future towards excitonic optoelectronic applications, such as excitonic lasing and exciton polariton condensation. In addition, two orders of Rydberg excitons are observed in the absorption spectra in both CsPbBr₃ and CsPbCl₃ perovskite at 12 K, as confirmed by the energy difference

of the exciton absorption peaks and the measured exciton binding energies. The observation of Rydberg excitons further suggests the excellent quality of our perovskite crystals, which provides a good platform for study many-body physics based on all-inorganic perovskite.

Chapter 4 Whispering Gallery Mode Photonic Lasing in All-inorganic Cesium Lead Halide Perovskite Nanoplatelets

4.1 Introduction

A laser is a device that can emit coherent light with strong intensity and perfect directionality. Lasers essentially work through a light amplification process by stimulated emission of radiation (137). Since the laser was invented in 1960, lasers have been widely used in a variety of technological and scientific fields, such as bioimaging, manufacturing, spectroscopy, and optical communications (138-140). Particularly, with the emergent progress in nanoscience and nanotechnology, small solid-state lasers, *i.e.*, where the physical size of one or multiple dimensions is comparable or smaller than the diffraction limit, have attracted considerable attention driven by the need for high-density data storage, optical integration, and high-resolution bioimaging, *etc* (141-143). Further technological advances based on lasers significantly rely on nanolasers with low threshold and high quality factor.

Recently, lead halide perovskites are regarded as ideal active media towards high performance lasers owing to their high quantum efficiency and solution processability. Since the first demonstration of amplified spontaneous emission (ASE) in solution-processed organic-inorganic perovskite films with low threshold and seamless wavelength tunability (62), considerable effort has been devoted to pushing the performance of perovskite lasing to be better and better. F. Deschler *et al.* firstly utilized the solution-processed $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ perovskite film embedded into two silver mirrors to realize lasing action at room temperature (61). In addition to the 2D film lasing, various nanostructure lasing based on perovskites have also been demonstrated in the past few years. As shown in Figure 4-1, Q. Zhang *et al.* firstly demonstrated perovskite lasing based on organic-inorganic hybrid lead halide perovskite

nanoplatelets (59). These organic-inorganic hybrid lead halide perovskite nanoplatelets exhibit sharp edges and well-defined hexagonal and triangle structures, serving as high quality active microcavities. Thus, near-infrared nanolasing with a low threshold of $37 \mu\text{J cm}^{-2}$ can be realized in such perovskite nanoplatelets.

Figure 4-1. (a) Schematic of optical measurement principle for perovskite lasing. (b) The far-field optical microscopy images of CH₃NH₃PbI₃ nanoplatelets under white light (top panels) and pump laser (bottom panels) excitations. (c) and (d) Characterization of the lasing action based on individual CH₃NH₃PbI_{3-a}Br_a and CH₃NH₃PbI₃ nanoplatelets. Figure is taken from Ref. (59).

After that, H.M. Zhu *et al.* reported the first demonstration of high performance nanowire lasers based on organic-inorganic hybrid lead halide perovskite (60). By adopting a one-step wet-chemical method, high-quality MAPbX₃ perovskite nanowire active microcavities are obtained, exhibiting ultralow lasing threshold (220 nJ cm^{-2}), high coherence with a Q factor of 3600 (laser pulse width: 100 fs @ 250 kHz; 0.24 nm @ 750 nm) and broad wavelength tunability covering the near-infrared to the visible regions. Such exceptional lasing

performance is believed to originate from the long carrier lifetime and low nonradiative recombination rates of the rectangular perovskite nanowires. However, the biggest concern about this organic-inorganic hybrid perovskites is their optical and structure instability, which may restrict the potential applications. Thus, their counterparts, the all-inorganic cesium lead halide perovskites, which exhibit similar optical properties but better stability, attract more and more attention towards high performance perovskite lasers (66-69, 144). After the demonstration of low threshold ASE based on CsPbX_3 quantum dots by S. Yakunin *et al.* (66) and Y. Wang *et al.* (144, 145), S. Eaton *et al.* firstly reported the nanolasing based on CsPbX_3 perovskite nanowires (67). However, compared with the organic-inorganic hybrid perovskite lasing, the CsPbX_3 nanowires exhibit much larger lasing threshold and lower spectral coherence possibly because of the imperfect nanowire microcavity. Further improvements on CsPbX_3 nanolasing are crucial towards the practical implementation of nanolasers. In this chapter, I will demonstrate our experimental results on CsPbX_3 perovskite lasing and more particularly how the lasing performance has been improved by utilizing well-defined square nanoplatelets as active microcavities.

4.2 Photonic Lasing Mechanism

Generally, photonic lasing is based on stimulated emission of photons when the optical gain medium reaches the population inversion regime. It is a process of photons inducing radiative relaxation of excited state electrons coherently. A photonic laser usually consists of an optical gain medium embedded in an optical resonator. The optical gain medium is usually a semiconductor where the population inversion is achieved under intense optical excitations, as shown in Figure 4-2a. While the optical resonator is used for providing the optical feedback of the coherent light. Photons with proper wavelengths will be confined due to the selection

of the optical resonator and constructively interfere with each other to produce amplification of coherent light.

To take a simple Fabry-Pérot cavity laser for example, as shown in Figure 4-2b, the cavity of length L usually consists of two end mirrors characterized by the reflectivities R_1 and R_2 . The propagating mode with wavelength λ in the Fabry-Pérot cavity should meet the following relationship with the cavity length:

$$L = \frac{\lambda m}{2n}$$

where m is an integer and n is the effective refractive index in the cavity. The shortest cavity length for lasing with a wavelength of λ is thus obtained when m is equal to 1. Owing to the finite reflectivity of the end mirrors, substantial mirror loss will occur near the end mirrors preventing from the occurrence of lasing. In order to achieve lasing, the round-trip optical gain should be able to overcome the mirror loss and the propagation loss, such that

$$\Gamma g > \alpha_m + \alpha_p = \frac{1}{2L} \ln\left(\frac{1}{R_1 R_2}\right) + \alpha_p$$

where Γ is the confinement factor, g is the material optical gain, α_m is the loss from the end mirrors and α_p is the propagation loss. As shown in this latter equation, the reflectivities of the end mirrors play an important role in the mirror loss.

Before the occurrence of lasing effect, the lifetime τ_p of a photon confined in the cavity is usually defined by the quality factor Q of the cavity,

$$Q = \frac{\lambda}{\Delta\lambda}$$

$$\frac{1}{\tau_p} = \frac{2\pi c}{Q\lambda}$$

Where $\Delta\lambda$ is the linewidth of the emission peak and c is the speed of light in vacuum. The photon lifetime which is determined by the linewidth of the cavity emission could be significantly increased if one can improve the quality factor Q of the cavity. More round trips could be achieved to generate more optical feedback by increasing the photon lifetime. In order to reduce the lasing threshold, one has to find a way to minimize the optical losses in the cavity including mirror loss and propagation loss. Improving the reflectivity of the end mirrors could serve as an effective way to significantly reduce the lasing threshold while the propagation loss could be reduced by improving the quantum efficiency of the active medium.

Figure 4-2. (a) Schematic of the stimulated emission process. (b) A typical Fabry-Pérot cavity for a laser.

In terms of cavity design for nanolasers, several kinds of cavities have been adopted in nanolasers such as 1D nanowire Fabry-Pérot cavity, 2D whispering gallery mode (WGM) cavity and photonic crystal microcavity, as shown in Figure 4-3. Particularly, compared with other cavities, WGM cavities possess the advantage of better quality factors due to the low loss in the resonator. Specifically, as WGM cavities are actually based on continuous total internal reflections, the mirror loss is significantly lower than that of Fabry-Pérot cavities, thus providing much higher quality factors. An early work on WGM cavity laser was firstly reported in a microsphere laser by Garrett *et al.* (146). With the development of fabrication techniques, the quality factors of WGM cavities dramatically increased to up to 10^8 , thus providing extremely low lasing threshold (147).

Figure 4-3. (a) A typical nanowire Fabry-Pérot microcavity. (b) WGM microcavity of square nanoplatelet, hexagonal nanoplatelet and nanosphere. (c) Photonic crystal microcavity. Figure is taken from Ref. (120).

To understand the light propagation in a WGM microcavity, we can take a 2D circular structure as an example, as shown in Figure 4-4. The light is confined in the circular cavity by multi-total internal reflections near the boundary. Light travels one round trip and satisfies the following equation:

$$m\lambda = Ln_{eff} \quad (5)$$

Where λ is the light wavelength, L is the circumference of the circular structure, m represents the angular mode number and n_{eff} is the effective refractive index. WGM microcavity can sustain both transverse magnetic (TM) and transverse electric (TE) modes. In order to simplify the description of the light propagation process, we take the surrounding material as air ($n=1$) and focus on the fundamental WGM. By accurately calculate the resonant wavelength inside the circular structure, we obtain (148):

For TE modes

$$\lambda_{TE} \approx \frac{2\pi rn_1}{m + 1.856m^{\frac{1}{3}} + \left(\frac{1}{2} - \frac{n_1}{\sqrt{n_1^2 - 1}}\right)}$$

For TM modes

$$\lambda_{TM} \approx \frac{2\pi r n_1}{m + 1.856m^{\frac{1}{3}} + \left(\frac{1}{2} - \frac{1}{n_1 \sqrt{n_1^2 - 1}}\right)}$$

Where n_1 is the cavity refractive index and r is the radius of the circular cavity. As n_1 should be larger than 1 so that light can be effectively confined in the cavity, TM modes usually resonate at a shorter wavelength than that of the TE modes. The theory can also be applied into other WGM cavities while the only difference is the travel length for a round trip.

Figure 4-4. Schematic of the light propagating in a circular WGM cavity where the dashed lines show the light leakage out of the WGM cavity.

4.3 Whispering Gallery Lasing in Perovskite Nanoplatelets

As shown in Chapter 3, the as-synthesized CsPbX_3 nanoplatelets naturally form high-quality WGM microcavities with a uniform square shape, sharp facets and a subwavelength thickness, providing excellent light confinement. We carried out lasing characterization in square perovskite nanoplatelets as schematically shown in Figure 4-5a. An individual perovskite nanoplatelet was pumped by a 400 nm pulsed laser with a repetition rate of 1kHz, resulting from frequency-doubling by a nonlinear BBO crystal from an amplifier laser source (Libra, Coherent company, center wavelength: 800 nm). The pump laser was focused by a

microscope objective (20 $\times$, NA: 0.45) leading to a laser spot of 40 μm in diameter to excite the whole nanoplatelets. The emission signal was collected by the same objective and sent to an Acton spectrometer (Spectra Pro 2500i) with a Princeton Instrument liquid nitrogen cooled CCD (Pixis 400B) for spectra measurements.

Figure 4-5. Lasing Characterization of Cesium Lead Halide Nanoplatelets. (a) The schematic of an individual CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}$ or I) nanoplatelet on mica substrate pumped by a 400 nm laser (~ 100 fs, 1 kHz). The yellow solid line shows the light propagation direction inside the square WGM cavity. (b) The measured emission spectra under five different optical pump fluencies, demonstrating the appearance of lasing. Inset: 2D pseudo-color plot of the nanoplatelet emission spectra under different pump fluencies. (c) A Lorentzian fitting of a lasing mode gives a FWHM of 0.15 nm, which corresponds to a quality factor of 3570. (d) Power-dependent lasing output intensity, showing a superlinear increase of the output intensity above a threshold of $\sim 2.2 \mu\text{J}/\text{cm}^2$ (peak power density of $2.2 \times 10^7 \text{ W}/\text{cm}^2$). (e) TRPL decay kinetics after photoexcitation at a pump fluence below ($P \sim 0.8P_{\text{th}}$) and above threshold ($\sim 1.2 P_{\text{th}}$),

showing a ~ 3.0 ns SPE decay process below P_{th} and a <30 ps lasing process above P_{th} . A lifetime of ~ 4.2 ns is shown at relatively low pump fluence ($\sim 0.1 P_{th}$).

