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**CONTINUOUS-WAVE LASING FROM PEROVSKITES
EMBEDDED MICROCAVITIES**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2021

CONTINUOUS-WAVE LASING FROM PEROVSKITES EMBEDDED MICROCAVITIES

ZHANG HONGBO

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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

2021

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Abstract

The emerging lead halide perovskite materials with a basic form of ABX_3 have aroused enormous interest due to their underlying rich physics and promising applications in optics, electronics, and optoelectronics. In particular, triggered by the unprecedented success in photovoltaics, lead halide perovskites have attracted more and more attention because of their superior properties such as a direct-band gap, strong excitonic effects, high quantum efficiency, and broadly tunable emission wavelengths. Besides, the facile solution processability and defect tolerance of metal halide perovskites guarantee low-cost light-emitting devices. In the past few years, significant efforts have been made to achieve lasing emission of metal halide perovskites under pulsed pumping. However, the study of continuous-wave (CW) perovskite laser, which is regarded as a significant milestone towards the electrically pumped laser, is still at the early stage. Thus, further optimization of light-emitting materials and optical confinement is highly demanded to advance the development of CW pumped perovskite lasers. In this thesis, I mainly focus on the preparation of high-quality lead halide perovskites and the systematic investigation of CW lasing from both organic and inorganic perovskites embedded in microcavities.

The high-quality single-crystalline methylammonium lead bromide ($MAPbBr_3$) nanoplates were grown by a facile two-step solution method, with the aim of the development of the efficient CW pumped laser. The phase transition from the cubic to tetragonal to orthorhombic phase have been recorded by *in-situ* temperature-dependent Raman spectroscopy, and the pronounced PL enhancement was observed at 80 K. Furthermore, the representative free exciton emission with an inhomogeneous broadening of 3.94 meV and the binding energy of 21.1 meV have been demonstrated by *in-situ* temperature-dependent PL spectroscopy from 13.5 to 73.5 K, indicating the brilliant optical quality of the single-crystalline $MAPbBr_3$ nanoplates.

By embedding the as-fabricated MAPbBr₃ into the vertical microcavity, CW lasing with a low threshold of 55.2 W cm⁻² and a high Q-factor of 1140 have been demonstrated at 80 K, which is attributed to strong optical confinement in the high-Q cavity and significant PL enhancement at low temperature. These findings envisage the future applications of single-crystalline metal halide perovskites in practicable laser devices.

All-inorganic cesium lead bromide (CsPbBr₃) quantum dots (QDs) are considered as promising candidates to achieve room temperature CW pumped lasing due to their large exciton binding energy, near-unity photoluminescence quantum yield, and high environmental stability. Here, the high-quality CsPbBr₃ QDs, prepared by a hot-injection method, were employed as the gain medium and sandwiched by two sets of high-reflectivity DBRs to form a high Q-factor vertical-cavity surface-emitting laser (VCSEL). The as-prepared CsPbBr₃ QDs were diluted and mixed with PMMA to ensure their sparse dispersion in the microcavity, showing single-mode CW lasing with a relatively low threshold of 8.8 W cm⁻² and high Q-factor of 1787 at room temperature. The CsPbBr₃ QDs VCSEL held outstanding environmental stability, which can sustain more than 5 min and conserve the lasing characteristic after one-year of storage in the ambient condition. This work sheds light on the realization of practical coherent light sources based on lead halide perovskites.

2D layered lead halide perovskites with the large exciton binding energy, efficient radiative recombination and outstanding environmental stability are regarded as supreme candidates for realizing ultralow threshold lasers. Here, the phenylethylammonium lead iodide [(PEA)₂PbI₄] thin flakes, exfoliated from the solution-processed millimeter-sized single crystal, were utilized as gain media to construct a VCSEL, which presents the robust single-mode CW lasing operation with an ultra-low threshold of 5.7 W cm⁻² at room temperature, attributed to strong optical confinement in the high-Q cavity. Moreover, the multi-mode emission has been

synchronously discussed, which can be explained by the change of the cavity length resulting from the unintentional roughness of the exfoliated flake. This work opens up a new window for developing novel 2D VCSELs based on the layered lead halide perovskites.

In summary, this thesis depicts the systematic exploration of CW lasers developed by both organic and inorganic perovskites sandwiched in microcavities with low or room-temperature operations. These findings provide a strategy to design and fabricate solution-based perovskite VCSELs and mark a significant step towards the next-generation of coherent light sources.

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Publications

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2. **Zhang, H.**; Du, B.; Wen, W.; Zhou, L.; Wu, L.; Chen, Y.; Zou, C.; Feng, S.; Shang, J; Cong, C.; Yu, T. Robust continuous-wave lasing from discrete CsPbBr₃ Quantum dots embedded microcavity. (To be submitted)
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Abbreviations

CW	continuous-wave
VCSEL	vertical-cavity surface-emitting laser
MAPbBr ₃	methyammonium lead bromide
CsPbBr ₃	cesium lead bromide
(PEA) ₂ PbI ₄	phenylethylammonium lead iodide
QD	quantum dot
PMMA	poly (methyl methacrylate)
1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
vdW	van der Waals
TMD	transition metal dichalcogenide
hBN	hexagonal boron nitride
BP	black phosphorus
PL	photoluminescence
LED	light emission diode
CVD	chemical vapor deposition
MBE	molecular beam epitaxy
AFM	atomic force microscopy
SEM	scanning electron microscopy
EDS	energy-dispersive X-ray spectroscopy

TEM	transmission electron microscopy
XRD	X-ray diffraction
CCD	charge coupled device
ASE	amplified spontaneous emission
FWHM	full width at half maximum
DBR	distributed Bragg reflector
WGM	whispering gallery mode
DFB	distributed feedback laser
FSR	free spectral range
FDTD	finite-difference time-domain method
LN ₂	liquid nitrogen
LHe	liquid helium
SE	spontaneous emission
FE	free exciton

Chapter 1

Introduction

1.1 Introduction to lead halide perovskites

In recent years, the problem of energy shortage has become a worldwide focus[1]. Since Miyasaka's group first reported hybrid organic-inorganic perovskites in 2009[2], perovskite solar cells have made rapid progress. Their performance has even surpassed many other types of solar cells, which have been developed for several decades. In the past years, the energy conversion efficiency of metal halide perovskites-based solar cells has been rapidly increased from 3.8%[2] to over 24%[3-8]. Due to their numerous advantages in solar cells, such as appropriate bandgap, high optical absorption rate, long carrier diffusion length, high carrier mobility, and low-cost processability, metal halide perovskites show tremendous potential in the advancement of the photovoltaic field.

Perovskite was first discovered by Russian geologists in 1839, as an ore containing calcium titanate (CaTiO_3), and then it was referred to as the substance with the same crystal structure. Their crystalline system has the ABX_3 compound, in which 'A' and 'B' are two different cations, and 'X' is an anion. In this structure, the metal B atom is located in the center of the cubic cell, the halogen X atom is located in the face center of the cube, and cation A is located in the vertex of the cube, as shown in Figure 1.1[9]. In general, perovskites can be classified into two types, which include inorganic oxide perovskites and halide perovskites[10]. The ferroelectric perovskites such as BaTiO_3 were reported in 1956, representing the first observation of photocurrent in oxide perovskites[11].

Halide perovskites include a big perovskite group, and they can be further divided into

organo-metal halide perovskites and alkali-halide perovskites[10]. The most representative organo-metal halide perovskites are methylammonium lead halide perovskites (MAPbX_3), which include the single halide perovskites ($\text{CH}_3\text{NH}_2\text{PbI}_3$, $\text{CH}_3\text{NH}_2\text{PbBr}_3$, $\text{CH}_3\text{NH}_2\text{PbCl}_3$)[12] and their hybrid alloys ($\text{CH}_3\text{NH}_2\text{PbI}_{3-x}\text{Cl}_x$, $\text{CH}_3\text{NH}_2\text{PbI}_{3-x}\text{Br}_x$, $\text{CH}_3\text{NH}_2\text{PbBr}_{3-x}\text{Cl}_x$)[13]. There are related organo-metal halide perovskites like formamidinium lead halide perovskites (FAPbX_3)[9], phenylammonium lead halide perovskites (PhAPbX_3)[14], and ethylammonium lead halide perovskites (EAPbX_3)[15]. Furthermore, lead can be replaced by tin or their alloys to form a perovskite structure like MASnX_3 or $\text{MAPb}_x\text{Sn}_{1-x}\text{X}_3$ [16]. As to alkali-halide perovskites, such as cesium metal halide perovskites[17], they usually show higher stability at high temperatures due to their all-inorganic composition.

Figure 1.1 The ABX_3 halide perovskite crystal structure. ‘A’ is the organic or cesium cation, ‘B’ is the metal cation, and ‘X’ is the halide anion. Reprinted with permission from: ref. [9], Copyright 2014, Royal Society of Chemistry.

Due to their outstanding optoelectronic properties such as optimal direct bandgap, promising quantum yields, excellent optical gain properties, and tunable emission wavelength, organo-metal halide perovskites have exhibited their great potential applications beyond solar cell, including LED, lasers, and photodetectors, which are summarized in Figure 1.2.

Figure 1.2 The potential applications of organo-metal halide perovskites. (NC: nanocrystal, NR: nanorods, NW: nanowires, QD: quantum dots, NP: nanoparticles, MC: millimeter-scale crystal). Reprinted with permission from: ref. [4], Copyright 2016, Royal Society of Chemistry.

1.1.1 Crystal structure of lead halide perovskites

The ideal crystal structure of organo-metal ABX_3 halide perovskites is a cubic unit cell. As shown in Figure 1.3, the size of cations and anions may cause the distortion of the crystal structure. In general, cation A is surrounded by four nearest-neighbor BX_6 octahedra, which consists of cation B and anion X[18]. When the size of the BX_6 octahedra and the cation is not matched, it would distort the crystal structure and affect the symmetry[15].

Figure 1.3 (a) The ideal cubic ABX_3 perovskite unit cell. (b) A view depicting cation A surrounded by four nearest-neighbor BX_6 octahedra. (c) Slanting of BX_6 octahedra due to the mismatched size effect. (green: cation A, blue: cation B, red: anion C). Reprinted with permission from: ref. [15], Copyright 2012, Elsevier.

The ABX_3 perovskites with the typical cubic structure, where corner-sharing BX_6 octahedra and A cations resided in the building cage of octahedra, could undergo structural phase transformations by the octahedron tilting and the cation shifting. A tolerance factor t and an octahedral factor μ can be used to evaluate the structural probability and stability of the ABX_3 perovskites[19]. From the definition, t is the ratio of the distance A-X to B-X[4]:

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$

Where R_A , R_B , and R_X are the ionic radii of the ion A, B, and X, respectively[20]. μ is defined as the ratio of R_B to R_X . As summarized in Figure 1.4, generally, the confine condition is $0.81 < t < 1.11$ and $0.44 < \mu < 0.90$ for halide perovskites[18]. When $0.89 < t < 1.0$, the cubic structure probably appears, and when $t < 0.89$, it turns to symmetric tetragonal or orthorhombic structures[4].

Figure 1.4 Octahedral and tolerance factors for 12 common organo-metal halide perovskites.

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As the structure could be affected by the strain between the cations and anions, the lead halide perovskite could have different phases [21]. According to the previous report, both the temperature[22-24] and pressure[25-27] can induce the ABX_3 perovskite analog phase transitions. For example, the representative structural evolution of MAPbBr₃ with the cooling and compression process is shown in Figure. 1.5. At ambient condition, there is no tilting for PbBr₆ octahedra in cubic $Pm\bar{3}m$ phase while MA cations are randomly disordered[28]. As temperature decreases, PbBr₆ octahedra undergo tilts and form the tetragonal $I4/mcm$ structure with the partially ordered MA cations[21,29]. With the further cooling process, MAPbBr₃ perovskite transforms into an orthorhombic $Pnma$ structure *via* further tilting of PbBr₆ octahedra, and the MA cations become fully ordered with head-to-tail configuration[30]. In brief, the structural phase transition in the ABX_3 perovskites is related to the tilts of PbBr₆ octahedra and rotation of the organic cation, suggesting a robust interaction between X anions and H atoms of A cation.

Figure. 1.5 Crystal structure evolution of MAPbBr_3 perovskite as (a) temperature decreases and as (b) pressure increase. Reprinted with permission from: (a) ref. [23], Copyright 2016, American Chemical Society; (b) ref. [25], Copyright 2015, American Chemical Society.