As shown in Figure 4-5b, the spontaneous emission (SPE), which is centered at 527 nm with a FWHM of 20 nm, is so weak that it cannot be distinguished in the same scale of the spectra taken above the lasing threshold. With the pump fluence increasing to $\sim 1.5 \mu\text{J}/\text{cm}^2$ (peak power density of $1.5 \times 10^7 \text{ W}/\text{cm}^2$), several narrow lasing peaks are observed around $\lambda = 530.0$ nm, which are the cavity modes selectively amplified by the optical feedback in the square cavity. By further increasing the pump fluence to $2.5 \mu\text{J}/\text{cm}^2$ (peak power density of $2.5 \times 10^7 \text{ W}/\text{cm}^2$), the lasing peak intensity increases dramatically along with a significant narrowing of the peak width $\delta\lambda$, suggesting the occurrence of lasing action. When the pumping fluence further increases to $3.0 \mu\text{J}/\text{cm}^2$ (peak power density of $3.0 \times 10^7 \text{ W}/\text{cm}^2$), the FWHM of the lasing peak is as narrow as $\delta\lambda = 0.15$ nm. To the best of our knowledge, the corresponding quality factor of 3600 is larger than that of previous reports in semiconductor active cavities, as shown in Table 4-1. The relationship between pump fluences and the lasing emission intensity (input-output curve) clearly exhibits a typical “S” shape which confirms the occurrence of lasing action based on a multi-mode laser theory, as shown in Figure 4-5d. Under low pumping power, the linear region is attributed to spontaneous emission while the superlinear region above $2.2 \mu\text{J}/\text{cm}^2$ corresponds to ASE. A full lasing action region is obtained by further increasing the pump fluence above $3.0 \mu\text{J}/\text{cm}^2$. The transition from the linear region (SPE) to the nonlinear region (ASE) happens at $P = 2.2 \mu\text{J}/\text{cm}^2$ (peak power density of $2.2 \times 10^7 \text{ W}/\text{cm}^2$) which is regarded as the lasing threshold. Furthermore, we conducted time-resolved photoluminescence (TRPL) measurements with a streak camera as a function of pump fluence to confirm the occurrence of lasing. As shown in Figure 4-5e, the SPE lifetime is as long as $\tau_{SPE} \sim 4.2$ ns at low excitation ($\sim 0.1 P_{th}$, green dots) while it shows a decrease trend with a time constant $\tau_{SPE} \sim 3.0$ ns at higher excitation fluence ($\sim 0.8 P_{th}$). Above the threshold

($\sim 1.2P_{th}$), a fast decay of less than 30 ps (limited by the instrument response of the streak camera) which dominates the carrier kinetic process was observed. This further confirms the lasing occurrence in the square perovskite cavity.

Table 3-1. Detailed comparison between the WGM lasing in CsPbX_3 and the lasing in other nanostructures.

Material	Peak position (nm)	Threshold($\mu\text{J}/\text{cm}^2$)	Quality factor of lasing line $Q_l = \lambda_l / \delta\lambda_l$	Reference
CdS NW	512	~ 1.0 at RT	~ 1280 at RT	Ref (149)
CdS NW	490	~ 0.2 at 4.2K	~ 1633 at 4.2K	Ref (150)
CdSe NW	723	NA	~ 1800 at RT	Ref (151)
InGaAs/GaAs NW	883	~ 22 at 4K	~ 206 at 4K	Ref (6)
InP NW	898	~ 130 at RT	~ 900 at RT	Ref (152)
$\text{CH}_3\text{NH}_3\text{PbI}_3$ NW	787	~ 0.4 at RT	~ 3600 at RT	Ref (60)
$\text{CH}_3\text{NH}_3\text{PbBr}_3$ NW	546	~ 0.6 at RT	~ 2400 at RT	Ref (60)
$\text{CH}_3\text{NH}_3\text{PbBr}_3$ WGM	557	~ 3.6 at RT	~ 430 at RT	Ref (153)
$\text{CH}_3\text{NH}_3\text{PbI}_3$ WGM	776	~ 37 at RT	~ 650 at RT	Ref (59)
$\text{CH}_3\text{NH}_3\text{PbI}_3$ NW	777	~ 11 at RT	~ 405 at RT	Ref (109)
CsPbBr_3 WGM	536	~ 2.0 at RT	~ 3600 at RT	*This work
$\text{CsPbBr}_{1-x}\text{I}_x$ WGM	680	~ 5.0 at RT	~ 4300 at RT	*This work

We further characterized the optical modes propagating inside the cavity. With a thickness of around 180 nm, both the WGM oscillation through four facets of the square cavity and the Fabry-Pérot mode oscillation between two facets of the square cavity can give rise to a lasing action. However, the WGM oscillation usually possesses much lower loss than that of

the Fabry- Pérot oscillation, thus leading to a lower threshold. Therefore, the WGM lasing is more favorable in our square cavity. To further confirm the lasing origin, we measured the PL/lasing image and conducted field calculation by using finite element method (Lumerical FDTD). Figure 4-6a and Figure 4-6b display the PL image of an individual CsPbBr₃ nanoplatelet below and above the lasing threshold, respectively. The whole body of the perovskite nanoplatelet exhibits a green emission below threshold, demonstrating the unidirectional out-coupling of the spontaneous emission. When the pump fluence is larger than the lasing threshold, the individual nanoplatelet show much stronger emission at the four corners, which further confirms the WGM lasing origin. Considering our square microcavity, Fabry- Pérot oscillation between parallel end facets of the nanoplatelet could also lead to lasing action. However, if the lasing action is from the Fabry- Pérot oscillation between parallel end facets of the nanoplatelet, there should be stronger emission at all the end facets of the nanoplatelet rather than stronger emission only at the corners. Thus, lasing action from Fabry- Pérot oscillation between parallel facets could be excluded. Another possibility is WGM lasing nature inside the square nanoplatelet. With total internal reflection, photons propagate and get reflected by the four end facets of the nanoplatelet. There will be some photon leakage at the end facts of nanoplatelet. However, at the corners of the nanoplatelet, total internal reflection can no longer sustain, leading to more losses compared with the end facets. As a result, stronger emission can be observed at the four corners than that of four end facets, leading to four bright spots at the corners of the nanoplatelet. This observed emission pattern is in good agreement with the calculated electric field distribution of the TM mode in a square WGM cavity using a finite domain time difference (FDTD) package (Figure 4-6c). The calculation illustrates that the optical field of the lasing mode is well confined inside the microcavity through WGM confinement, with a greater leakage at the four corners. This is in good agreement with our

experimental data where the experimental far-field emission image exhibits much stronger emission at the four corners.

Figure 4-6. Whispering-gallery-mode lasing characterization and numerical calculation.

(a) and (b) Photoluminescence emission image obtained by a CCD below and above the lasing threshold for an individual CsPbBr₃ perovskite nanoplatelet, respectively. Scale bar, 3 μm. (c) Simulated electric field distribution inside the square perovskite cavity for a TM optical mode. The pattern demonstrates that the cavity supports a WGM lasing. (d) The measured multimode lasing spectra of four perovskite nanoplatelets with different edge lengths ranging from 9 to 29 μm. The oscillation number of the lasing mode is indicated near the lasing peak in the case of the edge length of 9 μm. (e) The spacing between two lasing modes is extracted and plotted as a function of the inverse of edge length. Navy dots are the experimental data while the navy line shows the fitting of the experimental data.

We further investigated the relationship between the lasing mode and the nanoplatelet edge length. With the increase of the nanoplatelet edge length L from 9.0 to 29.0 μm, the mode spacing narrows from 3.0 nm to 0.9 nm (Figure 4-6d). To rule out the effect of the thickness

variation on the effective refractive index, we focused on CsPbBr₃ nanoplatelets with similar thicknesses (180±20 nm). The mode spacing extracted from Figure 4-6d exhibits a linear trend with respect to the inverse of the edge length (Figure 4-6e). In a cubic WGM resonator, the mode spacing $\delta\lambda_l$ can be written as (153):

$$\delta\lambda_l = \frac{\lambda_l^2}{2\sqrt{2}Ln_g}$$

According to the fitting, we extracted a group refractive index n_g of ~ 3.7, which agrees well with previous studies, suggesting the nature of WGM lasing (154). The obtained lasing peaks usually appeared at the lower energy side of the SPE. This feature has been widely observed in III-V and II-VI semiconductor nanolasers and can be attributed to an exciton self-absorption process during the photon propagation inside the cavity (155).

Multi-color lasing actions can be realized in similar square-shaped perovskite nanoplatelet crystals by composition modulations at room temperature, as shown in Figure 4-7a. The colour of the spontaneous emission in perovskite active mediums can in fact be tuned throughout the whole visible spectral range by changing the halide elements. Depending on the colour, the measured lasing threshold is around ~2.0-10.0 $\mu\text{J}/\text{cm}^2$, which is similar to traditional semiconductors and smaller than that of CsPbX₃ QDs WGM lasers with much larger cavity size as reported recently (155, 156). The far field images (inset, Figure 4-7a) above the lasing threshold clearly exhibit the occurrence of WGM lasing. As shown in the lasing spectra in Figure 4-7a, the lasing peaks are dominant over the spontaneous emission background, suggesting an excellent coupling efficiency of the spontaneous emission into the lasing process. The square perovskite crystals with different composition also exhibit superior quality for WGM cavity. Figure 4-7b depicts the zoom-in spectrum of the lasing mode of a CsPb(Br/I)₃ perovskite with a central emission wavelength of ~ 680 nm. The lasing peak could be well fitted by a Lorentzian function with FWHM of 0.14 nm, which corresponds to a quality factor

of ~ 4850 . The lasing spectrum is slightly asymmetric which is possibly due to the background subtraction. Compared with other reports on the lasing in nanostructures, the obtained laser quality factor of the as-synthesized perovskite crystal is the highest within this spectral range (Table 4-1). It should be noted that the high quality factor originates from the perovskite crystal itself which serves as an active cavity where no additional mirrors have been introduced to reduce the optical losses. Thus, it could be predicted that the lasing linewidth of the all-inorganic perovskite micro-laser could be further reduced by introducing an additional high- Q passive optical cavities. The obtained high quality lasing with excellent spectral coherence based on all-inorganic perovskite crystals can be ascribed to naturally formed high quality WGM resonator, highly luminescent all-inorganic cesium lead halide perovskite active mediums with stable excitons of large exciton binding energy.

With the naturally formed perovskite microcavity, we will demonstrate the Purcell effect in all-inorganic perovskite nanoplatelets which can enhance the perovskite emission in next section.

Figure 4-7. Multicolor whispering-gallery-mode microlaser based on inorganic perovskites with high-quality factor. (a) Lasing spectra and images of individual CsPbX_3 perovskite nanoplatelets with various halide compositions. Left to right: the halide element X in perovskite varies from $\text{Cl}_x\text{Br}_{3-x}$, Br, to $\text{Br}_x\text{I}_{3-x}$. Inset, emission images above the lasing threshold of perovskite with X changing from $\text{Cl}_x\text{Br}_{3-x}$, Br, to $\text{Br}_x\text{I}_{3-x}$. (b) A zoom-in spectrum

of a lasing mode of $\text{CsPbBr}_x\text{I}_{3-x}$ perovskite. The blue dots and red line are experimental data and Lorentzian function fitting curve, respectively. The full width at half maximum $\delta\lambda$ of the lasing mode is 0.14 nm.

4.4 Summary

In this chapter, I mainly introduced our work on high performance nanolasing based on as-synthesized cesium lead halide perovskite crystals. The cesium lead halide perovskite crystals exhibit well-defined square and rectangular shapes and sharp edges, naturally forming WGM microcavities. Under pulsed laser excitation, the CsPbBr_3 perovskite crystals exhibit high performance lasing with a low threshold of $2.2 \mu\text{J}/\text{cm}^2$ (peak power density of $2.2 \times 10^7 \text{ W}/\text{cm}^2$) and high quality factor of over 3500. According to the far-field lasing image and FDTD calculation, the lasing action is believed to originate from WGM. Furthermore, by measuring the lasing spectra on CsPbBr_3 perovskite crystals with different sizes, the lasing mode spacing are found to be proportional to the inverse of the edge length of the perovskite crystals, which further confirms the WGM origin of lasing in cesium lead halide perovskites. Multicolor lasing actions are also realized by composition engineering in cesium lead halide perovskite crystals. Such multicolor lasing actions also exhibit low threshold and high quality factor. The presented studies show that the perovskite semiconductor compounds exhibit outstanding and engineered excitonic properties, which may supply solutions to solve the weakness of current technological semiconductors from II-VI/III-V compounds, metal dichalcogenide to organic crystals. The large exciton binding energy, high absorption/emission efficiency ensures a large number of active exciton at room-temperature for device applications, particularly in excitonic and quantum photonic devices. Together with the well-controlled exciton at room temperature, the cubic lattice of the type of materials promises the achievement of high quality factor WGM cavities for further quantum physical and optics studies from weak to strong coupling regime.