1.1.2 Dimensionality of lead halide perovskites

Compared to 3D lead halide perovskites, two-dimension (2D) layered hybrid perovskites with the quantum well structures[31], where electrons and holes are strongly confined within the inorganic layers to form excitons at room temperature with high binding energies, display remarkable excitonic properties and high PL quantum yield[32-34]. Due to the quantum well structure, 3D bulk lead halide perovskites can be made into two-dimensional sheets with atomically thickness[10,35]. The layered perovskites can be denoted by a general formula $\text{R}_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ [36], where ‘R’ is the large organic cation such as n-butylammonium (BA^+), phenylethylammonium (PEA^+) and 1-naphthylmethylamine (NMA^+) and, ‘A’ can be CH_3NH_3

or other similar small cation, ‘B’ is a metal cation, and ‘X’ is a halide anion. When $n = 1$, the perovskites become a single-layer structure. When $n \rightarrow \infty$, the perovskites become bulk structure with the form of ABX_3 [37]. The schematic lattice structure of the layer perovskites is shown in Figure 1.6.a[36]. The electronic structures of the 3D $MAPbI_3$ and 2D $(BA)_2PbI_4$ are shown in Figure 1.6.b, which of 3D and 2D perovskites are much different. The valence band maximum (labeled as TVB in Figure 1.6.b) for $MAPbI_3$ is formed by the Pb 6s–I 5p σ anti-bonding orbital, and the conduction band minimum (labeled as BCB in Figure 1.6.b) results from the Pb 6p – I 5s σ anti-bonding and Pb 6p –I 5p π anti-bonding orbitals[38,39]. In the 2D $(BA)_2PbI_4$, the electronic orbitals of the in-plane and out-of-plane I atoms of I1 and I2 are splitting. The TVB contains the Pb 6s–I1 and I2 5p σ anti-bonding orbitals, but the BCB of Pb 6p–I1 5s σ anti-bonding and Pb 6p –I1 5p π anti-bonding orbitals displays greater dispersion than the Pb 6p–I2 5s one[38]. With the transition from 3D to 2D perovskites, the bandwidth becomes narrow and the gap is broadening, resulting in robust excitonic properties in 2D structure.

Figure 1.6 (a) The structure of $R_2A_{n-1}B_nX_{3n+1}$ layered perovskite ($n = 1, 2, 3$). (b) Electronic structure of 3D $MAPbI_3$ and 2D $(BA)_2PbI_4$ perovskites at TVB and BCB. Reprinted with permission from: (a) ref. [36], Copyright 2016, Wiley-VCH; (b) ref. [38], Copyright 2016, American Physical Society.

1.1.3 Electronic band structure of lead halide perovskites

Hybrid perovskites show particular electronic features of conventional inorganic semiconductors, where the valence band and conduction band are determined by the atomic orbitals of the B cations and X anions[40]. In the hybrid lead halide perovskites, the electronic configuration of the Pb cation and halide X are $6s^26p^0$ and np , respectively[41]. The valence band maximum is formed from the Pb 6s-X np σ anti-bonding combination. In contrast, the conduction band minimum is formed from the Pb 6p-X ns σ and Pb 6p-X np π anti-bonding orbitals[38,39], as demonstrated by an orbital diagram of Fig. 1.7.a for MAPbI₃ perovskite. By moving I to Br to Cl, the atomic orbitals change from 5p to 4p to 3p, and the valence band will be downshifted obviously while the conduction band will be upshifted slightly[41], the calculated band structures for different halides as shown in Fig. 1.7.b-d.

Figure 1.7 (a) Bonding diagram of the Pb-I interaction in MAPbI₃. (b-d) Calculated band structure for MAPbI₃, MAPbBr₃ and MAPbCl₃ at the SOC-GW level, respectively. Reprinted with permission from: (a) ref. [38], Copyright 2016, American Physical Society; (b) ref. [41], Copyright 2016, Royal Society of Chemistry.

Because the electronic properties of lead halide perovskites are governed by the B-X bond, the band structure can be tailored by merely adjusting the halogen compounds. For example, the bandgap of the hybrid CH₃NH₃PbI_{3-x}Br_x perovskites can be tuned from 1.6 – 2.3 eV, which is shown in Figure 1.8[42].

Figure 1.8 Photoluminescence spectra of CH₃NH₃PbI_{3-x}Br_x perovskites at room temperature. Reprinted with permission from: (a) ref. [42], Copyright 2016, American Chemical Society.

The emission wavelength of hybrid mixed-halide MAPbX₃ can be tuned from 400 to 800

nm, which has covered the whole visible region. Besides, replacing MA cation with others like FA can also adjust the band structure[16]. Figure 1.9 shows the schematic energy level diagram of some common organo-metal halide perovskites.

Figure 1.9 Schematic energy level diagram of 7 common organo-metal halide perovskites along with TiO₂. Reprinted with permission from: (a) ref. [16], Copyright 2015, Wiley-VCH.

1.2 Interaction of light and matter

1.2.1 The concept of excitons

As a semiconductor absorbs a high-energy photon, inter-band transition occurs, which generates an electron in the conduction band and a hole in the valence band. Due to the Coulomb interaction between the electron and hole, they can be bound together to generate a hydrogen-like system, which is an electrically neutral quasiparticle, known as an exciton. Exciton plays a vital role in the semiconductor, such as acceleration in the optical transition. In particular, there are two kinds of excitons in semiconductors: Wannier-Mott excitons and Frenkel excitons[43].

Wannier-Mott excitons, also called free excitons, are mainly observed in inorganic materials. As shown in Figure 1.10.a, the Wannier-Mott exciton in the crystal is formed by an electron and a hole orbiting around each other with the Coulomb interaction. The Wannier-Mott exciton generally owns a relatively large Bohr radius, encompassing many atoms. The Wannier-Mott exciton is delocalized, which is able to travel freely in the crystal, so-called ‘free exciton’. The delocalization of Wannier-Mott excitons leads to strong exciton-exciton interaction. On the contrary, as illustrated in Figure 1.10.b, the Frenkel exciton possesses a small Bohr radius, usually at the atomic scale, owing to the reduced screening effect. Thus, this kind of excitons is highly localized in the particular site, called ‘tightly bound exciton’, which is less mobile than the Wannier-Mott exciton. The Frenkel exciton can only move through the crystal by hopping from one to another atom. Therefore, the exciton-exciton interaction among Frenkel excitons is relatively weak[44].

Excitons will be stable only if the attractive potential of the electron-hole pair is large enough to overcome collisions with phonons. The binding energy is used to describe the energy demanded the breaking of the bound electron-hole pair to free carriers. According to the Bohr model, the binding energy is defined as[43]

$$E_n = -\frac{\mu}{m_0} \frac{1}{\epsilon^2} \frac{R_H}{n^2} = -\frac{R_x}{n^2}$$

where μ stands for the effective mass of the exciton, m_0 is the mass of the free electron, ϵ is the dielectric constant, R_H represents the Rydberg energy of the hydrogen atom (13.6 eV), n denotes the principal quantum number. The quantity $R_x = (\mu/m_0\epsilon^2)$ represents the exciton Rydberg energy. Then, the Bohr radius can be given by

$$r_n = \frac{m_0}{\mu} \epsilon n^2 a_H = n^2 a_x$$

where a_H is the Bohr radius of the hydrogen atom ($5.29 \times 10^{-11} \text{m}$) and $a_x = (m_0 \epsilon / \mu) a_H$ stands for the exciton Bohr radius. Thus, the ground state (i.e., $n = 1$) has the largest binding energy and smallest radius, while the higher excited states 2s, 2p, etc., have smaller binding energies. Only excitons with the binding energy larger than thermal excited phonon energy can exist at room temperature. Therefore, the Wannier-Mott exciton usually cannot exist at room temperature, while the Frenkel exciton is much stable in that case.

Figure 1.10 Schematic of two types of excitons in the crystal. (a) Wannier - Mott exciton with a large Bohr radius. (b) Frenkel exciton with a small Bohr radius. Reprinted with permission from: ref. [43], Copyright 2011, Oxford University Press.

1.2.2 Fermi's golden rule

Fermi's golden rule describes the transition rate from one energy state of a quantum system to other energy states, i.e., it can be used to describe the probability of a transition during the interaction between light and matter. When an electron interacts with light, the classical Hamiltonian is[45]

$$H = \frac{1}{2m} \left(p - \frac{e}{c} A \right)^2 + e\varphi + W$$

where A stands for the vector potential, φ denotes the scalar potential, m and e are the mass and electric charge of the electron, p and c are the momentum and vacuum speed of light, W represents external potential. Quantum model is induced when replacing p by $-i\hbar\nabla$,

$$H = \frac{1}{2m} \left(-i\hbar\nabla - \frac{e}{c}A \right)^2 + e\varphi + W$$

after expanding,

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{i\hbar e}{mc} (\nabla \cdot A + A \cdot \nabla) + \frac{e^2}{2mc^2} (A \cdot A) + e\varphi + W$$

choose Coulomb gauge, $\nabla \cdot A = 0$, then

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \frac{i\hbar e}{mc} (A \cdot \nabla) + \frac{e^2 A^2}{2mc^2} + e\varphi + W$$

considering weak-field approximation (i.e., neglect the term of $\frac{e^2 A^2}{2mc^2}$), then

$$H = -\frac{\hbar^2}{2m} \nabla^2 + e\varphi + W - \frac{e}{mc} (A \cdot p) = H_0 + V$$

H_0 is perturbed by the matter-field interaction potential, V . In the first-order perturbation, apply

vector potential $A = A_0 \epsilon \cos(k \cdot r - \omega t)$, then

$$\begin{aligned} V &= -\frac{e}{mc} (A \cdot p) = -\frac{e}{mc} A_0 \cos(k \cdot r - \omega t) \epsilon \cdot p \\ &= -\frac{e}{2mc} A_0 (e^{i(k \cdot r - \omega t)} + e^{-i(k \cdot r - \omega t)}) \epsilon \cdot p \\ &= U(k) e^{-i\omega t} + U(-k) e^{i\omega t} \end{aligned}$$

The transition matrix from initial m state to final k state, the matrix element U_{km} is:

$$U_{km}(k) = -\frac{eA_0}{2mc} \langle k | e^{ik \cdot r} \epsilon \cdot p | m \rangle$$

with the long-wavelength approximation, $e^{ik \cdot r} \sim 1$, U_{km} becomes:

$$\begin{aligned} U_{km}(k) &= -\frac{eA_0}{2mc} \frac{im}{\hbar} \epsilon \cdot \langle k | [H_0, r] | m \rangle \\ &= -\frac{ieA_0}{2c\hbar} (E_k - E_m) \langle k | \epsilon \cdot r | m \rangle \end{aligned}$$

$$= \mp \frac{iA_0}{2c} W_{km} \varepsilon \cdot e \langle k|r|m \rangle$$

where the electric dipole, μ_{km} , is defined as $e \langle k|r|m \rangle$, thus

$$U_{km}(k) = \mp \frac{iA_0}{2c} W_{km} \varepsilon \cdot \mu_{km}$$

According to first-order perturbation theory, the transition coefficient from initial m state to final k state will be:

$$c_k(t) = \frac{-i}{\hbar} \int_0^\tau dt' U_{km} e^{i(\omega_{km} \pm \omega)t'} = -U_{km} \frac{e^{i(\omega_{km} \pm \omega)\tau} - 1}{\hbar(\omega_{km} \pm \omega)}$$

We suppose the final states as a quasi-continuum with density of states, the total probability of transition is

$$\begin{aligned} P_T &= \sum_k P_k^m = \sum_k |U_{km}|^2 \frac{2 - 2 \cos(\omega_{km} \pm \omega)\tau}{[\hbar(\omega_{km} \pm \omega)]^2} \\ &= \sum_k |U_{km}|^2 \frac{\sin^2[(E_k - E_m \pm \hbar\omega)\tau/2\hbar]}{[(E_k - E_m \pm \hbar\omega)/2]^2} \\ &\approx \int dk |U_{km}|^2 \frac{\sin^2[(E_k - E_m \pm \hbar\omega)\tau/2\hbar]}{[(E_k - E_m \pm \hbar\omega)/2]^2} \\ &= \int dE_k |U_{km}|^2 \frac{\sin^2[(E_k - E_m \pm \hbar\omega)\tau/2\hbar]}{[(E_k - E_m \pm \hbar\omega)/2]^2} \\ &= \rho(E_m \pm \hbar\omega) |U_{km}|^2 \int_{-\infty}^{\infty} dE_k \frac{\sin^2[(E_k - E_m \pm \hbar\omega)\tau/2\hbar]}{[(E_k - E_m \pm \hbar\omega)/2]^2} \\ &= \frac{2\pi\tau}{\hbar} \rho(E_m \pm \hbar\omega) |U_{km}|^2 \end{aligned}$$

Finally, the rate of transition W_T , is obtained from dividing P_T by the transition time τ , notably, $\rho(E_m \pm \hbar\omega)$ is the density of photon states at a given energy

$$W_T = \frac{P_T}{\tau} = \frac{2\pi}{\hbar} \rho(E_m \pm \hbar\omega) |U_{km}|^2$$

which is known as the Fermi's golden rule.

1.3 The concept of laser

There are three significant elements in a laser, including the gain media, cavity, and pumping source. With an optical or electrical pumping source supplying the energy, the active media emits incoherent light. The emitted light is spatially confined and resonates within the cavity, forming a cavity mode. This cavity mode can produce stimulated emission when traveling through the gain media with the population inversion, resulting in coherent light. When the gain exceeds the loss, the light is amplified, and then lasing emission generates from the cavity. A typical laser input-output curve is plotted schematically in Figure. 1.11, where spontaneous emission factor (β) shows the relative strengths of the spontaneous emission and stimulated emission[46].