Chapter 5 Room Temperature Polariton Lasing in All-Inorganic Cesium Lead Halide Perovskites

5.1 Introduction

Exciton polaritons stem from the strong coupling between confined cavity photons and excitons (9, 10). As half-light, half-matter quasiparticles, exciton polaritons possess extremely light effective mass inherited from their photonic component, which is typically only $10^{-4} \sim 10^{-5}$ times the rest mass of electron. While their excitonic components provide them high nonlinearity. These two combined features give rise to the possibility for achieving BEC utilizing exciton polaritons at high temperatures (92, 105). BEC of exciton polaritons appears if the ground state of the lower polariton branch is macroscopically occupied when a critical threshold is achieved and the polariton occupancy distribution exhibits a Bose–Einstein distribution. However, polaritons usually possess finite lifetime, which results in the alteration of polariton occupancy distribution by some uncondensed excitons and non-equilibrium effects. Under such conditions, the polariton condensate can be considered as a non-equilibrium state with spontaneous coherence, which leads to a coherent polariton emission, the so-called polariton lasing, with relatively low threshold (27). In conventional photonic lasing scheme, the population inversion is compulsory to trigger the amplification of photons, which requires intense optical pumping. While in the polariton lasing scheme, population inversion can be exempted thanks to the mechanism of bosonic final-state stimulation. This unique feature leads to a relatively lower lasing threshold for polariton lasing, in comparison with vertical-cavity surface emitting lasing (VCSEL) which possesses similar cavity structure as polariton laser.

Figure 5-1. (a) Reflectivity spectrum of a GaAs microcavity at 5K, showing clear energy splitting when the exciton and cavity photon are in resonance. (b) The plotted reflectivity peak position as a function of the cavity detuning, showing a clear anticrossing feature. Figure is taken from Ref. (9).

In solid state systems, strong coupling between excitons and photons was firstly revealed by C. Weisbuch *et al* in a GaAs quantum well microcavity in 1992 (9). As shown in Figure 5-1, typical energy splitting and anticrossing feature can be observed in the GaAs quantum well microcavity, which confirms the strong coupling regime. Since then, a wide range of research work has been done on exciton polariton towards exciton polariton condensation and polariton lasing. Clear evidences of exciton polariton condensation were not observed until the work of J. Kasprzak *et al.* (30). As shown in Figure 5-2, upon reaching the threshold, polaritons massively occupy the ground state of the lower polariton branch to form polariton condensates and the distribution of polaritons follows the Bose-Einstein distribution. In addition, long-range spatial coherence of 16 μm was also observed to further confirm the occurrence of exciton polariton condensation. However, limited by the small exciton binding energy, exciton polariton condensation and lasing using such inorganic semiconductors with Wannier-Mott excitons, for example GaAs (157, 158), CdTe (30), ZnSe and more recently InP

(159), can only operate at low temperatures, which greatly hinders the potential applications of polariton lasing. On the contrary, robust excitons, as well as large oscillator strengths, promote further room temperature realizations of exciton polariton condensation and exciton polariton lasing in ZnO (44, 45) and GaN (43) (101). Nonetheless, inorganic planar microcavities usually require sophisticated epitaxial techniques to ensure the high quality of the microcavity as well as the optical gain medium, in which one has to combat the challenges of built-in strain and mismatch of thermal expansion coefficients. In contrast, organic materials exhibit Frenkel excitons with much larger exciton binding energy and ease of fabrication, provide alternative systems for achieving room temperature polariton emission (160-162) and polariton condensation, *e.g.*, crystalline anthracene (46), amorphous 2,7-bis[9,9-di(4-methylphenyl)-fluoren-2-yl]-9,9-di(4-methylphenyl) fluorine (TDAF) molecules (47), ladder-type conjugated MeLPPP polymer (48) and enhanced green fluorescent protein (49). Nevertheless, Coulomb interaction (163), which contributes primarily to polariton-polariton interactions, is significantly weaker in organic materials due to the Frenkel exciton nature, leading to inefficient polariton relaxation to ground state (164). Therefore, a much higher threshold and weaker nonlinearity are often obtained in organic microcavities (165), compared with inorganic microcavities. Under such conditions, it is crucial to find a suitable system which can provide ease of fabrication and low threshold towards exciton polariton condensation and exciton polariton lasing.

Figure 5-2. (a) 3D images of k-space emission as a function of pump power. (b) Energy versus in-plane wavevector plot of polaritons as a function of the pump power. Figure is taken from Ref. (30).

In addition, there have also been tremendous and long-lasting interests in the past decades in using hybrid organic-inorganic perovskites for polariton emission (166-169) and in investigating polariton condensation and polariton lasing operated at room temperature, as they combine the advantages of both inorganic and organic materials, such as ease of synthesis, large exciton binding energies and excellent optical properties determined by the inorganic component. T. Fujita *et al.* firstly utilized a distributed feedback microcavity coated with $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$ perovskite to demonstrate the strong coupling regime (166). As shown in Figure 5-3, by changing the grating pitch, the cavity detuning can be tuned to make the cavity photon in resonance with the perovskite exciton, thus reaching strong coupling regime. Energy splitting and clear anticrossing features can be observed to prove the existence of strong coupling regime. Later, strong coupling based on lead halide perovskites have also been realized by G. Lanty *et al.* (169-172) and H.S. Nguyen *et al.* (173, 174). However, up to now, only room temperature strong coupling regime in perovskite materials can be observed (166-

169), without any successful realization of polariton condensation, which is probably caused by the insufficient crystalline quality induced by solution chemistry. In Chapter 3 and 4, we have demonstrated that all-inorganic cesium lead halide perovskites grown by a vapor phase method possess superior optical gain properties with large exciton binding energy and tunable emission throughout the whole visible range. Thus, we believe that our all-inorganic perovskite crystals are promising candidates for investigating the physics of BEC in an easy-access solid-state platform and realizing low threshold room temperature polariton lasing. In this chapter, I will demonstrate the experimental realization of polariton lasing based on epitaxy-free CsPbCl₃ planar microcavities operated at room temperature. The demonstration of exciton polariton lasing is unambiguously evidenced by macroscopic ground state occupation, a superlinear power dependence, continuous blueshift of the ground state emission, significant decrease of the ground state emission linewidth and the occurrence of long-range spatial coherence.

Figure 5-3. (a) The transmission spectra of hybrid perovskite samples at room temperature under different gratings with different pitches under two different polarizations. (b) The peak energy in transmission spectra as a function of the cavity detuning. Figure is taken from Ref. (167).

5.2 Sample Preparation

An e-beam evaporator is used to fabricate the bottom DBR, which consists of 13 pairs of hafnium dioxide (54 nm) and silicon dioxide (73 nm). The active medium CsPbCl₃ perovskite nanoplatelet is grown on a mica substrate, as described in Chapter 3. The CsPbCl₃ perovskite nanoplatelet is then transferred onto the bottom DBR substrate by a dry tape transfer process. In fact, as the mica is a two-dimensional layered structure, the mica substrate could be totally removed by mechanical exfoliation with a scotch tape, leaving the perovskite active medium onto the tape. Consequently, the perovskite active medium could be left on the bottom DBR by printing the tape with perovskite onto the bottom DBR. After that, the bottom DBR with perovskite on top is put into the e-beam evaporator for the deposition of the top DBR which is composed of 7 pairs of hafnium dioxide (50 nm) and silicon dioxide (68 nm). In the end, perovskite microcavities could be obtained with various cavity lengths as the transferred CsPbCl₃ perovskite nanoplatelet exhibit various thicknesses.

5.3 Characterization of the Perovskite Microcavity

The fabricated perovskite microcavity, as shown in Figure 5-4a, is composed of a CsPbCl₃ perovskite nanoplatelet sandwiched by the bottom and top DBRs. The Fabry-Pérot resonance can be controlled by the thickness of the perovskite nanoplatelet. The characterization of the perovskite microcavity is conducted using a home-built optical setup where angle-resolved reflectivity and PL measurements can be performed (Figure 5-4b), as discussed in Chapter 2. After the whole microcavity fabrication process, the perovskite microcavity inherits the rectangular shape from the CsPbCl₃ nanoplatelet with a width of 12 μm, as shown in Figure 5-4c. The fluorescence image (Figure 5-4d) of the perovskite microcavity displays a stronger emission at the edges of the perovskite, suggesting the good 2D confinement induced by the microcavity. Figure 5-4d shows the room temperature

absorption and PL spectra of the CsPbCl₃ perovskite nanoplatelet on mica substrate, as well as the ground state emission of the CsPbCl₃ perovskite. The CsPbCl₃ perovskite exhibits a narrow and strong excitonic absorption peak at around 3.045 eV in the absorption spectrum (orange trace). Our results in Chapter 3 have in fact shown that the exciton binding energy of the CsPbCl₃ perovskite is around 72 meV, making it a promising candidate towards room temperature polaritonic applications (69). The room temperature PL emission (blue trace) of the CsPbCl₃ perovskite is centered at around 2.99 eV with a FWHM of 80 meV. After the perovskite nanoplatelet being sandwiched by two DBRs, the normal incidence emission (red trace) of the CsPbCl₃ perovskite shifts to lower energy of around 2.9 eV and significantly narrows to a FWHM of around 9.7 meV, which corresponds to a quality factor of $Q \sim 300$.

Figure 5-4. Microcavity structure and emission. (a), Schematic of the perovskite microcavity, which is composed of a CsPbCl₃ rectangular nanoplatelet sandwiched between a top and a bottom HfO₂/SiO₂ DBR. (b), Schematic of the angle resolved setup with Fourier

optics. Two Fourier lenses are shown as f_1 and f_2 . (c) and (d) Optical and fluorescence microscopy images of a rectangular-shaped CsPbCl_3 perovskite microcavity after fabrication. Scale bar, 12 μm . (e) Room temperature absorption and PL spectra of a CsPbCl_3 perovskite nanoplatelet. The absorption spectrum (Orange trace) of the CsPbCl_3 perovskite nanoplatelet on mica substrate exhibits a strong excitonic peak at ~ 3.045 eV. The PL emission spectrum (Blue trace) of the CsPbCl_3 perovskite nanoplatelet on mica substrate displays an emission at ~ 2.99 eV with a FWHM of 80 meV. The ground state emission (Red trace), along with Gaussian fitting (black dash line) of a CsPbCl_3 nanoplatelet after microcavity fabrication, demonstrates an emission at ~ 2.90 eV with a FWHM of ~ 9.7 meV.

5.4 Perovskite Polariton Lasing - Negative Detuning

5.4.1 Exciton Polariton Dispersion - Negative Detuning

Here, we use a CsPbCl_3 perovskite nanoplatelet with a thickness of 373 nm as the active medium. We probe the polariton behaviour of the fabricated CsPbCl_3 perovskite microcavity by angle-resolved reflectivity and PL spectroscopy (equivalently as a function of the in-plane wavevector $k_{\parallel}$) at room temperature ($T = 300$ K). Figures 5-5a and 5-5b depict the momentum-space spectra of angle-resolved reflectivity and PL, respectively. The angle-resolved PL spectrum is in good agreement with that of the reflectivity spectrum, apart from the minor energy difference caused by the slightly change of the excitation spots. In particular, no uncoupled exciton peak located at ~ 3.045 eV is observed, suggesting the efficient coupling between the perovskite exciton and the cavity photon. Meanwhile, we can hardly observe the upper polariton branch both in angle-resolved reflectivity and PL spectra, which is a widely met issue in microcavities with large Rabi splitting energy (175). This could be explained by thermal relaxation, strong absorption in the electron-hole continuum and the high reflectivity of the top DBR. However, the features of lower polariton branch in both reflectivity and PL spectra unambiguously confirmed strong exciton-photon coupling regime. Firstly, the

curvature of polariton dispersion tends to be smaller and smaller with the increase of angles. Secondly, an inflection point can be observed near an angle $\sim \pm 50^\circ$, which is caused by the onset of an anticrossing between the Fabry-Pérot cavity mode and the perovskite exciton in strong coupling regime. We also observe a parabolic-like dispersion in the angle-resolved reflectivity spectrum, which is ascribed to the bare cavity mode without any active medium, as shown in Figure 5-6. The feature is due to the much larger white light spot compared with a smaller sample size. The theoretical fitting (dashed white lines) from a coupled harmonic oscillator model is in good agreement with that of the measured polariton dispersions in the angle-resolved reflectivity and PL spectra, as shown in Figure 5-5a and Figure 5-5b. The solid white lines show the dispersions of the uncoupled CsPbCl₃ perovskite exciton ($E_{ex} = 3.045 \text{ eV}$) and the cavity photon mode obtained from the fitting. A large Rabi splitting energy of $\sim 2\Omega = 265 \text{ meV}$ with a negative exciton-photon detuning of $\Delta = -25 \text{ meV}$ are obtained from the theoretical fitting, which corresponds to a photon fraction of 0.55 at the minimum of the lower polariton branch.

Figure 5-5. Angle-resolved reflectivity and PL mappings of a CsPbCl₃ perovskite microcavity. (a) Angle-resolved reflectivity spectrum measured using a white light lamp. The dashed white lines depict the fitting dispersions of the lower (LP) and upper (UP) polariton branches from a coupled oscillator model. The solid white lines show the dispersions of the

cavity photon mode (C) and the uncoupled CsPbCl₃ perovskite exciton (X), extracted from the coupled oscillator model fitting. Another unfitted parabolic-like dispersion corresponding to the bare microcavity mode is observed, caused by the smaller sample size compared with the white light beam diameter. **(b)** Angle-resolved PL spectrum of the CsPbCl₃ perovskite microcavity. The detuning Δ is indicated inside the figure, which is extracted from the coupled harmonic oscillator model. Note, the slight energy difference between PL and reflectivity spectrum is caused by slightly different sample positions of the excitation spot on the sample.

Figure 5-6. Angle-resolved reflectivity dispersion of the bare microcavity without any perovskite inside, showing a resonant mode from SiO₂ spacer.

5.4.2 Exciton Polariton Lasing - Negative Detuning

In order to realize polariton lasing, the perovskite microcavity is excited by a non-resonant laser with center peak at 375nm, pulse duration of 100 fs and a repetition rate of 1 kHz. The laser spot is around 25 μm in diameter. Figure 5-7 depicts the mappings of angle-resolved PL spectra under different pumping fluences, which are corresponding to a factor 0.75, 1.0 and 1.3 of the threshold fluence ($P_{th} = 12 \mu\text{J}/\text{cm}^2$, peak power density of $1.2 \times 10^8 \text{ W}/\text{cm}^2$), respectively. The lower polariton dispersion exhibits wide range emission distribution along all the angles at low pump fluence of $0.75 P_{th}$ (Figure 5-7a). While it shows much stronger emission at normal incidence when the pump fluence increases to P_{th} (Figure 5-7b), suggesting the appearance of polariton condensation. Under even higher pump fluence of $1.3 P_{th}$ (Figure

5-7c), the ground state emission at $k_{\parallel}=0$ ($E_{LP}(k_{\parallel}=0)=2.90$ eV) totally dominates the emission from all the angles. This feature is in sharp contrast with that of photonic lasing which should show major emission from the minimum of the cavity mode dispersion ($E_C(k_{\parallel}=0)=3.02$ eV) (92). The occurrence of massively occupation at the ground state of the lower polariton dispersion is one of the key features of polariton condensation and polariton lasing.

Figure 5-7. Power dependent angle-resolved PL spectrum. (a) Angle-resolved PL spectrum measured at $0.75 P_{th}$, which displays a wide range of distributions at all the emission angles. (b) Angle-resolved PL spectrum measured at $1.0 P_{th}$, which shows predominant emissions at the ground state near $k_{\parallel}=0$ of the lower polariton branch. (c) Angle-resolved PL spectrum measured at $1.3 P_{th}$. The ground state emission near $k_{\parallel}=0$ shows a dramatic intensity increase and an energy blueshift.

In order to characterize the polariton behaviours quantitatively, we plot the ground state emission behaviours at $k_{\parallel}=0$ as a function of the pump fluence in a log-log scale, as shown in

Figure 5-8. The ground state emission intensity at $k_{\parallel}=0$ exhibits a sharp increase by three orders of magnitude when the pump fluence reaches above the threshold of $P_{th}=12 \mu J / cm^2$ (peak power density of $1.2 \times 10^8 \text{ W/cm}^2$). Notably, the lasing threshold is at least five times lower than that of previous reports at room temperature in epitaxy-free microcavities (46-48). In the meantime, with the increase of the pump fluence, the FWHM of the ground emission (blue trace in Figure 5-8b) slightly broadens first below the threshold, which is due to polariton-exciton interaction (176). Then it significantly drops from 10.3 meV to 3.4 meV when the pump fluence increases to $1.5 P_{th}$, suggesting a dramatic increase of the temporal coherence. Finally, the FWHM exhibits a broadening trend again, which can be caused by decoherence induced by polariton self-interactions and the different localized condensate modes (30). The evolutions of ground state emission intensity and FWHM clearly demonstrate the onset of polariton condensation. In addition, with the increase of pump fluence, the ground state emission of the lower polariton branch at $k_{\parallel}=0$ exhibits a continuous blueshift trend. This feature is a crucial evidence to confirm the occurrence of polariton condensation, which is resulted from the repulsive interactions between polaritons. As shown in Figure 5-8c, the energy blueshift of the ground state emission at $k_{\parallel}=0$ is plotted as a function of the pump fluence. The polaritons exhibit a maximum blueshift of 10 meV within the measured pump fluence region, which is far below the energy difference of 120 meV between the dispersion minimum of the cavity mode and the lower polariton branch. Two different blueshift slopes are observed with the increase of the pump fluence, showing a transition at the threshold. This can be explained by predominant polariton-reservoir interaction below the threshold and predominant polariton-polariton interaction above the threshold. In order to gain more insights into this behaviour, we apply a model by coupling the driven-dissipative Gross-Pitaevskii equation to a rate equation for a reservoir of excitons, neglecting for simplicity spatial dependence:

$$i\hbar \frac{d\psi}{dt} = \left[E_0 + \alpha |\psi|^2 + g_R n_R + \frac{i}{2} (\hbar r n_R - \Gamma) \right] \psi$$

$$\frac{dn_R}{dt} = P - (\Gamma_R + r |\psi|^2) n_R$$

where ψ shows the coherent polariton field, coupled to an equation for the density of higher energy excitations n_R (a reservoir). E_0 is the energy of the bare polariton resonance; α represents the strength of polariton-polariton interactions; g_R is the strength of interactions between polaritons and the high energy reservoir; r is the exciton polariton condensation rate; Γ is the exciton polariton dissipation rate; Γ_R is the reservoir decay rate; and P is the pumping rate. The equations are readily solved analytically, where the condensate mean-field population $|\psi|^2$ is non-zero above the threshold pumping rate $P_0 = \frac{\Gamma \Gamma_R}{\hbar r}$. Above the threshold, the polariton energy shift with pumping rate is given by

$$\Delta E = \frac{\hbar P \alpha}{\Gamma} - \frac{\Gamma_R \alpha}{r} + \frac{g_R \Gamma}{\hbar r}$$

And below the threshold, the polariton energy shift with pumping rate is given by:

$$\Delta E = \frac{g_R P}{\Gamma_R},$$

By fitting our experimental blueshift data and taking the parameters $\frac{g_R \Gamma}{\hbar r} = 10.6 \text{ meV}$ and

$\frac{\Gamma_R \alpha}{r} = 0.86 \text{ meV}$ as the relevant fitting parameters (it is also assumed that the theoretical

pumping rate P is linearly proportional to the experimental pump power), the fitted curve is in agreement with our experimental data. The slope of the energy shift with the pumping rate has a discontinuity at the threshold, since below and above threshold the condensate and reservoir populations have different growth rates with the pumping rate. In addition, the interaction

energy associated with polariton-polariton interaction and polariton-reservoir interaction is generally different.

Figure 5-8. Characterizations of CsPbCl₃ microcavity polariton lasing. (a) Ground state emission spectra at $k_{\parallel}=0$ under different pumping fluences. A sharp increase of emission intensity occurs beyond $1.0 P_{th}$, suggesting the transition to the nonlinear regime. The emission energy is observed to be blue-shifted with the increasing pump fluence. (b) Ground state emission intensity at $k_{\parallel}=0$ and FWHM as a function of pump fluence. A linewidth narrowing occurs near the threshold of $P_{th}=12 \mu\text{J}/\text{cm}^2$ (peak power density of $1.2 \times 10^8 \text{ W}/\text{cm}^2$, along with a sharp increase of emission intensity. (c) Energy blueshift with respect to the polariton emission energy at the lowest pump fluence as a function of pump fluence. The experimental blueshift of the ground state emission is shown as blue dots and the red solid line indicates the theoretical calculation of the blueshift. The blueshift trend below the threshold is attributed to polariton - reservoir interaction while the trend above the threshold corresponds to polariton-polariton interaction.

5.4.3 Long-Range Spatial Coherence of Perovskite Polariton Condensates

Another crucial evidence to demonstrate the occurrence of polariton condensation and polariton lasing is the build-up of long-range spatial coherence. In the linear regime, polaritons are expected to have a characteristic coherence length of the order of the thermal de Broglie wavelength $\lambda_{dB} = 760$ nm. While above the threshold, the polariton condensate is expected to possess long-range spatial coherence. To further confirm the occurrence of polariton condensation unambiguously, we check the long-range spatial coherence by interferometry measurements. For this purpose, the real space emission image of the polariton condensate is sent to a Michelson interferometer in which one of the arms is replaced by a retroreflector to invert the image in a centro-symmetrical configuration, as shown in Chapter 2. The use of the retroreflector enables the measurement of the first-order spatial coherence $g^{(1)}(\mathbf{r}, -\mathbf{r})$ based on the interference fringes contrast, or in other words the phase coherence between points localized at $\mathbf{r}$ and $-\mathbf{r}$ from the center of the polariton condensate. Figures 5-9a and 5-9b display the real space emission image of the polariton condensate and its inverted image, respectively. First of all, we observe several bright spots in the real space emission image, which are associated to the localization of the polariton condensate, possibly as a result of the photonic disorder inherited from the sample transfer process during the fabrication of the perovskite microcavity. Similar phenomena have been widely observed in organic and inorganic polariton condensates before (30, 46).

Figure 5-9. Demonstration of long-range spatial coherence. (a) Real space photoluminescence image measured above threshold from one arm of the Michelson

interferometer. Dashed line, sample edges. Scale bar, 4 μm . **(b)** Real space photoluminescence image obtained above threshold from the second arm by using a retroreflector to flip the image in a centrosymmetric way. Dashed line, sample edges. Scale bar, 4 μm . **(c)** Interference pattern after superposition of the images above threshold from the two arms of the Michelson interferometer. Clear interferences are readily identified with a distance as large as 15 μm , demonstrating the build-up of long-range spatial coherence. Dashed line, sample edges. Scale bar, 4 μm .

Figure 5-9c presents the interference image resulted from the superposition of the two previous images shown in Figures 5-9a and 5-9b, where unambiguous interference fringes are readily identified along a distance as large as 15 μm . This latter result is a clear demonstration of the build-up of a long range spatial coherence associated to the formation of a polariton condensate in our all-inorganic perovskite system. Finally, we further extend the Gross-Pitaevskii theory to account for spatial dynamics in the real space. Using the dispersion obtained from the coupled oscillator fitting and including some disorder, the localization effect can be successfully reproduced, as shown in Figure 5-10. The disorder was generated from a white noise convoluted with a Gaussian function, giving a disorder profile characterized by a spatial correlation length (taken to be 1 μm) and a root mean squared amplitude (taken to be 10 meV).

Figure 5-10. (a) Theoretically simulated photoluminescence dispersion below threshold and, (b) above threshold. Note that there is a slight blueshift of the emission with respect to the

energy minimum in (a). (c) Simulated real-space distribution of polaritons in a disordered environment, showing condensation at localized points.

5.5 Perovskite Polariton Lasing - Positive Detuning

5.5.1 Exciton Polariton Dispersion - Positive Detuning

In addition, we also fabricate a CsPbCl₃ perovskite microcavity based on a slightly thinner nanoplatelet (thickness of 360 nm), leading to slightly shorter cavity length. According to the cavity resonance condition, the shorter cavity length will give rise to a larger energy for the cavity mode. As shown in Figure 5-11, the measured angle-resolved reflectivity is in good agreement with the angle-resolved PL spectrum. The angle-resolved spectrum based on this slightly thinner perovskite microcavity shows quite similar behaviors as the previous perovskite microcavity presented in the previous section, with a flatter dispersion of the lower polariton branch. In fact, when the detuning changes from negative detuning to positive detuning, the exciton fraction of the lower polariton branch increases accordingly, making the lower polariton branch more exciton-like and flatter in comparison with the perovskite microcavity with a negative detuning. The flatter dispersion of the lower polariton branch can be resolved on both sets of data; along with the bare cavity mode in the PL (the laser spot is moved closer to the nanoplatelet's edge for the PL measurements as a result of sample degradation after the pulse laser measurements). A small fraction of the dispersion of a Bragg mode (BM) is also visible at large angles ($\pm 60^\circ$). We conclude that the strong coupling regime and polariton emission are reached for different detunings in inorganic CsPbCl₃ perovskite.