Figure 1.11 The typical nonlinear input-output relationship of the lasing emission.

1.3.1 Quality factor and linewidth

The Quality factor (Q-factor) indicates how long photons can remain in the cavity, with a definition as a ratio between the trapped photon energy and photon energy loss per cycle[47].

$$Q = 2\pi \frac{\text{trapped photon energy}}{\text{energy loss per cycle}} = 2\pi f \tau_c$$

where f and τ_c are the frequency and lifetime of the cavity mode.

The full width at half maximum (FWHM) of the cavity mode after resonating N cycles in the cavity is estimated as about $\delta w \approx w_s/N$, where w_s is the axial mode-spacing. For a standing-wave cavity with a length of L , the mode-spacing[47]

$$w_s = \frac{c}{2nL}$$

where c represents the speed of light in vacuum and n denotes the refractive index. Then, the FWHM of the cavity mode is approximate as

$$\delta w = \frac{c}{2nLN}$$

Thus, another expression of Q-factor is as follows

$$Q = \frac{w}{\delta w}$$

where w is the resonant frequency. As $w = cm/\pi nL$, Q-factor is approximately $Q \sim 2Nm/\pi$.

Therefore, the longer existence of cavity mode leads to a narrower linewidth.

1.3.2 Purcell factor

Purcell effect is the description of the enhancement of emission rate when emitting dipoles are coupled to the electromagnetic field inside the cavity. According to Fermi's golden rule, the transition of emitting dipoles at the oscillating electromagnetic field is enhanced due to the increase in density of the final states, leading to a faster emission rate. The enhancement factor is defined as Purcell factor

$$F = \frac{3}{4\pi} \left(\frac{\lambda}{n}\right)^3 \frac{Q}{V}$$

where λ illustrates the wavelength of cavity photons, n denotes the refractive index, Q is the Q-factor, and V represents the effective mode volume. In order to maximize the emission rate, small mode volume and high Q-factor is vital for designing an optical cavity.

1.3.3 Different types of cavities

As shown in Figure 1.12, optical cavities can be categorized as (a) Fabry-Pérot (F-P) cavity, (b) whispering gallery mode cavity (WGM cavity), (c) plasmonic cavity, and (d) disordered cavity due to the difference in constructing resonances. F-P cavity is a one-dimensional resonator with two reflecting facets, providing a precise optical path length for the resonating light. WGM cavity is a circular structure where light resonates within the internal surface via reflection. In a plasmonic cavity, dispersive surface plasmon promotes stimulated emission, which is sustained by the FP or WGM structure. The disordered cavity usually generates the random lasing, originated from random scattering feedback of light from within clustered scatters.

Figure 1.12 Various optical cavities. (a) Fabry-Pérot cavity. (b) Whispering gallery mode (WGM) cavity. (c) Plasmonic cavity. (d) Disordered cavity with random scattering.

1.3.5 Properties of vertical microcavity

The vertical microcavity in this thesis is a 2D Fabry-Pérot resonator, consist of the active medium sandwiched in two distributed Bragg reflectors.

1.3.5.1 Distributed Bragg reflectors

Distributed Bragg reflectors (DBRs) are dielectric mirrors with high reflectivity, which are constructed by multiple pairs of dielectric layers with alternating high and low refractive indices. Each dielectric layer has an optical thickness of $\lambda/4n$, where λ is the wavelength of the incident light, and n is the refractive index. As such, multiple constructive interference processes occur in the DBRs layer, resulting in a high reflectivity within a broad spectral range, known as stopband. The reflectivity in the stopband depends on the refractive index and number of the dielectric pairs, which can be calculated by[48]

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

where n_{ext} , n_c , n_L and n_H denote the refractive indexes of the external medium, cavity, as well as the low index dielectric and high refractive index dielectric layer, respectively. N is the number of dielectric pairs.

Figure 1.13 An example of the reflectivity spectrum of the $\text{TiO}_2/\text{SiO}_2$ DBRs with high reflectivity.

The width of the stopband Δs is another critical parameter for DBRs, which is influenced by the refractive index difference between the high and low refractive index layers as follows[49]

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

1.3.5.2 Fabry-Pérot Microcavity

A Fabry-Pérot microcavity consists of an active medium embedded in two DBRs with high reflectivity. The length between two DBRs is designed as

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

where N is a positive integer, λ is the optical wavelength, n_c is the effective group index of the cavity. The constructive interference takes place when the round-trip phase shift is multiple of 2π . Free spectral range (FSR) is defined as a wavelength spacing between neighboring modes as follows

$$\Delta\lambda = \lambda_m - \lambda_{m-1} \approx \frac{\lambda_m^2}{2n_c L}$$

where λ_m and λ_{m-1} are the wavelengths of the m^{th} and $(m+1)^{th}$ cavity mode. As such, the shorter length of F-P cavity makes larger FSR.

1.3.6 The fabrication and characterization of VCSEL

Vertical cavity surface-emitting laser (VCSEL) is a kind of semiconductor laser with perpendicular emission from the surface, which is was firstly proposed in 1979[50]. The room-temperature pulsed-operated VCSEL and continuous-wave (CW)-operated VCSEL were realized in 1984[51] and 1988[52], respectively. Figure 1.14 shows the representative structure of a VCSEL[53]. The inner cavity is constructed by a few quantum wells (QWs) as active layers, which are located at the center of the device. The conductive DBRs sandwich the active and provide optical feedback. Ohmic contacts on the top and the n-type substrate provide a path for the electrical current.

Figure 1.14 Schematic diagram and working mechanism of a conventional VCSEL. Reprinted with permission from: ref. [53], Copyright 2003, Springer.

VCSELs are different from edge-emitting lasers (EELs), which emit light from the cleaving edge with an elliptical beam profile (Figure 1.15)[54]. Compared with EELs, VCSELs have a lot of advantages, including low threshold, high power efficiency, small divergence in the emission profile, and high compatibility. Therefore, VCSELs are more promising in the application of integrated optoelectronics.

Figure 1.15 Schematic diagram of the typical EEL (left side) and VCSEL (right side). Reprinted with permission from: ref. [54], Copyright 2013, Springer.

1.3.6.1 The fabrication of VCSEL

The fabrication of conventional III-V semiconductor VCSELs usually demands cutting edge epitaxy techniques, such as molecular beam epitaxy (MBE)[55,56], metal-organic chemical vapor deposition (MOCVD)[57-60], and reactive ion beam sputtering[61].

During the fabricating process, current confinement is important in the active layer as small apertures, which can render certain insulating regions and efficiently avoid lateral spreading of the current. Thus, the flow of the injection current can be restrained. Figure 1.16 shows six typical methods for the current confinement, including: (a) ring-electrode structure, (b) proton-

bombardment structure, (c) buried-heterostructure, (d) air-post structure, (e) selective oxidation structure, and (f) oxidized DBR.[53]

Figure 1.16 Schematic diagram of different current confinement structures. Reprinted with permission from: ref. [53], Copyright 2003, Springer.

Optical confinement is another key factor that should be considered, which benefits the interaction between the optical field and the gain media. As shown in Figure 1.17, five kinds of structures for optical confinement are illustrated, including: (a) Fabry-Perot structure, (b) gain-guide structure, (c) buried heterostructure, (d) selective oxidation structure, and (e) anti-guiding structure. [53]

The typical structure of epitaxial VCSELs based on GaInAs/GaAs quantum wells is shown in Figure 1.18. The active layer, GaAs spacer layer, n-type DBR, and p-type DBR were grown by MOCVD, followed by plasma etching technique to form mesas. And oxide apertures are formed by AlAs wet-oxidation process.[62]

Figure 1.17 Schematic diagram of different optical confinement structures. Reprinted with permission from: ref. [53], Copyright 2003, Springer.

Figure 1.18 Schematic diagram of a typical epitaxial VCSEL. Reprinted with permission from: ref.[62], Copyright 2003, IEEE.

The main difference between VCSELs with dielectric DBRs and epitaxial DBRs is the pathway for current injection. As shown in Figure 1.19, the lateral injection current in VCSELs

with dielectric DBRs has to go through intra-cavity spreading layers, which would induce lateral heat flow. In contrast, epitaxial DBRs are electrically conductive, which enable vertical current injection into the active layers.[63] Therefore, VCSELs with epitaxial DBRs usually have low electrical resistance and high thermal conductivity, which is in favor of high light-emitting performance.

Figure 1.19 Schematic diagram of VCSELs with dielectric DBRs (a) and epitaxial DBRs (b). The arrows represent the current injection pathway. Reprinted with permission from: ref. [63], Copyright 2019, MDPI.

1.3.6.2 The characterization of VCSEL

For the characterization of VCSEL, the threshold is one of the most critical parameters, which indicates the onset of lasing emission. As shown in Figure 1.20.a, the kink in the nonlinear output-input curve represents the threshold of a GaInNAs VCSEL[64]. The threshold is mainly constrained by the losses result from optical scattering and diffraction, non-radiative recombination, and imperfections during the fabrication process. This nonlinear output-input relation also can be observed in optical pumping VCSELs, and the narrowing of the full width at half maximum (FWHM) can also take place simultaneously (Figure 1.20.c)[65]. The DBR for optical feedback should also be designed and fabricated carefully. The reflectance of stopband is usually higher than 99%, with a broad wavelength range completely covering the

PL spectrum of gain media (Figure 1.20.b)[66]. The stability of long-time operation is a crucial factor for practical application. As shown in 1.20.d, the emission intensity of a $\text{CH}(\text{NH}_2)_2\text{PbBr}_3$ VCSEL can sustain about 20 hours with 60 % of initial values, which is attributed to the isolation of oxygen and moisture[65].

Figure 1.20 (a) Classic nonlinear output power-injection current characteristics for a GaInNAs VCSEL. (b) Measured and simulated reflectance spectra for epitaxial GaN DBRs, as well as PL spectrum of $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film. (c) Light output-input relationship of an optical pumping $\text{CH}(\text{NH}_2)_2\text{PbBr}_3$ VCSEL. (d) Normalized emission intensity and linewidth of a $\text{CH}(\text{NH}_2)_2\text{PbBr}_3$ VCSEL versus time under constant optically pulse pumping. Reprinted with permission from: (a) ref. [64], Copyright 2011, IOP Publishing; (b) ref. [66], Copyright 2019, WILEY-VCH; (c) & (d) ref. [65], Copyright 2017, American Chemical Society.

The spatial coherence is another typical feature of lasing, which can be observed from the spatial emission of VCSEL. As shown in Figure 1.21.a, near-field images display weak and diffuse spontaneous emission below the threshold[66]. However, a crisp and bright beam is seen above the threshold, which is perpendicular to the device surface. The far-field pattern shows a nearly Gaussian beam profile with a small divergence angle of about 3° , indicating spatial coherence (Figure 1.21.b)[66]. The emission from the perovskite VCSEL typically shows linear polarization, which might originate from the unspecified built-in anisotropy in perovskite film and DBRs (Figure 1.21.c)[66]. The PL dynamics as a function of pump intensity is a useful method to identify the occurrence of lasing. As shown in Figure 1.21.d, the PL decay with a pumping intensity above threshold (green curve) is much faster than the decays with a pumping intensity below threshold (black curve) and around threshold (red curve), indicating the appearance of the stimulated emission[67].

Figure 1.21 (a) Reprinted with permission from: (a) ref. 24, Copyright 2012, Nature Publishing Group; (b) ref. 12, Copyright 2011, American Physical Society

1.4 Organization of the thesis

The lead halide perovskite materials have aroused enormous interest because of their superior properties such as a direct-band gap, strong excitonic effects, high quantum efficiency and broadly tunable emission wavelengths. In addition, the facile solution processability and defect tolerance of metal halide perovskites are conducive to the development of practical, low-cost light-emitting devices, which will enable the new-generation optoelectronic applications and bring fascinating features into the present semiconductor lighting technology such as low energy consumption and highly compact light sources for on-chip optical circuit beyond electronics. In the past few years, great effort has been made to achieve lasing emission from metal halide perovskites under pulsed pumping. However, the studies of continuous-wave (CW) perovskite laser, which is regarded as a significant milestone towards the electrically pumped laser, are still in an early stage. The integration of metal halide perovskite into the vertical-cavity surface-emitting lasers (VCSELs) is a potential solution to the development of novel lasers with low threshold and high-power efficiency, which will promote the advancement of electrically driven perovskite lasers.

The research objectives for this thesis are to fabricate both organic and inorganic perovskites with high quality, study their optical properties at both low temperature and room temperature, and develop lasers based on perovskites embedded in microcavities upon continuous-wave excitation. If successfully achieving the targets, this thesis can provide a general strategy to design and fabricate perovskite-based VCSELs, which will undoubtedly build the bridge for electrically driven perovskite lasers, boost the widespread development of the next-generation integrated photonics, and push the frontier of nanotechnology.

In Chapter 1, the background about the lead halide perovskites, the fundamental concepts of light-matter interaction, and the basic physics of laser are reviewed here.