Figure 5-11. Angle-resolved dispersion on a 360 nm thick perovskite microcavity. Angle-resolved reflectivity (a) and photoluminescence (b) measured below the polariton lasing threshold, at positive detuning ($\Delta = +70$ meV). The dispersions of the lower polariton (LP) and the Bragg mode (BM) are observed in reflectivity and PL, and the additional bare cavity mode (when no perovskite is embedded in the microcavity) is only observed in PL. The coupled oscillator model fits of the lower polariton (LP) and upper polariton (UP) dispersions are displayed along with the dispersions of the uncoupled exciton (X) and cavity (C) modes. The extracted Rabi splitting is 273 meV.

As shown in Figure 5-11, the coupled harmonic oscillator model fittings agree well with the experimental reflectivity and PL results. The dashed white lines show the theoretical polariton dispersions and the solid white lines are the dispersion of exciton and cavity mode. From the theoretical fittings, we extract a positive detuning of $\Delta = +70$ meV and a Rabi splitting energy of around 273 meV.

5.5.2 Transition from Strong Coupling to Weak Coupling Regime

Here, we use the same pulsed laser to pump the perovskite microcavity with a positive detuning of $\Delta = +70$ meV to reach the nonlinear regime. As one can see from the angle-resolved PL spectra in Figure 5-12a, the lower polariton branch exhibits predominant emission at $k_{\parallel} = 0$ ($E_{LP}(k_{\parallel} = 0) = 2.94$ eV) upon reaching the threshold, corresponding to the onset of polariton

lasing. When the pump fluence further increases to $1.6 P_{th}$ ($P_{th} = 55 \mu\text{J}/\text{cm}^2$, peak power density of $5.5 \times 10^8 \text{ W}/\text{cm}^2$), the ground state emission at $k_{\parallel} = 0$ totally dominates and the intensity increases by two orders of magnitude. When the pump fluence increases to $5.0 P_{th}$ (Figure 5-12c), the emission from the lower polariton branch becomes pretty weak, and a flat dispersion locating at a lower energy ($\sim 2.90 \text{ eV}$) than the minimum of the lower polariton branch ($\sim 2.95 \text{ eV}$) is observed. We attribute this additional flat dispersion to the electron-hole plasma (EHP) emission in the weak coupling regime which is accompanied by a band-gap renormalization at high pump fluence as previously observed in ZnO microcavities (177). Such transition will be discussed in detail.

Figure 5-12. Transition from strong coupling to weak coupling regime in momentum space. (a)-(c), Angle resolved photoluminescence spectrum obtained at $1.0 P_{th}$, $1.6 P_{th}$ and $5.0 P_{th}$, showing a transition from the polariton condensate regime to the weak coupling regime

with a sharp decrease of the emission intensity at the lower polariton ground state.

In addition to the emission evolution in the momentum space, we observe a very different emission diagram in the real space with the increase of the pump fluence, which further confirms the transition from strong coupling regime to weak coupling regime. As shown in Figure 5-13a, the emission of the perovskite microcavity reflects the laser spot intensity distribution at a pump fluence of $0.9 P_{th}$, whereas it shows dominant emission localized on a $4\ \mu\text{m}$ diameter spot within the laser spot diameter of about $25\ \mu\text{m}$ when the pump fluence increases to $1.6 P_{th}$. This could be caused by disorder that induces fluctuations of the polariton mode energy. Such phenomenon has been widely observed in other microcavity systems (30, 46). Below the threshold, disorders usually show little effect in the polariton distribution in real space. However, above the threshold, disorders play a strong role in shifting the polariton distributions in real space, causing the lasing to occur preferentially at localized points. When the pump fluence increases to $5.0 P_{th}$, we observe a very different emission diagram in the real space where the emission from the condensate totally disappears and the emission from the edge of the belt-like perovskite nanoplatelet becomes totally dominant and increases by thirty times. We ascribe such features as the appearance of photonic lasing at high pump fluence of $5.0 P_{th}$, in contrast to the polariton lasing at low pump fluence region, which will be confirmed by further analyses.

Figure 5-13. Transition from strong coupling to weak coupling regime in momentum space. (a)-(c), Real space images obtained at $0.9 P_{th}$, $1.6 P_{th}$ and $5.0 P_{th}$, showing a broad emission distribution below threshold, while above threshold, a localized polariton condensate shows up in the body of the platelet. By further increasing the pump fluence to $5.0 P_{th}$, the polariton condensate vanishes while a two orders of magnitude stronger emission appears at the edges of the platelet.

In order to better understand the emission properties observed under different pump fluences, we present in Figure 5-14 an analysis of the measurements shown in Figure 5-12 and Figure 5-13, in particular the power dependence of the emission intensities (Figure 5-14a), linewidths (Figure 5-14b) and peak energy positions (Figure 5-14c). We first observe, in the strong coupling regime at $P_{th} = 55 \mu\text{J}/\text{cm}^2$ (peak power density of $5.5 \times 10^8 \text{ W}/\text{cm}^2$), a transition associated with a sharp increase of the polariton emission intensity, a narrowing of the FWHM and a continuous blueshift in emission energy due to polariton-polariton interactions. This transition defines the pump threshold of the polariton laser induced by the spatially localized

polariton condensate observed in the real space image in Figure 5-13b at $1.6 P_{th}$. Then, the increase of the pump fluence well above the polariton lasing threshold, *i.e.*, above $100 \mu\text{J}/\text{cm}^2$, leads to the vanishing of the polariton condensate. A related decrease of the emission intensity at the lower polariton ground state energy and increase of the emission linewidth are observed. This decrease of the emission intensity could be explained by the change of cavity direction from vertical direction along the growth of DBR to horizontal direction along one of the perovskite nanoplatelet axis. Meanwhile, the EHP emission appears and dominates the signal above $P_{th2} = 108 \mu\text{J}/\text{cm}^2$ (peak power density of $1.08 \times 10^9 \text{ W}/\text{cm}^2$), mainly at the belt edges. The latter pump fluence defines a second threshold for the transition to the weak coupling regime in the perovskite sample. This statement is further confirmed by the continuous redshift of the EHP emission and the superlinear behavior of the EHP emission intensity above P_{th2} (Figure 5-14b and Figure 5-14c, respectively). Furthermore, we measure the real space emission spectra below and above the second threshold of P_{th2} , as shown in Figure 5-15. The perovskite microcavity exhibit quite broad and weak emission at low pump fluence of $1.6 P_{th}$. However, as a result of the nanoplatelet itself serving as a natural Fabry-Perot cavity, it shows multiple narrow and strong peaks occur at a high pump fluence of $5.0 P_{th}$, confirming the appearance of photonic lasing. This statement can be further confirmed by the equal mode spacing of 4.7 meV between two lasing peaks, as shown in Figure 5-15, which is in good agreement with a Fabry-Pérot cavity length (nanoplatelet edge length) of $48 \mu\text{m}$ and a refractive index of 2.7 . Additional precise studies of the EHP emission still need to be done to determine why it shows lasing along the nanoplatelet axis rather than along the vertical direction of perovskite microcavity.

Figure 5-14. Characterizations of the polariton lasing in a 360 nm thick perovskite microcavity. (a) Ground state emission intensity and FWHM at $k_{\parallel} = 0$ as a function of the pump fluence. A typical S shape power dependent emission relationship suggests the occurrence of polariton lasing with a first threshold P_{th} of $55 \mu\text{J}/\text{cm}^2$ (peak power density of $5.5 \times 10^8 \text{ W}/\text{cm}^2$), while the emission intensity decreases sharply crossing a pump fluence P_{th2} of $108 \mu\text{J}/\text{cm}^2$ (peak power density of $1.08 \times 10^9 \text{ W}/\text{cm}^2$). The FWHM first slightly increases (from 10.1 meV to 11.4 meV) below the threshold P_{th} and narrows from 11 meV to 3.5 meV when crossing the threshold P_{th} , and then increases until 19 meV with the further increase of the pump fluence. (b) Ground state emission peak position at $k_{\parallel} = 0$ as a function of the pump fluence. The emission peak position in the strong coupling regime shows continuous blueshift with two different slopes below P_{th2} . When crossing the second threshold P_{th2} of $108 \mu\text{J}/\text{cm}^2$ to weak coupling regime, the energy position of another arisen peak corresponding to the EHP emission shows redshift with the increase of the pump fluence. (c) Edge emission intensity as a function of the pump fluence, extracted from the real space images of the perovskite microcavity. A clear threshold P_{th2} of $108 \mu\text{J}/\text{cm}^2$ (peak power density of $1.08 \times 10^9 \text{ W}/\text{cm}^2$) was observed for

the emission in the lateral modes.

These additional results constitute a clear proof that the lasing behaviour observed in our perovskite samples corresponds to a polariton lasing effect induced by the formation of a polariton condensate, and not to the more classical photonic lasing effect observed in the weak exciton-photon coupling regime.

Figure 5-15. The real space emission spectra of the perovskite microcavity at $1.6 P_{th}$ and $5.0 P_{th}$. When the pump fluence is $1.6 P_{th}$, the perovskite microcavity exhibits quite broad and weak emission at the EHP emission energy. Multiple narrow and strong peaks with equal mode spacing show up at a pump fluence of $5.0 P_{th}$, which is corresponding to the appearance of photonic lasing.

5.6 Summary

In this chapter, we have unambiguously demonstrated the evidences of polariton lasing based on CsPbCl_3 microcavities at room temperature, including the superlinear increase of emission intensity, linewidth narrowing, continuous blueshift of emission, buildup of long-range spatial coherence and the transition from strong coupling regime to weak coupling

regime. The successful realization of polariton lasing within a low Q microcavity, along with its ease of fabrication and the inorganic nature of its active medium, significantly alleviates the stringent requirements to approach the fundamental physics of BEC. Our findings open a new platform with compelling properties toward realization of large-area, low-cost, and high-performance polariton devices and potentially toward an electrically pumped BEC coherent light source at room temperature.

Chapter 6 Room Temperature Long-Range Polariton Condensate Flow in Cesium Lead Halide Perovskites

6.1 Introduction

Novel technological applications significantly favor alternatives to electrons towards low-power consuming and high-speed devices. It is commonly acknowledged that, the charge carrier of electrons in current circuits will be replaced by photons to form photonic circuits which ideally will possess much higher operation speed and low losses. However, the nonlinearity in pure photonic devices are relatively small, leading to their operations at high powers regime.

The advance of novel integrated optoelectronic devices depends on three fundamental elements: transport, switching and logic gates (*178-181*). All of these three basic elements dramatically rely on the propagation of carriers. Exciton polaritons, which are neither pure photons or electrons, but a mixture of both, serve as such ideal carriers towards the basic elements of novel integrated optoelectronic devices. As light-matter quasiparticles, exciton polaritons combine the advantages of excitons and photons, which enable them as an intermediate bridge between electronic system and pure photonic system. Thanks to the part-light and part-matter nature, exciton polaritons inherit from their photonic components the low effective mass, thus having a much faster propagation speed than that of electrons (*182*). While the constituent excitons provide them high nonlinearity from the strong polariton-polariton interactions. Significantly, exciton polaritons are bosonic quasiparticles with low effective mass, which can allow polaritons to condense into a single quantum state, as discussed in

chapter 5. The single quantum state nature and fast propagation nature of polariton condensates provide them huge potentials for their use in all-optical integrated circuits.

In 2010, A. Amo *et al.* reported a new type of all-optical spin-selective polariton switch utilizing the propagation of exciton polariton in a GaAs quantum well microcavity (178). Generally, the polariton spin switch strongly relies on the polariton-polariton interactions which result in the blueshift of the polariton dispersions. The mechanism of such polariton switches can be described as follows. The GaAs microcavity is pumped with a continuous wave incident laser operating at low pump power. The incident laser is slightly above the polariton energy at a given in-plane wavevector and therefore polaritons are excited with this given in-plane wavevector. In this case, the polariton optical switch corresponds to the OFF state due to a low population of polaritons. When the pump power of the incident laser increases, the strong polariton-polariton interaction results in blueshift of polaritons which can bring the incident laser in resonance with polariton dispersion, thus leading to a large fraction of polariton population. This corresponds to the ON state where a strong polariton emission is observed. In addition, as polaritons are spin degenerate, they possess two possible spin projection values on the structure axis, either $S_z = -1$ or $S_z = +1$. As the polariton-polariton interaction between polaritons with same spin is much larger than that of polaritons with opposite spins, it is possible to build an all-optical spin-selective switch utilizing exciton polaritons, as shown in Figure 6-1a. To do so, the same group utilizes two external lasers where one acts as the pump beam with a spot diameter of 60 μm and another one as the probe beam with a spot diameter of 6 μm . The pump beam excites the GaAs microcavity with an incident angle in the off-state configuration while the probe beam excites a small area inside the pump beam area to bring this small local area into the ON state configuration. Due to the non-zero incident angle of both the pump and probe lasers, the polaritons inherit the in-plane wavevector from the incident lasers. Polaritons within the probe beam area at ON state could then propagate and interact

with the polaritons outside the probe beam area in order to generate significant blueshifts and lead the rest of the pump beam area into ON state. Based on the significant interaction difference between polaritons with same spins and opposite spins, the resulting all-optical polariton switch could be spin-selective by changing the circular polarizations of the pump and probe beams, as shown in Figure 6-1.