In Chapter 2, the experimental techniques, including the sample preparation, morphology characterization and spectroscopy analysis, are briefly introduced.

In Chapter 3, the phase transition of solution-grown MAPbBr_3 nanoplates is systematically investigated by Raman spectroscopy, and lasing emission from the MAPbBr_3 embedded microcavity at low temperature is studied.

Chapter 4 focuses on the demonstration of CW CsPbBr_3 quantum dots-based vertical-cavity surface-emitting laser, which operates at room temperature and shows highly environmental stability.

In Chapter 5, the ultralow threshold lasing emission from 2D $(\text{PEA})_2\text{PbI}_4$ perovskites at room temperature is presented. The single-crystalline $(\text{PEA})_2\text{PbI}_4$ thin flake is exfoliated from the bulk solution-processed crystal and sandwiched in the microcavity as the active gain media.

Chapter 6 is the conclusion and outlook of this thesis.

Chapter 2

Experiment methods

2.1 Preparation of lead halide perovskites and their devices

2.1.1 Growth of lead halide perovskites

There are mainly two kinds of methods to synthesize metal halide perovskites, which can be known as solution-processed methods and vapor processed methods. The morphology of perovskites highly depends on the synthesis methods, where the thin films, large single crystals, micro/nano-structures, and nanocrystals have been controllably fabricated.

2.1.1.1 Solution-processed methods

The available solution-processed methods to fabricate metal halide perovskite thin films include the one-step method and two-step method, which is divided by coating a mixed organic halide (e.g., $\text{CH}_3\text{NH}_3\text{I}$ (MAI)) and Pb-containing precursor (e.g., PbI_2) solution or coating organic halide after fabricating a Pb-containing precursor thin film.

As shown in Figure 2.1, for the typical one-step method, organic halide (e.g., $\text{CH}_3\text{NH}_3\text{I}$) and Pb-containing precursor (e.g., PbI_2) are dissolved in a polar aprotic solvent, such as dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), or gamma-butyrolactone (GBL), and then coated on the substrate directly[16]. For the two-step method, Pb-containing precursor film is first formed by coating, and then a 2-propanol solution of organic halide is added to form perovskites.

Figure 2.1 One-step and two-step methods to deposit perovskite thin films. Reprinted with permission from: ref. [68], Copyright 2012, American Institute of Physics.

Similar to the perovskite polycrystalline films, large single crystal perovskites can also be synthesized by solution-processed methods. By employing a temperature gradient top-seeded-solution-growth approach, Dong *et al.* reported the millimeter-scale single-crystal perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ with long electron-hole diffusion lengths ($>175\ \mu\text{m}$). The setup is shown in Figure 2.2.a[69]. Ku *et al.* also developed a two-step solvent method to synthesize centimeter-sized $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite single crystals, where the nucleation and growth are taken place in the different containers. The growth process is fast, which takes a few hours from a tiny seed to a centimeter-scale crystal. (Figure 2.2.b)[70]. Besides, Shi *et al.* used a simple antisolvent vapor-assisted crystallization method to synthesize $\text{CH}_3\text{NH}_3\text{PbX}_3$ single crystals with volumes more than 100 millimeters[71]. The slow diffusion of an antisolvent (dichloromethane) results in the growth of the sizable $\text{CH}_3\text{NH}_3\text{PbX}_3$ single crystal with long carrier diffusion and low trap-state

density. The crystallization process is shown in Figure 2.2c.

Figure 2.2 (a) The setup for the growth of millimeter-scale single-crystal perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. (b) Schematic of the two-step solvent growth of large $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals. (c) Schematic diagram for the antisolvent vapor-assisted crystallization process. Reprinted with permission from: (a) ref. [69], Copyright 2015, American Association for the Advancement of Science; (b) ref. [70], Copyright 2016, Royal Society of Chemistry; (c) ref. [71], Copyright 2015, American Association for the Advancement of Science.

The single crystalline micro/nano-structures of metal halide perovskites also can be synthesized by solution-processed methods. Liao *et al.* modified the antisolvent vapor-assisted method to produce high-quality single-crystal perovskite square microdisks, constructing self-assembled whispering-gallery mode (WGM) nanolasers at room temperature[72]. The

preparation scheme of square microdisks is illustrated in Figure 2.3.a. By using a surface-initiated solution growth strategy, Zhu *et al.* prepared high-quality single-crystal nanowires, which can lead to room-temperature lasing with low thresholds (220 nJ cm^{-2}) and high-quality factors ($Q \sim 3600$) (Figure 2.3.b)[73].

Figure 2.3 (a) Preparation process of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ square microdisks. The right panel displays the absorption and emission spectra of microdisks. The insets are optical and fluorescence images of a microdisk with a width of $5 \mu\text{m}$. (b) Schematic illustration for the synthesis of single-crystal lead halide perovskite nanowires. Reprinted with permission from: (a) ref. [72], Copyright 2015, Wiley-VCH; (b) ref. [73], Copyright 2015, Nature Publishing Group.

Furthermore, perovskite nanocrystals have been prepared by solution-processed methods. Ling *et al.* modified the ligand-assisted precipitation method by using octylammonium bromide

($\text{C}_8\text{H}_{17}\text{NH}_3\text{Br}$) as the long-chain capping ligand to confine the nanoplatelet morphology and successfully fabricated colloidal organo-metal halide perovskite nanoplatelets[74]. The schematic process is shown in Figure 2.4.a. Imran *et al.* improved the hot-injection method to prepare APbX_3 ($\text{A} = \text{MA}, \text{FA}, \text{Cs}$) quantum dots (QDs) with regular composition and near-unity quantum yield, owing to the fast reaction between desired cations and halide ions (Figure 2.4.b)[75].

(a)

(b)

Figure 2.4 (a) Synthesis of colloidal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanoplatelets. (b) Hot injection method for

the fabrication of Lead Halide Perovskite QDs. Reprinted with permission from: (a) ref. [74], Copyright 2015, Wiley-VCH; (b) ref. [75], Copyright 2018, American Chemical Society.

2.1.1.2 Vapor processed methods

The vapor evaporation methods can also prepare lead halide perovskites with high quality. Chen *et al.* employed a low-temperature vapor-assisted solution process to fabricate polycrystalline perovskite thin film, as shown in Figure 2.5, which exhibits full surface coverage, uniform surface, and microscale grain size[76].

Figure 2.5 Fabrication of perovskite thin film by vapor-assisted solution strategy. Reprinted with permission from: ref. [76], Copyright 2014, springer nature.

Using the chemical vapor deposition (CVD) method, perovskite micro/nano-structure can also be synthesized. Xiong's group successfully employed a two-step chemical vapor deposition to fabricate organo-metal halide perovskite nanowires[77] and nanoplatelets[78,79], which show a strong room-temperature lasing behavior. Figure 2.6 illustrates the setup of the method. They first synthesized Pb-containing precursor nanowires or nanoplatelets by the CVD method and then converted the nanowires or nanoplatelets to the perovskite phase through a gas-solid hetero-phase reaction.

Figure 2.6 The setup of two-step chemical vapor deposition for low dimensional perovskite single crystals. Reprinted with permission from: ref. [78], Copyright 2011, Wiley-VCH.

In this thesis, we mainly use the solution-processed methods to prepare the single crystalline MAPbBr₃ nanoplates, CsPbBr₃ quantum dots, and (PEA)₂PbI₄ single crystals, in consideration of the facile operation and low-cost process.

2.1.2 Mechanical exfoliation

In 2004, Prof Geim and his colleagues [80] developed the Scotch tape method to exfoliate the graphite to single-layer graphene, which is the milestone for the study of 2D materials. Such a kind of mechanical exfoliation method can be extended to various layered materials with weak van der Waals interactions, including hexagonal boron nitride (hBN), transition metal dichalcogenides (TMDs), black phosphorus (BP), and so on. Due to the weak van der Waals interactions between the long-chain ligands (R), this mechanical exfoliation method can also be applied to the 2D layered perovskites (R₂A_{n-1}B_nX_{3n+1}) to obtain thin flakes. During the exfoliation process, a small piece of the bulk crystal is placed on the Scotch tape, followed by folding several times for preliminary exfoliation. After that, another clean Scotch tape attaches to the original one with some gentle pressure and then is peeled off quickly. This step repeats several times until the exfoliated flakes with the required thickness are obtained. Finally, the scotch tape with thin flakes is pressed softly onto the substrate. Thin flakes will be transferred onto the substrate after peeling off the Scotch tape. When observed from the microscope, these thin crystals own various optical contrast on the 300 nm SiO₂/Si substrate because of the

interference[81,82]. The exfoliation process and some examples of the exfoliated 2D thin crystals with various thicknesses are given in Figure 2.7. In this thesis, $(\text{PEA})_2\text{PbI}_4$ thin flakes are obtained *via* the mechanical exfoliation method.

Figure 2.7 (a) Schematic illustration of the mechanical exfoliation method. (b) Partially exfoliated flakes of graphite via the scotch tape method. (c-e) Optical images of mechanically exfoliated thin crystals of graphene, molybdenum disulfide (MoS_2), and BP with different thicknesses, respectively. Reprinted with permission from: ref. [83], Copyright 2011, Springer International Publishing.

2.1.3 Electron beam evaporation

Electron beam evaporation (E-beam evaporation) is one of the physical vapor deposition processes to deposit metals and dielectric materials into uniform thin films. The evaporation source is composed of a cathode, an electron accelerator, and a coating material as an anode. In a high vacuum, the electron gun filament is heated up and emits hot electrons. The electrons are accelerated when going through the electric field, by which they obtain great kinetic energy and bombard the source materials. The kinetic energy is converted into heat to vaporize the

source materials, and then the uniform film is formed. By adjusting the power of the electron beam, the evaporating rate of coating materials can be controlled precisely, which is especially beneficial to the evaporation of metals and oxides with high melting point and purity, for example, Ni, Mo, W, Ti, Pt, MoO₃, WO₃, SiO₂, and Al₂O₃, etc. This technique has been widely used in the fabrication of optical films, conductive films, semiconductor films, ferromagnetic films, etc. Compared with conventional thermal evaporation techniques, electron beam evaporation has higher flux density and power, which is able to evaporate materials with an extremely high melting point and a higher evaporating rate. Besides, the electron beam positioning is accurate, which can avoid the contamination of the crucibles. The particles of the source materials evaporated by the electron beam own the high kinetic energy, which is in favor of high-quality uniform films. Therefore, e-beam evaporation is an excellent choice to fabricate high-quality DBRs. Figure 2.8 displays the configuration of a Cello E-beam evaporator used to deposit SiO₂, TiO₂, and Ta₂O₅ in this thesis.

Figure 2.8 *The setup of a Cello E-beam evaporator (Ohmiker-50B). Reprinted with permission from: (a) ref. [84], Copyright 2018, Nanyang Technological University.*

2.2 Morphology characterization

2.2.1 Atomic force microscopy

Atomic force microscopy (AFM) is an analytical technique that can be utilized to probe the surface morphology of materials. As shown in Figure 2.9, the surface structure and properties of materials are measured by detecting the weak atomic interaction between the sample surface and a micro-tip. A pair of extremely sensitive micro-cantilevers are fixed at the end, and a tiny tip at the other side is close to the sample. When the gap between them is small enough, the Van Der Waals force will cause deformation to the micro-cantilever, detected by a laser sensor. When the sample is scanned, sensors will monitor these changes. The force distribution information can be collected so that the surface morphology, structure information, and thickness can be obtained with the nanoscale resolution, which is very important to distinguish the layer number of two-dimensional materials.

In general, the AFM has two working modes, and both are based on a feedback circuit to adjust the position of the probe. In the non-contact mode, the cantilever is driven by the piezoelectric ceramics at the intrinsic frequency. When the tip and sample are close enough, the interaction between them will obstruct the vibration of the cantilever, thereby reducing the amplitude. The amplitude can be maintained by adjusting the distance between the cantilever and the sample at a particular value by the feedback circuit. In contact mode, the probe is attached to the sample surface, and the feedback circuit adjusts the height of the tip to make the bending degree of the cantilever unchanged, and the morphology of the sample is obtained. In general, the resolution of AFM could reach the nanometer scale.

Figure 2.9 Schematic of the AFM measurement. Reprinted with permission from: ref. [85], Copyright 2008, Royal Society of Chemistry.

2.2.2 Scanning electron microscopy

According to the Matter-wave theory of de Broglie, an electron can be considered as a short wave, where the de Broglie wavelength can be denoted by $\lambda = \hbar/p$ (p : momentum, $\hbar$: Planck constant), calculating that an electron with an energy of 10 keV has a de Broglie wavelength of about 0.12 Å. Thus, the accuracy of scanning electron microscopy (SEM) can reach the nanometer scale. SEM system mainly includes the vacuum system, power supply, control system, and working platform. The high vacuum of the chamber ensures the stability and collimation of the electron beam, and the working platform has an anti-vibration system and an anti-magnetic interference system to ensure the stable operation of the instrument. As illustrated in Figure 2.10, the emitted electron beam is accelerated by the electric field for higher energy. With the adjustment of condenser lenses, which are formed by the electromagnetic field, the electron beam is focused on the specimen surface. The upper lenses are used to tune the probing current and spot size. After electrons hitting the specimen surface,

the generated secondary electrons are collected by the detector. After signal processing, the image of the specimen surface is exhibited on the screen.