Figure 6-1. The operation of an all-optical polariton switch. (a) The polariton density exhibits a transition with the increase of the pump power. At low pump power, the system is at off-state due to the low polariton population. While at high pump power, polariton-polariton interaction gives rise to a significant blueshift which bring the polaritons in resonance with the

incident laser to generate high polariton population into on-state. **(b) and (c)** The experimental real-space images of emission under σ^+ polarization detection with σ^+ pump and σ^+ probe, respectively. **(d)** The experimental real space image when both the pump and probe with the same σ^+ polarization focus on the sample. **(e)** The experimental real space images when the pump and probe with opposite circular polarization focus on the sample. Figure is taken from Ref. (178).

In addition to the all-optical spin-selective switch based on the propagation of exciton polaritons, T Gao *et al.* also reported a new type of all-optical polariton switch based on the propagation of polariton condensate in 2012 (180). As polariton condensate is formed in a single quantum state, the unique properties of polariton condensate, such as long-range coherence, makes this new type of all-optical switch promising for further novel design towards all-optical quantum information devices. The polariton condensate switch is based on a 1D GaAs wire microcavity, where polariton condensates are guided to propagate along the long axis of the wire. The unique structure of 1D microcavity provides more freedom to be adapted into integrated circuits (179). The 1D GaAs wire microcavity is pumped by two off-resonant laser beams at normal incidence with one beam acting as the pump beam and the other one acting as the gate beam, as shown in Figure 6-2. The polariton condensates were created at the strong pump beam region and act as the sources of polaritons which are ballistically ejected to the other end of the wire microcavity. As shown in Figure 6-2b, the created polariton condensate can freely propagate along the wire. Such polariton condensate propagation could be gated and controlled by adding a weak gate beam at the propagation path of the polariton condensates. Due to the strong polariton-polariton interactions, the weak gate beam can modify the landscape and induce a barrier to block the polariton condensates along their propagation path. Intensity attenuations in transmission approaching 90% have been achieved based on such polariton condensate switches (180).

Figure 6-2. The working principle of a polariton condensate switch. (a) The polariton condensate can freely propagate to the wire end. **(b)** The polariton condensate is blocked by a barrier caused by the gate beam. Figure is taken from Ref. (180).

As one can see, polariton propagation plays an important role in the basic elements of all-optical polariton devices. Long-range polariton propagation is highly demanded for linking multiple polariton devices. Generally, if polaritons could propagate faster and farther, more cascability and higher operation speed could be achieved for the all-optical integrated circuits. In this case, it is desirable to have a system which can support higher speed and longer distance polariton propagation, especially polariton condensate propagation showing long-range coherence.

In 2010, E. Wertz *et al.* reported extremely long-range flow of polariton condensates in a 1D GaAs microwire microcavity (183). The polariton condensate can propagate up to 200 μm without losing its intrinsic coherence, which can be attributed to the long polariton lifetime of 15 ps. In addition, the polariton condensate propagation direction can be easily controlled in such a 1D microcavity by adjusting the excitation spot and collection spot, as shown in Figure 6-3. However, the majority of works on polariton condensate flow are still based on GaAs microcavity. Limited by the small exciton binding energy (~ 5 meV), the GaAs system can only operate at liquid helium temperatures which largely hinders the potential implementations

of polariton condensate flow into all-optical polariton devices. Meanwhile, the propagation speed in GaAs systems is only around $2.5 \mu\text{m}/\text{ps}$. More recently, room temperature polariton condensate superfluidity have been observed in an organic microcavity along with the flow of polariton condensate (42). Despite the high group velocity of organic polaritons, only short-range coherent polariton condensate flow limited within $10 \mu\text{m}$ has been observed in organic microcavities due to the strong disordered environment and short polariton lifetime (117). For the advance of all-optical integrated circuits, it is highly desirable to find a system which can support long-range polariton condensate flow at room temperature. In this chapter, I will demonstrate that such long-range and fast polariton condensate flow can be realized in all-inorganic perovskite microcavity at room temperature.

Figure 6-3. Polariton condensation in microwires. (a) and (c) Momentum space spectra above the condensation threshold of polaritons located at different sides $30 \mu\text{m}$ away from the pump spot. (b) Momentum space spectra of polaritons at the pump spot. Figure is taken from Ref. (183).

6.2 Mechanism of Polariton Condensate Propagation

Upon reaching the threshold, polaritons can massively occupy the ground state of the lower polariton branch to form polariton condensates. In this case, the polariton condensate

should occupy the minimum of the lower polariton branch and possess zero in-plane momentum. To propagate, the polariton condensates must achieve a non-zero in-plane momentum, the latter being related to the pump spot size. In 2008, M. Wouters *et al.* developed a theoretical model to describe the dynamics of polariton condensates under different pump spot sizes (184). Generally, with a large pump spot, polariton condensation takes place near $k_{\parallel} = 0$ of the lower polariton branch. Due to the polariton-polariton repulsive interactions, an anti-trapping potential is created by ballistically accelerating polaritons away from the center. Thus, as shown in Figure 6-4a, polariton condensates usually distribute along a region of $k_{\parallel} < k_c$ (k_c is a non-zero in-plane wavevector), thus inducing a condensate momentum broadening. This is in sharp contrast with that of equilibrium polariton condensates which have an in-plane wavevector at $k_{\parallel} = 0$. In addition to the anti-trapping potential which induces the momentum broadening of the polariton condensate wavevector, disorders in microcavity can also lead to significant modulation of the polariton condensates wavevector, which can lead to a non-zero wavevector distribution (184).

When the pump spot size is much smaller than the characteristic propagation length of polaritons, a strong blueshift of polariton energy is created by strong polariton-polariton interaction which is limited inside the pump spot. Such strong local blueshift creates a force to expel polariton condensates, which will experience a lateral acceleration and gain a finite in-plane wavevector to propagate outside the pump spot. In this case, the momentum space emission of polaritons above the threshold concentrates on a ring with radius k_c while polaritons inside the pump spot contribute to the weak emissions at $k_{\parallel} < k_c$. Almost no emission can be observed for $k_{\parallel} > k_c$. Consequently, the k space spectra as a function of polariton energy is dominated by the emission from polaritons with in-plane wavevector of k_c , as shown in Figure 6-4b.

Figure 6-4. Simulations of polariton condensation under different pump spot sizes. (a, c) The simulated k-space polariton condensation spectrum for a large pump spot and small pump spot, respectively. (b, d) The polariton population as a function of the in-plane wavevector for a large pump spot and a small pump spot, respectively. Figure is taken from Ref. (184).

6.3 Fabrication of the Microwire Microcavity

We use an e-beam evaporator to fabricate the bottom DBR, which consists of 20.5 pairs of tantalum pentoxide (60.2 nm) and silicon dioxide (87.5 nm), as shown in Figure 6-5a. A thin layer of SiO_2 (65 nm) is deposited onto the bottom DBR acting as the spacer. The active medium CsPbBr_3 microwire is synthesized on a mica substrate and is then transferred onto the bottom DBR through a dry transfer technique, as discussed in Chapter 3. After the CsPbBr_3 microwire is transferred onto the bottom DBR, a thin layer of PMMA (55 nm) is spin-coated to protect the perovskite. The bottom DBR with perovskite microwires is then sent into the e-beam evaporator again to deposit the top DBR, which consists of 8.5 pairs of tantalum

pentoxide (60.2 nm) and silicon dioxide (87.5 nm). Similarly, as perovskite microwires possess different thicknesses on mica substrate, 1D CsPbBr₃ microwire microcavity could be obtained with different cavity lengths, thus showing different detunings.

6.4 Characterization of the CsPbBr₃ Perovskite Microwire Microcavity

Unlike previous inorganic systems such as GaAs and CdTe which significantly rely on cutting-edge epitaxial techniques, the CsPbBr₃ microwire we use here is grown by an epitaxy-free chemical vapor deposition method, which has been discussed in Chapter 3. As shown in Figure 6-5b, the effective perovskite microcavity retains the rectangular shape of the CsPbBr₃ microwire with length of $\sim 30\ \mu\text{m}$ and width of $\sim 2\ \mu\text{m}$. The thickness of the perovskite microwire is around $\sim 120\ \text{nm}$. After the whole fabrication process, the perovskite microcavity still exhibits bright green emission under fluorescence microscopy as shown in Figure 6-5c. The realization of polariton devices at room temperature significantly demands stable excitons against thermal fluctuation. Previous studies have shown that CsPbBr₃ possesses stable excitons with a large exciton binding energy of 40 meV (69), as confirmed by the room temperature absorption spectrum of CsPbBr₃ shown in Figure 6-5d. The absorption spectrum of CsPbBr₃ thin film on mica substrate (red trace) shows a strong exciton absorption peak at $\sim 2.406\ \text{eV}$ while room temperature PL spectrum (blue trace) of CsPbBr₃ exhibits a peak at $\sim 2.353\ \text{eV}$ with a FWHM of 60 meV. After the CsPbBr₃ microwire is integrated into the microcavity, the emission (olive trace) from normal incidence (corresponding to in-plane wave number $k_{\parallel}=0$) shifts to 2.297 eV and the FWHM significantly narrows to 2.0 meV corresponding to a high quality factor of ~ 1150 (Figure 6-5d and Figure 6-5e). The high quality factor suggests that perovskite excitons are well-confined in the microcavity, which is crucial towards strong coupling between excitons and cavity photons.

Figure 6-5. (a) The schematic of the CsPbBr₃ microwire microcavity structure, showing x, y, and z axes. (b) and (c) The microscope and fluorescence images of CsPbBr₃ microwire microcavity after the fabrication process. The scale bar is 5 μm . (d) Room-temperature absorption and PL spectra of the CsPbBr₃ perovskite. Red trace shows the absorption spectrum of the CsPbBr₃ perovskite on mica substrate with have a strong exciton absorption peak at ~2.406 eV. Blue trace displays the PL emission spectrum of the CsPbBr₃ perovskite on mica substrate with a peak at ~2.353 eV and a FWHM of 60 meV. Olive trace presents the ground-state emission of the CsPbBr₃ microwire embedded into the microcavity, which shows a peak at ~2.297 eV with a FWHM of ~2.0 meV. (e) The measured emission from normal incidence fitted by a Gaussian function, showing a FWHM of 2.0 meV corresponding to a Q factor of ~1150.

6.5 Polariton Condensation in a CsPbBr₃ Microwire Microcavity

6.5.1 Polariton Dispersion

We then investigate the polariton behaviour in the CsPbBr₃ microwire microcavity by angle-resolved PL spectroscopy at room temperature. In conventional 2D microcavities, the confinement is only along the z axis of the microcavity leading to the wavevector quantization: $k_z = \pi/L_c$, where L_c is the effective cavity length. While in 1D microcavities, the additional lateral confinement along y direction introduces an additional quantization: $k_{y,j} = (j+1)\pi/L_y$, where L_y is the effective lateral length along the width direction (y axis) and j is a new quantization number, $j = 0, 1, 2, \dots$, giving rise to multiple photonic branches which can couple to the exciton state. The relationship between the energy and the wavevector of the cavity modes along the length of the wire (x axis) can be expressed as (93):

$$E_{1D}^c(j, k_x) = E_0 \sqrt{1 + \left[\frac{(j+1)\pi}{L_y} \right]^2 \frac{1}{k_z^2} + \left(\frac{k_x}{k_z} \right)^2}$$

where $E_0 = \hbar c k_z / n_c$. While along the y axis, the energy of each cavity mode is constant but shows electric-field distribution under different k_y . In such case, the resulting polariton dispersion exhibits multiple continuous branches along the x axis, while showing multiple discrete states along the y axis. As shown in Figure 6-6b, the measured polariton dispersion mapping shows continuous distribution along with the emission angle (with one-to-one mapping to the wavevector $k_{\parallel}$) when the long axis x of the CsPbBr₃ microwire is set in parallel to the entrance slit of the spectrometer (Figure 6-6a). Two lower polariton branches are observed in the polariton dispersion mapping, resulting from the strong coupling between the perovskite exciton and the 1D photonic branches of the 1D microcavity. As in inorganic microcavities with large Rabi splitting energy (43, 44, 103, 185-187), the upper polariton

branch cannot be identified and to better evidence the strong coupling in the microwire, a measurement is performed with a microscope objective of larger numerical aperture in order to detect larger emission angles. The curvature of the measured dispersion of the lower polariton branch then clearly shows an *S* shape and a decreasing curvature with the increase of angles (Figure 6-7), unambiguously demonstrating the strong coupling regime. The dashed curves in Figure 6-6b correspond to the theoretical polariton dispersion calculated by the coupled oscillator model while the solid white lines correspond to the uncoupled exciton energy (X) and cavity modes (C), respectively. As shown in Figure 6-6b, the theoretical fitting gives a large Rabi splitting energy of $2\Omega = 120$ meV with a negative detuning of -80 meV and a negative detuning of -40 meV for the two coupled cavity modes, respectively. The dispersions are also theoretically well-matched by assuming particle-in-a-box type wavefunctions and energies for photons confined by the width of the microwire, being coupled to excitons with negligible dispersion as shown in Figure 6-6c. Figure 6-6e displays the measured polariton dispersion when the short axis *y* of the CsPbBr₃ microwire is set in parallel to the entrance slit of the spectrometer (Figure 6-6d). It shows some discrete polariton states which is due to the electric field distribution of cavity mode induced by the optical confinement from the small width of the CsPbBr₃ microwire as discussed before. Similarly, the polariton discrete states can be well reproduced in theory as shown in Figure 6-6f.

Figure 6-6. Angle-resolved photoluminescence mappings of the CsPbBr₃ perovskite microwire microcavity. (a) The long axis of the CsPbBr₃ microwire is set in parallel to the entrance slit (red arrow). (b) The measured polariton emission dispersion when the long axis x is in parallel to the entrance slit of the spectrometer. The dashed white lines represent the theoretical fitting dispersion of the lower (LP) and upper (UP) polariton branches. The solid white lines are the dispersions of cavity photon mode (C) and uncoupled CsPbBr₃ perovskite exciton (X) obtained from the two-coupled harmonic oscillator model fitting. (c) The theoretically calculated polariton dispersion when the long axis x is parallel to the entrance slit of the spectrometer. (d) The short axis y of the CsPbBr₃ microwire is in parallel to the entrance slit (red arrow). (e) The measured polariton dispersion when the short axis y is parallel to the entrance slit, showing multiple discrete states. (f) The theoretically calculated polariton dispersion when the short axis y is parallel to the entrance slit.

Figure 6-7. Evidence of the strong coupling regime in the perovskite microcavity operating. The polariton dispersion with emission angle up to 64° is shown, when the long axis of the microwire is parallel to the entrance slit.

6.5.2 Polariton Condensation in a CsPbBr₃ Microwire Microcavity

The perovskite microwire microcavity is further pumped by a pulsed Ti: Sapphire laser at 400 nm and 1 kHz repetition rate to reach the nonlinear regime. As shown in Figure 6-8a, the lower polariton branches are observed with a broad distribution over a wide range of angles at low pump power density of $0.75 P_{th}$ ($P_{th} = 0.8 \mu\text{J}/\text{cm}^2$, peak power density of $8.0 \times 10^6 \text{ W}/\text{cm}^2$). Compared to the theoretically calculated lower polariton dispersion (the white dashed line in Figure 6-8a) under low pump power density, a clear blueshift trend of the polariton energy is observed, which is due to the enhanced polariton–reservoir interaction with the increase of polariton density below the threshold. With the increase of pump power density to $1.3 P_{th}$, the polariton dispersion is dominated by much stronger symmetric emissions at around $\pm 20^\circ$, which suggests the onset of polariton condensation. The polariton condensate at non-zero $k_{||}$ have been reported in GaAs microcavities (183, 188). The repulsive interaction causes a strong blueshift in energy of the polariton condensate which is limited inside the excitation spot. This strong local blueshift creates a force to expel polariton condensate, which

experiences a lateral acceleration and gains a finite in-plane wavevector to propagate outside the excitation spot.

Figure 6-8. Characterization of polariton condensation at room temperature. (a) The polariton dispersion at $0.75 P_{th}$, showing a broad emission distribution at all the angles. (b) The polariton dispersion at $1.30 P_{th}$ showing symmetric dominant emission at around $\pm 20^\circ$. The polariton condensation with non-zero $k_{||}$ inclines the role of polariton propagation. (c) The simulated polariton dispersion mapping at $1.3 P_{th}$. (d) The evolution of emission intensity and linewidth as a function of pumping fluence. (e) The power dependent energy blueshift with respect to the polariton energy at the lowest pump fluence. (f) and (g) Real space image and its inverted image of the perovskite microwire microcavity at $1.3 P_{th}$. The scale bar is $4 \mu m$. (h) The superposition of the real space image and its inverted image of the perovskite microwire microcavity at $1.3 P_{th}$. Clear interferences can be observed within a distance of $25 \mu m$, confirming the build-up of the long-range spatial coherence.

In order to describe the nonequilibrium polariton condensation in our system, we apply a similar model to our previous work in chapter 5, which was originally motivated by M. Wouters *et al.* (184). The model is to account for the pulsed excitation used in the present

experiment, which is based on the coherent polariton field ψ , coupled to a density of higher energy excitations n_R (a reservoir) (103):

$$i\hbar \frac{d\psi(x,t)}{dt} = (E_0 + \alpha |\psi(x,t)|^2 + g_R(n_R(x,t) + n_I(x,t)) + \frac{i}{2}(\hbar n_R(x,t) - \Gamma))\psi(x,t)$$

$$\frac{dn_R(x,t)}{dt} = P(x,t) - (\Gamma_R + r|\psi(x,t)|^2)n_R(x,t)$$

α represents the polariton-polariton interaction strength; E_0 represents the energy of the bare polariton resonance; g_R illustrates the strength of interactions between polaritons and higher energy reservoirs of excited states (excitons or electron-hole pairs); r represents the polariton condensation rate; Γ_R is the reservoir decay rate; Γ represents the polariton dissipation rate; and P represents the pumping rate. In previous works, it has been shown that under pulsed excitation it is often relevant to account separately for the dynamics of higher energy excitations not coupled to the polariton field that can nevertheless introduce a blueshift. This inactive reservoir, n_I , decays slower than the active reservoir n_R , as it does not experience depletion through coupling to the polaritons. Treating $P(x,t)$ as an instantaneous pulse, which is valid when its duration is shorter than the polariton lifetime, we assume that $n_R(x,0) = P(x,0)$ initially and that $n_I = b_I P(x,0)$ throughout the polariton lifetime, where b_I is a constant.

As one can see in Figure 6-8c, the polariton condensation behaviour can be well reproduced in theory. Further analysis of polariton propagation will be discussed later. To investigate the onset of polariton condensation in detail, we plot the polariton emission intensity and linewidth as a function of pump fluence in Figure 6-8d, an increase by two orders of magnitude of the emission intensity and a rapid decrease of the emission linewidth are observed when the pump fluence crosses the threshold of $P_{th} = 0.8 \mu\text{J}/\text{cm}^2$ (peak power density of $8.0 \times 10^6 \text{ W}/\text{cm}^2$). Another important feature to demonstrate polariton condensation is the

continuous blueshift with the raising of pump power as shown in Figure 6-8e. Two different blueshift slopes are observed corresponding to polariton-reservoir interaction and polariton-polariton interaction, which is similar to the CsPbCl₃ microcavity as discussed in Chapter 5. We observe a maximum blueshift of 11 meV which is two times smaller than the energy difference between the cavity mode and the polariton dispersion (~ 30 meV). To unambiguously demonstrate the appearance of polariton condensation, we further check the spatial coherence of the emission above the threshold by interferometry measurements. We send the real space emission of the polariton condensate to a Michelson interferometer with a retroreflector configuration (30). The first-order spatial coherence $g^{(1)}(\mathbf{r}, -\mathbf{r})$ can be probed by the interference fringes' contrast between points located at $\mathbf{r}$ and $-\mathbf{r}$. Figure 6-8f and Figure 6-8g display the polariton condensate emission image and its inverted image, respectively. Clear interference fringes can be readily identified with a distance of 25 μm as shown in Figure 6-8h, which suggests the build-up of long-range diagonal order.

6.6 Polariton Condensate Flow in a CsPbBr₃ Microwire Microcavity

Further investigations on the propagation of the polariton condensate are conducted by pumping a small area (3 μm^2) at the end of the microwire microcavity (red dash circle) as shown in Figure 6-9a. The polariton condensates are created in the pump spot area and the blueshift potential expels the condensate to propagate to the other end of the microwire. Polariton condensates can further get reflected and propagate back from the other end of microwire to interfere with the incoming polariton condensates from the pumping spot area. It gives rise to a clear interference pattern throughout the whole wire, as shown in Figure 6-9b, and confirms that at least some polaritons have propagated approximately 60 μm . Additional

evidences of clear interference fringes can also be observed when the pumping spot is located at the center of the microwire, as shown in Figure 6-9c.

Figure 6-9. Real space image of the perovskite microcavity above the threshold. (a) Schematic of the pumping spot (blue) and collection spot (red) on the microwire microcavity. **(b)** The measured real space image of the microwire microcavity when the pump spot locates at the right end of the wire. **(c)** The measured real space image of the microwire microcavity when the pump spot locates at the middle of the wire.

To further confirm that the obtained interference pattern results from the propagation of polariton condensate, we carry out the Michelson interferometry with a retroreflector configuration. As shown in Figure 6-10, when the real space image of the polariton condensates above the threshold and its inverted image are superposed, clear interference fringes can be identified at the end of the wire which confirms that the spatial coherence is still preserved during the propagation process from one end of the wire to the other end. Furthermore, we check the polariton dispersion in the k space to confirm the propagation of polariton condensate, as shown in Figure 6-11. The far-field emission spectrum measured at 20 μm (red circle in Figure 6-9) away from the pumping spot exhibits nonsymmetric behaviour with main emission angle at -15° (in equivalent to wavevector $k_{||}$) which can be explained by the dominant polariton

propagation direction to the other end of the wire. With a well-defined incident in-plane wavevector, condensed polaritons can thus propagate outside the pumping area along the wire. The far-field emission spectrum matches well with the theory as shown in Figure 6-11b. The broadening of the measured polariton dispersion could be attributed to disorders in our perovskite microcavity. Similarly, the in-plane wavevector of the propagating polaritons can be well controlled by changing the pumping spot position to the other end (opposite to the blue circle in Figure 6-9a). Consequently, as shown in Figure 6-11c, the far field emission shows an opposite behaviour in wavevector compared with that of in Figure 6-11b.

Figure 6-10. Long-range spatial coherence of propagating polariton condensate. The pump spot (small area of $3 \mu\text{m}^2$) was moved to the end of the CsPbBr₃ microwire.

Figure 6-11. Polariton condensate propagation at room temperature. (a) and (b) The measured and simulated polariton emission mappings as a function of emission angle respectively when the pump spot locates at the right end of the perovskite wire, showing dominant emission at $\sim -15^\circ$. (c) The measured polariton emission mappings as a function of emission angle respectively when the pump spot locates at the left end of the perovskite wire, showing dominant emission at $\sim 15^\circ$.

To model the spatial dynamics of polaritons above threshold, we directly solve the two equations in the model as shown in section 6.5, first considering the case of pulsed excitation near the microwire end. The observation of interference fringes depends on the chosen polariton decay rate in the calculation. The group velocity of polaritons can be obtained from the polariton dispersion according to

$$V_g = \frac{1}{\hbar} \frac{\partial E}{\partial k_{\parallel}}$$

We can deduce that the polariton condensate group velocity is around $10 \mu\text{m}/\text{ps}$. Consequently, to traverse the length of the wire ($30 \mu\text{m}$) and return to cause interference after being reflected a polariton needs to survive for a period of the order of 5 ps or more (depending on where along the microwire we are looking for interference fringes). This corresponds to a decay rate of around 0.15 meV . In practice not all polaritons need to survive to observe clear interference fringes so the experiment can be matched considering slightly higher decay rates, as shown in Figure 6-12. Estimating that the polariton decay rate is around 0.2 meV upon comparison with experiment, we obtain a real polariton lifetime of 3 ps which is much larger than that of other microcavities working at room temperature (42). Detailed comparison between perovskite polariton condensates and other semiconductor polariton condensates are shown in Table 6-1, where most of the systems only can operate at low temperatures.