Figure 2.10 Schematic diagram of the SEM system. Reprinted with permission from: ref. [86], Copyright 2013, Springer US.

2.2.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is a potent tool to form an image for tiny specimens in nanoscale/sub-nanoscale. Different from SEM, TEM images are formed by the electron transmitted through the specimen. Therefore, high energy electrons and thin specimen are required (≤ 100 nm). The TEM has a similar configuration to the SEM. As shown in Figure 2.11, After electrons are emitted from the electron gun and accelerated, they are confined to a parallel beam by a pair of electromagnetic lenses. Some of the electrons in the beam, which travel at relatively larger angles with respect to the optic axis, are restricted from falling on the sample by a condenser aperture of controllable size placed below the condenser lenses. The

thin specimen is placed between the twin objective lens system. After electrons transmitted through the specimen, a condenser aperture is used to exclude the forwarded scattered electrons. After all, the transmitted electrons are collected for forming images. Compared with SEM, TEM provides higher spatial resolution and carries more information, such as composition and crystallography.

Figure 2.11 Schematic diagram of the TEM system. Reprinted with permission from: ref. [87], Copyright 2014, University of Calcutta.

2.2.4 X-ray diffraction

X-ray diffraction (XRD) analysis is an analytic technique to probe the crystallographic structure of a material. As shown in Figure 2.12, the specimen is irradiated by the X-rays from a rotating electron gun, and then the intensities and angles of the scattering X-rays are recorded. Because the crystal is formed by the ordered arrays of atoms, the constructive interference of the X-ray electromagnetic wave takes place only with some specific angle. The interference is determined Bragg's law: $2d \sin \theta = n\lambda$, where d represents the interplanar distance of the crystal, θ denotes the incident angle, n is a natural number, and λ is the wavelength of the X-ray. By recording the scattering angles and intensities, the X-ray diffraction patterns are obtained, revealing the lattice spacings of the crystal.

Figure 2.12 Schematic diagram of the XRD measurement. Reprinted with permission from: ref. [88], Copyright 2019, Cambridge University Press.

2.3 Optical characterization

2.3.1 Raman Spectroscopy

Raman spectroscopy is an analytical technique based on the Raman scattering effect discovered by an Indian scientist C.V. Raman. By analyzing the scattering spectrum with different frequencies under the incident light, the information of molecular vibration and rotation can be obtained. Figure 2.13.a summarizes the energy change of infrared absorption (IR) and various scattering processes. The scattered light of elastic scattering has the same wavelength as that of the incident light, such as Rayleigh scattering. As the energy exchange takes place between the incident photon and the medium, the energy of the scattered light and incident light will be different. With a scattering wavelength longer or shorter than that of the incident light, this kind of scattering process is an inelastic process, called Raman scattering (Figure 2.13.b). The inelastic processes can be further distinguished as Stokes Raman scattering (energy loss) and anti-Stokes Raman scattering (energy gain). When the energy of the incident light is near the transition energy between the excited and ground states, it is called Resonance Raman scattering with an enhancement in intensity. The energy changes in all Raman scatterings are in good agreement with the phonon energy, which is an intrinsic property and independent of the incident light. By analyzing the peak position, line width, polarization, and intensity of the Raman spectrum, the vibrational or rotational energy level of a material can be known, which could be used to identify the material and analyze its vibration properties. Therefore, the Raman spectrum is also called the "fingerprint" of a material. Notably, Raman scattering must follow a selection rule, *i.e.*, only the phonon vibration with changes in the polarizability is Raman-active. In contrast, the phonon vibration with changes in the oscillating dipole is IR-active[89]. The representative Raman-active vibrational modes are shown in Fig. 2.3.c.

Figure 2.13 (a) Energy diagram of infrared absorption and scattering processes. (b) Schematic diagram of inelastic scattering. (c) Representative Raman-active vibrations.

In this thesis, a Witec alpha300 confocal system with a backscattering configuration is used for the Raman measurement, which is equipped with various excitation continuous-wave lasers (e.g., 488 nm, 532 nm, and 633 nm) and the Koehler white-light illumination, as illustrated in Fig. 2.14. An X-Y piezoelectric stage is used to support the specimen, where the Z-axis is controlled by a motor. Therefore, mapping in the X-Y plane or the line-scanning in Z-direction

can be realized. The excitation source is reflected by the beam splitter and focused on the sample *via* an appropriate objective lens. The back-scattered light is collected with the same objective lens and sent to a charge-coupled device (CCD) equipped with an ultra-high throughput spectrometer. The Rayleigh scattering is blocked by a filter for the distinction of the Raman signals.

Figure 2.14 Configuration of a Witec alpha300 system. Reprinted with permission from: ref. [90], Copyright 2019, MDPI.

2.3.2 Photoluminescence Spectroscopy

Photoluminescence (PL) refers to a re-emission process after the absorption of a high energy photon. In a direct bandgap semiconductor, electrons transit from the valence band to the conduction band and leave holes in the valence band under the illumination of excitation light, as shown in Figure 2.15.a. The electrons in the conduction band and holes in the valence band rapidly fulfill their lowest excited states (*i.e.*, the conduction band minimum and the valence band maximum, respectively) through the relaxation process. The densities of states of the carriers relaxed to near band edge exhibit a Boltzmann distribution (Figure 2.15.b). When the excited state electrons relax to low energy levels, the recombination of electrons and holes

generates photons. The emitted photons with various energies can be measured in the spectrum with different wavelengths and intensities. Compared with the direct bandgap semiconductor, the recombination of the carriers in the indirect bandgap semiconductor demands the assistance of a phonon to overcome the mismatch of momentum conservation (Figure 2.15c). PL spectrum is usually used to analyze the electronic band structure of materials, revealing the information on material composition and dislocations. As such, photoluminescence spectroscopy is a non-damage and straightforward tool for the characterization of light-emitting materials. In this thesis, all the PL measurements at room temperature are conducted by the WITec alpha 300 Confocal system.

Figure 2.15 Schematic diagram of PL spectroscopy. (a) The transition and recombination process of the carriers in a direct bandgap semiconductor during photoluminescence. (b) Level occupancies with a Boltzmann distribution due to the relaxation of electrons and holes. (c) The transition and recombination process of carriers in an indirect bandgap semiconductor during photoluminescence. Phonon assistance is necessary for momentum conservation. Reprinted with permission from: ref. [43], Copyright 2001, Oxford University Press.

2.2.3 Linkam stage

Linkam stage is a cryogenic vessel with a vacuum environment and controllable temperature, which is convenient for the *in-situ* temperature-dependent Raman/PL measurements from 300 to 80 K with the help of liquid nitrogen (LN₂). Linkam cooling stage can be easily equipped onto WITec alpha 300 Confocal system by simply replacing the X-Y piezoelectric stage. The schematic illustration of the Linkam stage is shown in Fig. 2.16, where the yellow circle represents the window for optical measurements.

Figure 2.16 Schematic image of a temperature-controlled Linkam cooling stage. Reprinted with permission from: ref. [91], Copyright 2011, Copernicus Publications for the European Geosciences Union.

2.2.4 Customized Magneto-Raman/PL System

In order to study the optical property of our samples below 80 K, the custom-designed

magneto-Raman/PL system (attocube) with a commercial WITec confocal Raman spectroscope is employed here for further PL measurement. As shown in Fig 2.17, the customized Magneto-Raman/PL System consists of an external optical path (Witec confocal Raman/PL system), temperature component (liquid helium container), magnetic system (superconducting magnet), and the sealed X-Y-Z piezo stage. With the help of liquid helium and a temperature controller under the stage, the system can run from 4.3 to 100 K. The superconducting magnet is able to offer a high magnetic field up to 9 T along the vertical direction. Samples are fixed on the non-magnetic stage with three degrees of freedom, allowing a spatial Raman/PL mapping. The external optical path is a general backscattering configuration, similar to the room temperature Raman system illustrated in Figure 2.14. The excitation source is a CW 532 nm laser, and the spectrometer is equipped with two gratings of 600 and 1800 g/mm, meeting the requirement of PL and Raman measurements, respectively.

Figure 2.15 Schematic diagram of the custom magneto-Raman/PL system. (1) Witec

confocal Raman/PL system. (2) Cryogenic container for liquid helium. (3) Magnet system offering a vertical magnetic field. (4) X-Y-Z piezo stage for supporting the specimen. Reprinted with permission from: ref. [92], Copyright 2013, American Physical Society.

Chapter 3

Continuous-wave lasing from MAPbBr₃ nanoplates embedded microcavity

3.1 Introduction

Metal halide perovskites are generally in the basic form of ABX₃, where A represents organic/inorganic cations, such as methylammonium (MA⁺), formamidinium (FA⁺) and cesium (Cs⁺), B is a metallic cation, like lead (Pb²⁺) and tin (Sn²⁺), and X is a halide ion (i.e., Cl⁻, Br⁻, and I⁻). This category of semiconducting materials integrates unique properties of ultralong photocarrier diffusion length, large absorption coefficient, high quantum efficiency, and facile solution processability, thus leading to intriguing applications in photovoltaics[93-95], light-emitting diodes[96,97], photodetectors[98,99] and micro-/nanolasers[72,77,100]. Perovskites offer core opportunities for lasing emission, which benefits from their broadly tunable emission wavelengths and efficient radiative photocarrier recombination at high injection density[101]. Lasing emission in perovskites has been extensively studied under optical pumping with pulse lasers. For instance, Xing *et al.* has demonstrated the amplified spontaneous emission (ASE) in perovskite thin films with various compositions.[102] Using hybrid-perovskite nanowires as gain materials and a high quality (Q) factor Fabry-Perot cavity, Zhu *et al.* demonstrated nanolasers with a low threshold.[73] Using colloidal quantum dots as gain media, Kovalenko and his colleagues have realized ASE and whispering gallery mode lasers.[103]

Despite in-depth understandings into lasing emission under pulse excitation, only a few experimental demonstrations of continuous-wave (CW) lasing have been reported, which is regarded as a significant milestone towards the electrically pumped laser. Using MAPbI₃ thin

films coupled with a distributed feedback (DFB) cavity, Giebink and his colleagues demonstrated CW lasing emission by using a spontaneously formed mixed-phase system to concentrate photocarriers for sustaining population inversion at cryogenic temperature.[104] Recently, Adachi and his colleagues achieved stable CW lasing in quasi-2D perovskites by carefully fabricating a high Q-factor distributed feedback cavity and optimizing materials with suppressed singlet-triplet exciton annihilation.[105] The realization of CW lasers relies on a high Q-factor artificial cavity and carefully engineered highly crystalline materials with suppressed defect density and other non-radiative recombination processes. In particular, single-crystalline micro-/nanostructures with low defect densities are expected as an ideal platform for achieving robust CW lasing emission.[106,107] However, in previous reports, these single-crystalline structures only served as free-standing micro-/nanolasers, which exhibited relatively weak optical confinement. Vertical-cavity surface-emitting lasers (VCSELs) constructed by high-reflectance distributed Bragg reflectors (DBRs) is an effective configuration for providing a strong confined optical field to realize low-threshold CW lasers[108]. Especially, this kind of cavity, combining with solution-processed single-crystalline perovskites, is capable of achieving high optical gain and confinement simultaneously demanded low-threshold CW lasing.

In this chapter, we demonstrate CW lasing emission by embedding solution-grown single-crystalline MAPbBr₃ nanoplates in a vertical microcavity. A low threshold of 55.2 W cm⁻² has been realized in our VCSELs with a Q factor of 1140 based on these single-crystalline perovskite structures. The CW lasing emission has been observed at 80 K, where the MAPbBr₃ presents an orthorhombic phase with significant photoluminescence enhancement. The transition from tetragonal to orthorhombic phase in MAPbBr₃ nanoplates occurs at 140 K, which is characterized by *in-situ* temperature-dependent Raman spectroscopy. CW lasing in this system can be understood in terms of single-crystalline structures with low defect densities,

high optical confinement supported by the high Q-factor cavity, and suppressed parasitic recombination caused by phonon scattering at cryogenic temperature. This work highlights the importance of integration of single-crystalline materials and high-quality artificial microcavity in the realm of CW lasing based on metal-halide perovskites.

3.2 Experimental details

3.2.1 Synthesis of MAPbBr₃ nanoplates.

We modified the surface-initiated solution growth strategy[73,109] to prepare the single-crystal MAPbBr₃ platelets from a lead acetate (PbAc₂) thin-film reacted with a Methylammonium bromide (CH₃NH₃Br) solution in isopropanol (IPA) at room temperature. Typically, 35.9 mL methylamine (33% in ethanol) and 29.8 mL of hydrobromic acid (HBr, 48 wt% in water) were slowly mixed in an ice bath followed by stirring for 2 hours. Water was then evaporated in the water bath at 100 °C, and the product CH₃NH₃Br was washed with diethyl ether three times. At last, the CH₃NH₃Br was dried at 60 °C in an oven for 24 hours. The precursor PbAc₂ film was fabricated by drop-casting 100 mg/mL PbAc₂·3H₂O aqueous solution on a substrate (glass or SiO₂, ~1 cm²), and then dried in an oven for 30 min at 65 °C. The mass loading is about 1 mg/cm². The PbAc₂ thin film was carefully placed in 1mL CH₃NH₃Br/IPA solution (5 mg/mL) for about 20 hours to synthesize MAPbBr₃ (CH₃NH₃Br₃) platelets. The PbAc₂-casted facet kept down during the immersing process.

Figure 3.1 Schematic of the preparation process of MAPbBr₃ nanoplates. The blue block represents the cover glass substrate, the grey block represents the PbAc₂ layer, and the yellow block represents the prepared MAPbBr₃ nanoplates.

3.2.2 Fabrication of MAPbBr₃ VCSEL

The device was constructed on the commercial silica (300 nm)/silicon (0.5 mm) substrate. The high-purity (99.9%) SiO₂ and TiO₂ sources were utilized for fabricating both the bottom and top DBRs by an e-beam evaporator (Cello, Ohmiker-50B) with a high vacuum ($\sim 10^{-6}$ torr). In between, our synthesized MAPbBr₃ platelets were transferred on the bottom DBR *via* a dry transfer method. In detail, the Scotch tape was used to cover the prepared MAPbBr₃ platelets on the growth substrate for 5 min, then slowly peeled off. The tape with MAPbBr₃ platelets was carefully attached to the bottom DBR surface for another 5 min. After the tape was removed rapidly, the MAPbBr₃ platelets were deposited on the DBR.

3.2.3 Morphological and optical characterization

Scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) were obtained from a Zeiss Auriga Dual-Beam FIB/SEM system. The optical images and fluorescence images were attained from an Olympus microscope with a Mercury lamp.

The PL and Raman measurement was conducted by a confocal microscope system (WITec, Alpha 300). The 488 nm excitation laser source was used for PL measurement, while the 633 nm excitation laser source was used for Raman measurement. A 50 $\times$ objective (Nikon, LU Plan, NA = 0.55, WD= 10.1 mm) was used to focus the laser beam, with a spot size of 1.2 μ m on the sample surface. The *in-situ* temperature-dependent measurement was controlled by the Linkam optical DSC600 system, which provided a vacuum chamber to support the sample. The reflectivity spectra were collected from the backscattering configuration of the confocal microscope system, in which a white-light source was used to irradiate the sample perpendicularly with a 20 $\times$ objective lens (Zeiss, NA = 0.4, WD= 3.1 mm).

The PL measurement at lower temperatures from 13.5 K to 73.5 K was performed by a

custom-designed confocal microscope system (Attocube), with the excitation of a CW 532 nm laser.

3.3 Result and discussion

3.3.1 Basic characterization of MAPbBr₃ nanoplates

MAPbBr₃ (CH₃NH₃PbBr₃) nanoplates were fabricated in a modified solution-based approach (Figure 3.1). In particular, CH₃NH₃⁺ cation is surrounded by four nearest neighbor [PbBr₆]⁴⁻ octahedra consisting of Pb²⁺ cation and Br⁻ anion, and these octahedra share corners in their orthogonal directions to form [PbBr₃] frameworks.[110] X-ray diffraction (XRD) is a useful instrument to probe the crystal structure of crystalline materials. Figure 3.2 shows the collected powder XRD patterns of single-crystalline nanoplates on SiO₂ substrate at room temperature. The position of these sharp peaks shows the right consistency with the previous report, and the narrow width of each peak indicates the excellent crystal quality of the as-fabricated nanoplates[111]. Because the MAPbBr₃ single crystal accepted the cubic phase (*Pm* $\bar{3}$ *m*) at room temperature, the strongest peak locating at $2\theta = 15.0^\circ$ is corresponding to the (001) plane.

Figure 3.2 Powder XRD pattern of MAPbBr₃ nanoplates on SiO₂ substrate at room temperature.

Figure 3.3 (a) Schematic setup of PL measurement. The crystal structure of MAPbBr₃ is illustrated at the bottom. (b) Normalized PL spectra of solution-grown MAPbBr₃ nanoplates at room temperature (RT) and 80K. (c) Optical image and (d) fluorescence image of the perovskite nanoplates. (e) SEM image of a single MAPbBr₃ nanoplate. (f, g) Br and Pb distribution images for the MAPbBr₃ nanoplate in (e), respectively. Scale bar: 30 μ m for (c) and (d), 5 μ m for (e), (f) and (g).

The crystal structure and the schematic of photoluminescence (PL) measurements are shown in Figure 3.3.a. The MAPbBr₃ nanoplate was characterized by a confocal micro-PL configuration with a 488 nm laser. A polarizer was used to confirm the linear optical feature of the incident light. The PL spectra of MAPbBr₃ are plotted in Figure 3.3.b. The PL emission is centered at 529 nm at room temperature and shifts to 545 nm when the sample is cooled down to 80 K. The redshift and narrowing of the emission are mainly due to the phase transition and the reduced electron-phonon coupling.[112,113] As the optical image shown in Figure 3.3.c, our prepared MAPbBr₃ nanoplates have a regular rectangular shape with sizes ranging from 5 to 20 μm . Figure 3.3.d shows its corresponding fluorescence image. The morphological features of MAPbBr₃ nanoplates were further characterized by a scanning electron microscope (SEM, Figure 3.3e). The energy-dispersive X-ray spectroscopy (EDS) technique was used for the elemental analysis of MAPbBr₃ nanoplates. The EDS elemental mappings of Br and Pb (Figures 3.3.f and g) show the homogeneous distributions of these elements in nanoplates with a ratio of 3:1 (detailed EDS spectrum in Figure 3.4), which is in accordance with the expected stoichiometry. The EDS spectrum shows a high C atom%, which is attributed to the synthesis process of MAPbBr₃ nanoplates. The nanoplates were grown from IPA solvent and were rinsed by IPA after the growth process. Therefore, the residual IPA on the sample surface induced a high C atom% in the EDS spectrum.

Figure 3.4 EDS spectrum of our fabricated MAPbBr₃ nanoplates. The inset shows the atomic ratios of elements in the spectrum.

3.3.2 Phase-transition characterization of MAPbBr₃ nanoplates

Figure 3.5 Phase-transition characterization of as-grown MAPbBr₃ nanoplates. (a) Temperature-dependent Raman spectra at low frequency. (b) Temperature-dependent Raman spectra at high frequency. Two typical modes are presented in the right panel, where the red arrows denote the atomic displacements. (c) Raman shifts for N–H symmetric bending modes [$\delta_s(\text{NH}_3^+)$] (blue dots) and asymmetric bending modes [$\delta_{as}(\text{NH}_3^+)$] (red squares) as a

function of temperature. (d) Peak linewidth (FWHM) for $\delta_s(\text{NH}_3^+)$ and $\delta_{as}(\text{NH}_3^+)$ as a function of temperature.

Temperature-dependent Raman spectroscopy is a high-efficiency approach to probe the evolution of atomic vibrations of as-prepared MAPbBr₃ nanoplates associated with the phase transition. To exclude the disturbance of PL emission to Raman signals, a 633 nm laser was used for the Raman measurements. *In-situ* temperature Raman spectra in the low-frequency range are shown in Figure 3.5.a, which were collected from 300 to 80 K with the step of 20 K. At room temperature, Raman scattering peaks are inconspicuous. When the temperature is cooled down to 220 K, a broad and flat trait emerges at $\sim 75 \text{ cm}^{-1}$, which results from the half dynamic disorder of the organic MA groups. When the temperature reaches 140 K, the sharp peaks arise, which corresponds to the tetragonal-to-orthorhombic phase transition. This distinct region from 50 cm^{-1} to 200 cm^{-1} is caused by the vibrations of inorganic PbBr₆ octahedra.[114,115] Figure 3.5.b shows the temperature-dependent Raman peaks ranging from 600 to 1800 cm^{-1} , which are attributed to MA cations vibration. The Raman peak at 914 cm^{-1} is assigned to the MA rocking mode [$\rho(\text{MA})$]. The Raman spectra ranging from 905 - 1017 cm^{-1} display undistinguished peaks at room temperature. As the temperature decreases to 220 K, the narrow peak at 914 cm^{-1} can be observed, which can be attributed to the constriction of the inorganic cages during the phase transition from cubic to tetragonal phase.[116] In particular, when the temperature further decreases to 140 K, the Raman peak becomes sharp and intensive dramatically. Similar behavior was also observed in the Raman peak at 967 cm^{-1} , which was attributed to the C-N stretching mode [$\nu(\text{C-N})$].[23] The higher frequency range beyond 1300 cm^{-1} is related to the bending (δ) of the NH_3^+ and CH_3 groups. For instance, the symmetric N-H bending mode [$\delta_s(\text{NH}_3^+)$] appears at 1476 cm^{-1} , while the asymmetric bending mode [$\delta_{as}(\text{NH}_3^+)$] is located at 1590 cm^{-1} . By carefully analyzing the temperature-dependent frequency, both $\delta_s(\text{NH}_3^+)$ and $\delta_{as}(\text{NH}_3^+)$ undergo redshifts from 300 to 160 K (cubic to

tetragonal phase) without any significant kink. However, when the temperature decreases from 140 to 80 K (orthorhombic phase), $\delta_s(\text{NH}_3^+)$ displays a redshift while $\delta_{as}(\text{NH}_3^+)$ shows the opposite trend (Figure 3.5.c). Recent studies have suggested the hydrogen-bonding interactions between the MA cations and halide anions of the PbBr_6 octahedra vary during the phase evolution. Such phase-sensitive bonding strength variation can be employed to determine the phase-transition temperature.[39,116-118] In the cubic and tetragonal phase, the hydrogen bonds are only formed betwixt the NH_3^+ functional group and the PbBr_6 framework, but the CH_3 group is free of the inorganic cage. Therefore, the redshifts of $\delta_s(\text{NH}_3^+)$ and $\delta_{as}(\text{NH}_3^+)$ in the cubic and tetragonal phases are due to the weakening of the N-H bond. Amid the tetragonal-orthorhombic phase transition, the CH_3 forms the hydrogen bonds with PbBr_6 octahedra, which locks the CH_3 group with the inorganic cage and results in the reorientation of the NH_3^+ group.[116] Therefore $\text{H}_\text{N}\cdots\text{Br}$ bonding becomes weakened in the orthorhombic phase, which releases the $\delta_{as}(\text{NH}_3^+)$ mode and thus leads to a blueshift, whereas it restricts the $\delta_s(\text{NH}_3^+)$ mode to result in a redshift. As presented in Figure 3.5.d, the line widths of $\delta_s(\text{NH}_3^+)$ and $\delta_{as}(\text{NH}_3^+)$ become narrow when the temperature decreases because the inorganic cages are contracted, and the degrees of freedom are restricted. A sudden drop takes place at 140 K because additional $\text{H}_\text{C}\cdots\text{Br}$ bonds are formed and work together with $\text{H}_\text{N}\cdots\text{Br}$ bonds to lock MA cations arranging orderly in the orthorhombic phase. These strong hydrogen bonding interactions result in distinctive optical properties in the low-temperature orthorhombic phase.

The transformation of MAPbBr_3 crystal structure via the chemical bonding interactions at various temperatures affects the electronic properties. In order to further investigate the evolution of the electronic structure during the phase transition, we study the photoluminescence characteristics of MAPbBr_3 nanoplates by decreasing the temperature. The temperature-dependent PL measurement was conducted from 300 to 80 K, with a step of 20 K. As shown in Figure 3.6.a, the contour map of temperature-dependent PL exhibits the

remarkable boundaries at 240 K and 140 K, which is related to the representative transition temperatures. During the cooling process, the PL intensity is enhanced enormously (Figure 3.6.b). From 300 to 240 K (blue region, cubic phase), only slight PL intensity enhancement was observed, while further cooling leads to much more significant enhancement. The intensity is enhanced by 15 times at 160 K (tetragonal phase) and 40 times at 80 K (orthorhombic phase), respectively. An uncommon redshift of the PL emission peak can be seen in each individual phase during cooling (Figure 3.6.c). However, a blueshift can be observed around the phase transition temperature, which indicates the bandgap boarding of MAPbBr₃ when the phase transformation is taking place with a decrease of temperature.[116] Considerably, the blue shift of PL emission peak is much more distinct between the transition from the tetragonal to orthorhombic phase compared with the transition from cubic to tetragonal phase. These results are consistent with our previous temperature-dependent Raman measurements, which confirm the formation of H_C⋯Br bonds confining the structural arrangement of MA cations and PbBr₆ octahedra in the low-temperature orthorhombic phase. In addition, considering the much larger enhancement of PL intensity in tetragonal and orthorhombic phases, MAPbBr₃ favors the direct bandgap feature in these ordered phases, while it shows the indirect bandgap character in the cubic phase[116].