Figure 6-12. Theoretically calculated time integrated intensity pattern of polaritons generated by pulsed excitation at one end of the microwire. The different plots consider different polariton decay rates. The decay rate must be small enough for a significant fraction of polaritons to traverse the microwire and be reflected for interference fringes to appear as clearly as in the experiment. Parameters: $\hbar r = 0.02 \mu\text{eV}$, $g_R = 0.082 \mu\text{eV } \mu\text{m}^2$, $\alpha = 0.5 g_R$; the pump spot was taken as a Gaussian with widths $2 \mu\text{m}$ and $1.5 \mu\text{m}$ along and perpendicular to the microwire axis, respectively.

Table 4-1. Detailed comparison between perovskite polariton condensate and other semiconductor polariton condensates.

	Distance	Lifetime	Group Vel.	Temp.	Reference
Polariton Microwires (GaAs)	200 μm	30 ps	2 $\mu\text{m}/\text{ps}$	10 K	Ref (183)
Condensate Transistor (GaAs)	60 μm	18 ps	2.5 $\mu\text{m}/\text{ps}$	40 K	Ref (180)
Long Lifetime Polaritons (GaAs)	100 μm	100 ps	?	7 K	Ref (189)
Polariton Superfluid (organic)	<10 μm	0.1 ps	19 $\mu\text{m}/\text{ps}$	Room Temperature	Ref (42)
Superluminal X-waves (GaAs)	40 μm	10 ps	1.2 $\mu\text{m}/\text{ps}$	10 K	Ref (190)
Perovskite Polaritons	60 μm	3 ps	10 $\mu\text{m}/\text{ps}$	Room Temperature	This work

6.7 Summary

In conclusion, we have successfully fabricated a 1D CsPbBr₃ perovskite microwire microcavity by e-beam evaporation. The length of this perovskite microwire microcavity is 30 μm while the length is around 2 μm . This CsPbBr₃ perovskite microwire microcavity exhibits excellent green emission and operates in strong coupling regime, confirmed by angle-resolved PL spectroscopy. Due to the small width of the microwire, lateral confinement is induced to give rise to multiple photonic modes. As a result, the perovskite microcavity exhibits two lower polariton branches, which is due to strong coupling between perovskite exciton and multiple photonic modes. This lateral confinement is further confirmed by angle-resolved PL spectroscopy when placing the short axis of the perovskite microwire in parallel with the entrance slit of the spectrometer, which exhibits multiple discrete states as a result of the electric field distribution of the multiple photonic modes. By fitting our experimental data with a coupled harmonic oscillator model, we obtain a large Rabi splitting energy of ~ 120 meV.

By pumping our one-dimensional perovskite microcavity with a pulsed laser, polariton condensation in green region can be achieved, which is distinct from previous inorganic semiconductors in the deep blue region. The occurrence of polariton condensate is unambiguously evidenced by a superlinear power dependence, blueshift of the ground-state emission, narrowing of the line width and the build-up of long-range spatial coherence. In addition, unlike conventional polariton condensation which massively occupies the ground state of lower polariton branch, we observe the polariton condensate at high state of the lower polariton branch because of the propagation of the polariton condensate. Furthermore, by pumping the end of the perovskite microwire, clear interference fringes can be observed throughout the whole perovskite microwire body, which suggests the long-range polariton condensate flow of 60 μm at room temperature. Known that the group velocity of perovskite polaritons is around 10 $\mu\text{m}/\text{ps}$ from the polariton dispersion, we estimate a long polariton lifetime of 3.0 ps from theoretical calculations.

Chapter 7 Conclusion and Future Work

7.1 Conclusion

In this dissertation, my work starts from the synthesis of all-inorganic cesium lead halide perovskites with high quality, which lays the foundation for the later researches in tailoring the emission into different light matter coupling regimes. At the early stage of my PhD in 2014, despite the successful growth of all-inorganic cesium lead halide perovskite nanocrystals, significant challenges still remained in synthesizing all-inorganic cesium lead halide perovskite with excellent crystallinity, including nanostructures and large films. To overcome the sample growth challenge became one of our motivations in this dissertation. As shown in chapter 3, we indeed can solve the challenge and synthesize all-inorganic cesium lead halide perovskites with high quality. All-inorganic cesium lead halide perovskite square nanoplatelets and large films can be synthesized in a home-built CVD system by a vapor phase synthesis method. The nanoplatelets usually possess thicknesses ranging from 50 nm to several μm and lateral dimension ranging from 3 to tens of μm . While the lateral dimension of perovskite films can be as large as centimeter scale. The synthesis is based on a van der Waals epitaxy technique which greatly relieves the stringent requirement of lattice matching, thus leading to high quality perovskite crystals. Furthermore, the measured XRD diffraction patterns of the cesium lead halide perovskites exhibit extremely narrow linewidth of 0.1° , which further confirms the excellent crystallinity.

By changing the halide composition, the emission of cesium lead halide perovskites can be continuously tuned from 1.77 eV to 3.0 eV, covering the whole visible range. The absorption spectra of most of the cesium lead halide perovskites exhibit strong exciton absorption peak at room temperature, which suggests the large exciton binding energy. Temperature-dependent absorption spectroscopy is conducted on CsPbBr_3 and CsPbCl_3 perovskites. Large exciton

binding energies of ~ 40 meV and 72 meV can be extracted from the temperature-dependent exciton absorption peak linewidth analysis. This conclusion is further confirmed by the absorption spectra of CsPbBr₃ and CsPbCl₃ perovskites at 12 K, which exhibit two orders of Rydberg excitons. The large exciton binding energy makes cesium lead halide perovskites as promising candidates towards investigating strong light matter interaction physics and potential room temperature applications, which are the basis of the following work in this dissertation on exciton polaritons.

In Chapter 4, the as-synthesized cesium lead halide perovskite nanoplatelets exhibit square or rectangular shapes with sharp edges, which naturally forms whispering gallery microcavities. For example, CsPbBr₃ nanoplatelets exhibit strong WGM lasing emission with low threshold of $2.0 \mu\text{J}/\text{cm}^2$ (peak power density of $2.0 \times 10^7 \text{ W}/\text{cm}^2$) and high quality factor of ~ 3600 . The WGM lasing origin is confirmed by the relationship between the lasing mode spacing and the inverse of the edge lengths, as well as by the real space lasing emission image which exhibits strong lasing emission at the four corners of the nanoplatelet. Multicolor lasing actions can also be realized by composition engineering in cesium lead halide perovskite crystals, showing low thresholds ranging from $2.2 \mu\text{J}/\text{cm}^2$ (peak power density of $2.2 \times 10^7 \text{ W}/\text{cm}^2$) to $10.0 \mu\text{J}/\text{cm}^2$ (peak power density of $1.0 \times 10^8 \text{ W}/\text{cm}^2$) and maximum quality factor over 4800. The obtained high quality lasing are believed to be promoted by the naturally formed high quality WGM resonator and the highly luminescent all-inorganic cesium lead halide perovskite active mediums with stable excitons of large exciton binding energy.

Possessing such large exciton binding energy, all-inorganic perovskites are ideal candidates towards strong light-matter interaction regime. By embedding the all-inorganic cesium lead chloride perovskites into 2D planar microcavities with two highly reflective DBRs, strong coupling regime is realized at room temperature, which is confirmed by the polariton dispersions. A large Rabi splitting energy of ~ 270 meV is extracted from the polariton

dispersions. Under a pulsed laser excitation, polariton condensation and lasing is achieved in the CsPbCl₃ microcavity upon reaching a threshold of $\sim 12 \mu\text{J}/\text{cm}^2$ (peak power density of $1.2 \times 10^8 \text{ W}/\text{cm}^2$). This conclusion is further strengthened by a superlinear power dependence, macroscopic ground-state occupation, the FWHM narrowing, blueshift of the ground-state emission and the build-up of long-range spatial coherence. In addition, another crucial evidence for the polariton condensation and lasing is the observation of transition from strong coupling regime to weak coupling regime. In a CsPbCl₃ microcavity with a positive detuning, with the increase of pump fluence, the microcavity firstly exhibits polariton condensation, followed by the vanishing of the polariton condensate and the appearance of an electron hole-plasma emission at lower energy. In addition, the red shifting trend of the lower energy emission further confirms the electron-hole plasma nature. These combined evidences unambiguously demonstrate the realization of polariton lasing in the CsPbCl₃ microcavity at room temperature. With the ease of fabrication and good performance, perovskite microcavities will play important roles to compensate traditional III/V systems towards room temperature polaritonic applications.

With the ease of bandgap engineering, we are able to tune the emission of microcavity by composition modulation of the perovskite. In chapter 6, 1D CsPbBr₃ microcavities with green emission are successfully fabricated. The 1D CsPbBr₃ microcavity is also confirmed to operate in the strong coupling regime. Owing to the unique 1D structure, two lower polariton branches are observed. Under the pulsed laser excitation, the 1D CsPbBr₃ microcavity exhibits low threshold of $0.8 \mu\text{J}/\text{cm}^2$ (peak power density of $8 \times 10^6 \text{ W}/\text{cm}^2$) for polariton condensation. The momentum space dispersion above the threshold clearly shows polariton condensation with non-zero in-plane wavevector, which indicates the propagation of polariton condensate. By pumping one of the end of the perovskite wire, clear interference fringes can be observed through the whole wire body, which further confirms the long-range flow of polariton

condensate up to 60 μm without losing the coherence. By modelling the polariton condensation dynamics, a long lifetime of ~ 3.0 ps can be extracted. Our results suggest considerable promise for perovskite microcavity towards the real implementation into all-optical polaritonic circuits.

7.2 Outlook for Future Works

7.2.1 Electrically Pumped Polariton Emission and Lasing based on Perovskite Microcavity

Although optically pumped polariton emission and polariton lasing have been reported in many different systems, electrically pumped polariton emission and lasing at room temperature is still a big challenge to overcome, as the current schemes mainly rely on III-V systems which demand cutting edge epitaxy techniques. C. Schneider *et al.* reported the room temperature realization of polariton lasing in a GaAs system which is fabricated by molecular beam epitaxy (50). After that, P. Bhattacharya *et al.* reported the room temperature realization of polariton lasing in a GaN microcavity which is also fabricated by molecular beam epitaxy (191). Further advance on electrically pump polariton lasing significantly demands ease of fabrication and high performance. Perovskite materials are such promising candidates to realize this objective. Given the success of light emitting diodes in perovskite materials with efficiency exceeding 12% (56), as well as the successful realization of optically pumped polariton lasing at room temperature, lead halide perovskites can hopefully play important roles in the electrically pumped polariton lasing. Further efforts are required to find a way to combine the light emitting diode structure with microcavities and improve the emitting efficiency.

7.2.2 Realization of Room Temperature All-Optical Polariton Switches

Novel technologies significantly favour all-optical operation over electrical operation owing to the much higher operating speed. Polaritons are such promising carriers towards all-optical integrated circuits. Due to the polariton-polariton interaction, polaritons will exhibit blueshift behaviour which is the basic mechanism for polariton switches. Early works on polariton switches stem from GaAs system. A. Amo *et al.* reported an all-optical spin-selective polariton switch operated at liquid helium temperature, which is based on the propagation of polaritons (178). Owing to the significant interaction difference between polaritons with same spins and opposite spins, the polariton switch could be spin-selective. After that, T. Gao *et al.* reported a polariton condensate switch at liquid helium temperature based on the propagation of polariton condensate (180). In 2013, D. Ballarini *et al.* reported a polariton transistor in GaAs system at liquid helium temperature (181). Logic gates were also realized by utilizing the polariton transistor. However, future advances still demand devices operating at room temperature and with high performance. As shown in this dissertation, excellent polariton propagation behaviour can be realized in perovskite microcavities at room temperature. Thus, we believe that perovskite microcavities are excellent candidates to realize polariton switch and logic gates at room temperature.

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3. J. Wang[#], **R. Su**[#], J. Xing, D. Bao, C. Diederichs, S. Liu, T. C. H. Liew, Z.H. Chen, Q.H. Xiong. “Room Temperature Strong Coupling in Two-dimensional Organic-Inorganic Perovskite”. *ACS Nano*, 12, 8, 8382-8389 (2018) (# equal contribution)
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