Figure 3.6 Temperature-dependent photoluminescence characterization. (a) The contour map of the temperature-dependent PL. The dash lines are used to mark phase transition temperatures as 140K (upper) and 240K (lower), respectively. The excitation power is 200 nW. (b) Integrated Intensity and (c) Peak position of photoluminescence emission as a function of temperature. The yellow, green, and blue regions represent orthorhombic, tetragonal, and cubic phases, respectively.

Figure 3.7 Study of the intrinsic photophysics of MAPbBr₃ nanoplates. (a) Temperature-dependent PL spectra recorded from 13.5 to 73.5 K. (b) Integrated PL intensity as a function of temperature, which is fitted with the Arrhenius-like equation (red curve). (c) FWHM of PL emission as a function of temperature, the solid red line represents the linear fitting.

In order to have better insight into the intrinsic photophysics and eliminate the thermal perturbation, the cryogenic temperature photoluminescence spectrum of the MAPbBr₃ single-crystalline nanoplates have been investigated. As shown in Figure 3.7.a, *in-situ* temperature-dependent PL spectra are recorded from 13.5 to 73.5 K under the excitation of a 532 CW laser. At 13.5 K, the dominantly sharp peak of the PL spectrum locates at 552 nm, corresponding to 2.25 eV, attributed to recombination of the free exciton (FE), while the wide and weak band at the low-energy side is assigned to recombination of the localized excitons on the trap state. According to the previous report[119,120], such a narrow emission related to FE vanishes completely in the cryogenic temperature PL spectra of the spin-coated thin film, which are dominated by trap state bands originated from the inhomogeneities of the surface or interface on the boundary of grains. Thus, this free exciton emission is the fingerprint for the single-crystalline lead halide perovskite, indicating the low-defect density of the crystal.

Because the orthorhombic phase is stable below 140 K, intrinsic physical factors of perovskite single crystal, including exciton binding energy and exciton-phonon interaction, can be reckoned from the *in-situ* temperature-dependent PL spectra. Figure 3.7.b displays the thermal evolution of the integrated PL intensity of the FE band, which can be fitted by the Arrhenius-like equation:[121]

$$I(T) = \frac{I_0}{1 + Ae^{-E_b/k_bT}}$$

Where I_0 represents the emission intensity at 0 K, A is a fitting parameter, E_b is the binding energy of the exciton, and k_b stands for the Boltzmann constant. From the fitting, the estimation of E_b is 21.1 meV, consistent with the reported value obtained from the MAPbBr₃ single crystal[120,122].

Figure 3.7.c shows the thermal evolution of the FWHM (Γ) of the FE band of MAPbBr₃ perovskites at cryogenic temperature. Since the intrinsic phonon broadening is mostly affected

by the electron-phonon interaction, so the strength of which can be appraised from the FE width. In general, the evolution of Γ with the temperature can be fitted with the independent Boson model:[123]

$$\begin{aligned}\Gamma(T) &= \Gamma_0 + \Gamma_{ac} + \Gamma_{LO} \\ &= \Gamma_0 + \gamma_{ac}T + \frac{\gamma_{LO}}{e^{E_{LO}/k_B T} - 1}\end{aligned}$$

Where Γ_0 is the temperature-independent inhomogeneous broadening at 0 K, Γ_{ac} and Γ_{LO} represent the homogeneous broadening caused by the acoustic phonon scattering and the optical phonon (LO) scattering, respectively. The corresponding coupling strengths between exciton and phonon are γ_{ac} and γ_{LO} , and E_{LO} stands for the energy of the LO phonons. At temperatures below 80K, the broadening mechanism is governed by the coupling to an acoustic phonon, while the contribution of optical phonon is negligible[122,124]. Thus, it is reasonable to fit the FWHM with a linear function. The estimated values of Γ_0 and γ_{ac} are 3.94 meV and 0.08 meV/K, respectively, which are agreed well with the previous report[119,122]. Such a low value of inhomogeneous broadening suggests the excellent optical quality of the single-crystalline MAPbBr₃ nanoplates with low-density defects.

3.3.3 Structure of the vertical microcavity

The excellent emission properties of our MAPbBr₃ samples at the low temperature give us an opportunity to realize CW pumped lasing. Owing to its intrinsically short resonance loop, a VCSEL configuration with a large gain factor and low optical loss could be an excellent choice for achieving lasing from our MAPbBr₃ nanoplates. In the previous report, separate multilayer distributed Bragg reflector (DBR) mirrors with high reflectivity were used to construct the vertical microcavity lasers with perovskites.[65,125,126] DBR is constructed by multilayers of alternative dielectric materials with a diverse refractive index. In theory, the

thickness of each dielectric layer is determined by the equation:

$$L = \frac{\lambda}{4n}$$

where λ is the wavelength of the reflected optical wave, n is the refractive index of the dielectric layer. The dielectric layers are profitable to highly efficient reflectors due to constructive interference. As shown in Figure 3.8.a, we pre-deposited a 100 nm SiO₂ layer for avoiding the possible strain effect, followed by depositing 12 pairs of alternating quarter-wavelength-thick TiO₂/SiO₂ layers with a large refractive index contrast to form high reflective bottom DBRs. Subsequently, the perovskite nanoplates were transferred onto bottom DBRs *via* a dry transfer method (see Experimental Section). Then, top DBRs with 8 pairs of SiO₂/TiO₂ layers were fabricated to build up a high-quality perovskite VCSEL. Figure 3.8.b presents a typical cross-sectional SEM image of our vertical microcavity. The regular structures with distinct boundaries can be recognized. The brown block is used to mark the TiO₂ layer with a thickness of 52 nm, and the blue block presents the SiO₂ layer with a thickness of 98 nm. The embedded MAPbBr₃ nanoplates are located between two SiO₂ layers of the bottom DBRs and the top DBRs, respectively. The reflection spectrum of bare TiO₂/SiO₂ microcavity, as shown in Figure 3.8.c, exhibits the broad stopband (460 nm ~ 560 nm) with the high reflectivity ($R > 98.5\%$), which covers the anticipated optical gain window of MAPbBr₃ nanoplates. The atomic force microscope (AFM) image and the corresponding height profile of embedded MAPbBr₃ nanoplates are presented in Figures 3.8.d and e, respectively. The measured thickness of the perovskite nanoplate is around 402 nm, which is sufficient to sustain Fabry-Pérot oscillations. Therefore, the additional spacer is not necessary.

Figure 3.8 Structure of a vertical microcavity with dielectric distributed Bragg reflector (DBR) mirrors. (a) Schematic of a MAPbBr_3 embedded microcavity on the SiO_2/Si substrate containing 12 pairs of bottom $\text{TiO}_2/\text{SiO}_2$ DBRs and 8 pairs of top DBRs. (b) Typical cross-sectional scanning electron microscope (SEM) image of the microcavity. (c) Reflectivity spectrum of bare $\text{TiO}_2/\text{SiO}_2$ microcavity. (d) Atomic Force Microscope (AFM) image of the embedded MAPbBr_3 nanoplate. (e) The corresponding height profile of the selected zone in (d). Scale bar: $1\mu\text{m}$ for (b) and $5\mu\text{m}$ for (d).

3.3.4 MAPbBr₃ perovskite lasing characteristics at 80 K.

Figure 3.9 MAPbBr₃ perovskite VCSEL characteristics at 80 K. (a) Representative emission spectra at the range from 535 to 555 nm under varied pump intensity. (b) Input-output characteristic of the laser under continuous excitation with the wavelength of 488 nm, demonstrating a distinct threshold at about 55 W cm⁻². Blue dots represent the FWHM of the emission spectrum, which decreases to 0.44 nm after traversing the threshold. (c) Intensity polar plot of lasing (black square), exhibiting linear polarization with DOP to be 92%.

The emission characteristics of the perovskite VCSEL are presented in Figure 3.9. The representative PL spectra of the VCSEL devices at 80 K are shown in Figure 3.9.a, which is excited by a 488 nm (CW) laser. As the excitation power density is below the threshold (8.49 W cm⁻²), only the broad spontaneous emission was observed. When the excitation power

density increases to around the threshold (55.2 W cm^{-2}), some sharp peaks emerge besides the spontaneous emission. As the excitation power density continuously increases to 138 W cm^{-2} , the sharp peak around 547.1 nm becomes much stronger, which is attributed to major lasing emission. The other two low-intensity modes may result from the surface roughness of the perovskite nanoplate and the local anisotropy in DBR, which can cause changes in the cavity length. As shown in Figure 3.9.b, the light input-output characterization exhibits the transition from the broad spontaneous emission to the predominant lasing emission with the increase in excitation intensity. The emission intensity as a function of excitation power shows an obvious kink at 55.2 W cm^{-2} , signifying the onset of lasing. The blue dots represent the full width at half maximum (FWHM) of the emission, which narrows from 4.3 nm to 0.44 nm after traversing the threshold. The Q-factor is about 1140, which could be simply calculated from the sharp emission peak at 547.1 nm with the FWHM of 0.48 nm . As presented in Figure 3.9.c, the lasing emission is linearly polarized with the degree of polarization $[\text{DOP} = (I_{\text{max}} - I_{\text{min}})/(I_{\text{max}} + I_{\text{min}})]$ about 92%. Moreover, a few modes normally exist in a resonant cavity, and the intensity of the specific lasing mode develops much more rapidly than that of the others with the increase of the excitation power. The competition of different cavity modes is a fingerprinting feature of a laser device with a consistently distributed medium.[127] The coherent light is generated due to the coexistence of the identical phase, directionality, and polarization in the incident and emitting waves.

The threshold with the pump intensity of 55.2 W cm^{-2} is strikingly low, which reaches the lowest magnitude comparing to the existent CW pumped perovskite lasers.[104] [106,128] DBR can efficiently reflect optical wave and enhance the emission, contributing to the high Q-factor and effectively optical confinement effect in VCSEL structure. By comparing the PL emission of MAPbBr_3 nanoplates on SiO_2 with that on bottom DBR, we could find the intensity is enhanced by 2.5 times (Figure 3.10). Even though no obvious lasing behavior was observed

in our samples at room temperature (Figure 3.11), in comparison to other perovskite nanostructure-based lasers without the external cavity, such as nanowires[106], a threshold of 6 kW cm^{-2} at 77 K, our perovskite nanoplates sandwiched in microcavity have a much lower threshold of 55.2 W cm^{-2} at 80 K. The low threshold CW lasing in our case benefits from three unique advantages, including: (i) single-crystalline perovskite gain materials with suppressed defect density and undesired non-radiative recombination, (ii) strong optical confinement supported by high Q microcavity, and (iii) orthorhombic phase with the greatly enhanced PL efficiency due to the direct bandgap nature and suppressed phonon scattering at cryogenic temperature.

Figure 3.10 PL spectra of MAPbBr₃ nanoplates on DBR (red curve) and SiO₂ (black curve) substrate.

Figure 3.11 Power dependent photoluminescence of a MAPbBr_3 embedded microcavity at room temperature, where no representatively sharp peak was observed.

3.4 Conclusion

High-quality MAPbBr_3 nanoplates have been successfully prepared by a modified solution-grown method in the ambient atmosphere, which is easy and low cost because it does not require the glove box or vacuum environment. The phase transition of the prepared MAPbBr_3 crystal has been systematically probed by temperature-dependent Raman scattering, which has further confirmed the crystal in orthorhombic phase at 80 K. Considering the outstanding light-emitting performance at low temperature, the MAPbBr_3 nanoplates were employed as the gain medium, which was sandwiched by two sets of high-reflectivity DBRs to form a high Q-factor vertical cavity surface emitting laser. Ultralow threshold CW lasing has been observed at 80 K, which is verified by the intensity kink of the light input-output curve, the linewidth narrowing, and the linear polarization. This work paves a way to realize ultralow threshold lasing of lead halide perovskites with CW optical pumping and represents a major step towards practical coherent light applications based on the rising gain media of lead halide perovskites.

Chapter 4

Continuous-wave lasing from all-inorganic CsPbBr₃ quantum dots embedded microcavity

4.1 Introduction

Metal halide perovskites are a fantastic family of semiconductors with a basic structure of ABX₃ in usual, where A can be organic cation like methylammonium (CH₃NH₃⁺), formamidinium (NH₂CH=NH₂⁺), or inorganic cation like cesium (Cs⁺), B is a metallic cation including lead (Pb²⁺) or tin (Sn²⁺) and X represents halide anion such as iodide (I⁻), bromide (Br⁻) or chloride (Cl⁻). Inspired by the unprecedented success in solar cells[9,37,129], metal halide perovskites have attracted more and more attention due to their superior properties of ultralong photocarrier diffusion length, large absorption coefficient, high quantum efficiency, facile solution processability and defect tolerance[130], which leads to the promising applications in novel photonic and optoelectronic devices such as light-emitting diode (LED)[131,132], photonic detectors[133,134], and optical sensors[135]. As a direct bandgap semiconductor, such excellent performances are benefited from their broadly tunable emission wavelengths, efficient radiative recombination, and strong excitonic effects, which are also widely believed as crucial characteristics for developing practical lasers[136]. In the past few years, many efforts have been made to achieve lasing emission from metal halide perovskites. For example, Xing *et al.* has reported the tunable amplified spontaneous emission (ASE) in CH₃NH₃PbX₃ (X = I, Br, Cl) perovskite thin films[102]. Using CH₃NH₃PbI_{3-a}X_a nanoplatelets as the gain material, nanolasers at room temperature have been demonstrated in the self-built whispering-gallery resonance cavity.[79] By employing colloidal perovskite quantum dots as

gain material, Wang *et al.* have observed ultra-stable stimulated emission and fabricated whispering gallery mode lasers.[137]

In advance of perovskite lasing emission under the pulse laser excitation, experimental demonstrations and in-depth understandings of continuous-wave (CW) lasing from lead halide perovskites are still at the infant stage, but highly demanded as prerequisites for realizing electrically pumped lasers. Recently, limited attempts of CW perovskite lasers have been reported[104,106,128]. By coupling MAPbI₃ thin films with a distributed feedback (DFB) cavity, Giebink and his colleagues obtained CW lasing emission from a mixed-phase system at 102 K.[104] Zhu *et al.* also realized the CW lasing in CsPbBr₃ nanowires at 77 K, which originated from exciton-polariton interactions.[106] Gu and his colleagues demonstrated a room-temperature CW laser based on the directly printed CH₃NH₃PbI₃ thin film as a high Q-factor second-order DFB cavity.[128] However, most of the existing CW lasers are operated at low temperatures with multi-mode or exhibit severe degradation in a few minutes under continuous pumping at room temperature. Therefore, CW perovskite lasers with room-temperature operation, environmental stability, and single-mode emission are highly desired.

Contemporarily, to meet the needs of the wide range of practical applications in the integrated optical circuit[138], fiber-optic communication[139], quantum computing[140], coherent light source and higher-capacity storage[141], vertical-cavity surface-emitting laser (VCSEL) is one of the most considerable and favored lasers since its capacity to construct compatible planar arrays, high spatial directivity perpendicular to the surface, excellent beam emission, and silicon-based substrate preference. Intrinsically, a classic VCSEL is formed by sandwiching gain material between two distributed Bragg reflectors (DBRs). Structurally, the DBRs are constructed by pairs of quarter-wavelength-thick dielectric oxides with different refractive indexes, which can provide high reflectivity resulting from the synergistic effect of

constructive interference. As a result, the cavity formed by DBRs would trap the light as a standing wave and support the optical oscillation. In most conventional III-V VCSELs, the device fabrication requires complicated epitaxial techniques, in which the challenge of lattice-mismatching and built-in strain must be overcome carefully[142]. All inorganic CsPbBr₃ quantum dots (QDs), which own the near-unity photoluminescence quantum yield[143] and much higher stability in the ambient condition compared with organic hybrid perovskites[144], are definitely the ideal gain materials worked for high-performance, market-ready VCSELs.

In this chapter, we demonstrated a solution-processed CsPbBr₃ QDs embedded VCSEL under CW pumping at room temperature. With the help of a high Q factor microcavity, a single-mode lasing emission has been observed at an ultra-low threshold of 8.8 W cm⁻², which is comprehensively lower than the lasing threshold values reported in existing perovskite QDs lasers. The apparent features of spectral narrowing, nonlinear evolution of the emission intensity, and directional emission systematically manifest the emergence of lasing emission. The fabricated CsPbBr₃ QDs VCSEL exhibits excellent stability, which not only sustains single-mode lasing at room temperature for 300s under continuously optical pumping without any obvious degradation, but also reserves its outstanding lasing performance after one-year preservation. These findings not only provide a strategy to design and fabricate planar solution-based perovskite VCSEL, but also marks a significant advancement towards the next-generation of coherent light sources.

4.2 Experimental details

4.2.1 Synthesis of CsPbBr₃ QDs

We modified the hot-injection strategy to prepare CsPbBr₃ QDs. Typically, PbBr₂ (0.72 mmol), oleic acid (2.0 ml), oleylamine (2.0 ml), and octadecene (20 ml) were mixed in a two-neck flask and heated to 100 °C with strong stirring for 30 min. The container was kept in a

vacuum by filling and evacuating N₂. after all PbBr₂ dissolving with the Continuously heating to 160 °C, the thermal Cs-oleate precursor solution (2 ml) was injected. A few sec later, the reaction was stopped by an ice bath. The product CsPbBr₃ QDs were collected and washed with cyclohexane by centrifugation at 10000 rpm several times. Finally, the as-prepared CsPbBr₃ QDs were conserved in 10 ml of cyclohexane.

4.2.2 Fabrication of CsPbBr₃ QDs VCSEL

The device was constructed on the commercial silica (300 nm)/silicon (0.5 mm) substrate. The high-purity (99.9%) SiO₂, TiO₂, and Ta₂O₅ sources were utilized for fabricating the bottom and top DBRs by an e-beam evaporator (Cello, Ohmiker-50B) with a high vacuum ($\sim 10^{-6}$ torr), respectively. Before being spin-coated on the bottom DBRs, our synthesized CsPbBr₃ QDs were diluted to 1000 times and mixed with PMMA.

4.2.3 Morphological and optical characterization

Scanning electron microscopy (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) were obtained from a Zeiss Auriga Dual-Beam FIB/SEM system. Transmission electron microscopy (TEM) images were acquired from JEM-ARM200F Analytical Electron Microscope (JEOL). Atomic force microscopy (AFM) images were acquired from an Asylum Research Cypher ES Scanning Probe Microscope.

The PL and Raman measurements were conducted by a confocal microscope system (WITec, Alpha 300). The 488 nm excitation laser source was used for PL measurement, while the 633 nm excitation laser source was used for Raman measurement. A 50× objective (Nikon, LU Plan, NA = 0.55, WD= 10.1 mm) was used to focus the laser beam, with a spot size of 1.2 μm on the sample surface. The low-temperature PL measurement was conducted by the Linkam DSC600 cooling stage with a vacuum chamber. The reflectivity spectra were collected from the backscattering configuration of the confocal microscope system, in which a white-light

source was used to irradiate the sample perpendicularly with a 20× objective lens (Zeiss, NA = 0.4, WD= 3.1 mm).

4.2.4 Theoretically simulation

The simulated reflection spectrum and electric field distribution were calculated with Lumerical FDTD Solutions.

4.3 Result and discussion

4.3.1 Basic characterizations of the synthesized CsPbBr₃ quantum dots

We synthesized the CsPbBr₃ Quantum dots (QDs) via a modified hot injection solution method.[145] In particular, the cesium precursor, like Cs-oleate, was first synthesized by solution method at a nitrogen atmosphere, and kept at 150 °C in solution. The PbBr₂ related precursor was prepared *via* a similar step and held at 160°C in solution. Then the hot cesium precursor was injected quickly into the PbBr₂ related precursor solution. After centrifuging and washing, the CsPbBr₃ QDs were attained. As shown in Figures 4.1.a and b, the as-fabricated CsPbBr₃ QDs exhibit yellow in solution, which radiates strong green light after illuminated by a UV lamp. Figure 4.1.c displays the TEM image of the CsPbBr₃ QDs under a large magnification. The statistic results of as-fabricated CsPbBr₃ QDs collected from the TEM image are shown in Figure 4.1.d, where the histogram for the size distribution of the CsPbBr₃ QDs matches with a normal distribution. The CsPbBr₃ QDs show a cubic shape with a dominant edge length of about 10 nm. Basic optical characterization is convenient and reliable to examine the quality of as-fabricated CsPbBr₃ QDs samples. Typically, under the excitation of 488 nm CW laser at room temperature, the CsPbBr₃ QDs on the SiO₂/Si substrate exhibit the PL emission with a narrow linewidth of 15 nm at 519.2 nm (Figure 4.1.e), which is corresponding to the excitonic emission at 2.39 eV. Besides, the Raman spectrum excited by a 633 nm continuous wave laser is shown in Figure 4.1.f, where there are three obvious Raman-

active modes at 72.1, 125.3, and 310.7 cm^{-1} , respectively. Coincident with the previous study, the peak at 72.1 cm^{-1} is ascribed to the vibrational mode of $[\text{PbBr}_6]^{4-}$ octahedron[114]. Notably, the transverse-optical (TO) phonon mode at 125.3 cm^{-1} related to the Pb–Br stretching vibration slightly stiffens compared to the previous report[146], which is possibly due to the lattice distortion as the size of CsPbBr_3 QDs decreases. The weak and broad peak at 310.7 cm^{-1} can be attributed to the second-order phonon mode of the $[\text{PbBr}_6]^{4-}$ octahedron.[147]

Figure 4.1 Basic characterizations of the synthesized CsPbBr_3 quantum dots. Optical image (a) of CsPbBr_3 quantum dots in solution and fluorescence image (b) excited by the ultraviolet light. (c) Typical TEM image of CsPbBr_3 quantum dots, scale bar: 50 nm. (d) Histogram for the size distribution of the CsPbBr_3 QDs obtained from TEM image analysis. The solid line is a fit with a normal distribution, the given mean size (9.8 nm) and standard deviation (0.97 nm) are obtained from the fitting method. (e) PL spectrum of CsPbBr_3 quantum dots at room temperature. The emission peak is at around 519.2 nm. (f) Raman spectrum of CsPbBr_3

quantum dots at room temperature, the arrows denote the Raman peaks at 72.1, 125.3, and 310.7 cm⁻¹, respectively.

4.3.2 Construction and characterization of the microcavity

Due to the outstanding light-emitting performances at room temperature, the CsPbBr₃ QDs was exploited as an optical gain medium for the lasing study. In order to achieve highly efficient lasing, it is critical to satisfying the rigorous demand of sufficient optical gain and affordable losses. The VCSEL constructed by two DBRs with high reflectivity (> 99%) has been adopted for the lasing characterization. As shown in the schematic diagram of planar microcavity (Figure 4.2.a), the bottom DBRs consist of twelve pairs of quarter optical-wavelength-thick SiO₂/TiO₂ (98 nm/52 nm) layers to assure extremely high reflectivity. It is worth mentioning, the deposition of the bottom DBRs was not conducted until one layer of SiO₂ was deposited in advance to lessen the strain effect from the SiO₂/Si substrate. To achieve the discrete distribution, the as-synthesized CsPbBr₃ QDs solution was diluted to 1000 times. After mixing the diluted CsPbBr₃ QDs with poly (methyl methacrylate) (PMMA) sufficiently, the mixture was spin-coated on the bottom DBRs with a thickness of about 400 nm. Notably, the PMMA plays an essential role in protecting the fragile perovskite QDs, conserving their electronic and optical quality, as well as operating as the spacer to support Fabry-Pérot resonance. Finally, the top DBRs containing ten pairs of quarter optical-wavelength-thick SiO₂/Ta₂O₅ (88 nm/60 nm) layers were deposited via e-beam evaporation. We chose Ta₂O₅ instead of TiO₂ to fabricate the top DBRs due to its lower intrinsic melting point, which could avoid the drastic increase of the temperature in the chamber and protect the delicate perovskite samples. Figure 4.2.b shows the typical cross-sectional scanning electron microscope (SEM) image of the as-fabricated piece. The interfaces between the dielectric oxide layers can be recognized clearly in the periodic structures of the cavity. The normalized reflection spectra of top and bottom DBRs have been measured, as shown in Figure 4.2.c, the reflectivities of which

are 98.7 and 99.6%, respectively. It is vital for VCSEL to overcome the short optical gain length *via* the high reflection mirrors. The broad high-reflectivity region of the stopband from 490 to 570 nm covers the overall spontaneous emission of CsPbBr₃ perovskites and results in strong optical confinement. Figure 4.2.d shows the comparison of the representative PL spectrum (black trace) of CsPbBr₃ QDs on the SiO₂/Si substrate and the lasing emission (red trace) of CsPbBr₃ ODs in the cavity. Compared with the spontaneous emission spectrum of CsPbBr₃ on the SiO₂/Si substrate, the full width at half maximum (FWHM) of the lasing emission spectrum of CsPbBr₃ embedded in the microcavity is narrowed from 15 nm to 0.3 nm while the peak redshifts from 519.2 nm to 536.1 nm, which can be attributed to the strong optical confinement of the cavity. As shown in Figure 4.2.e, the enlarged perpendicular reflection spectrum of CsPbBr₃ embedded in the microcavity (in black) exhibits a dip at 536.1 nm with a width of about 0.5 nm, which is related to the typical cavity photon mode. The lasing emission spectrum with a well-defined single-mode (in red) is also presented in Figure 4.2.e, which locates at the same position of the dip, with a narrower width of about 0.3 nm, suggesting a characteristic quality factor Q of about 1787.

Figure 4.2 *Structure and characterization of the microcavity. (a) Schematic image of the CsPbBr₃ quantum dots VCSEL. (b) Typical cross-sectional scanning electron microscope (SEM) image of the microcavity. Scale bar: 1 μ m. (c) Reflectivity spectrum of top DBRs (Ta₂O₅/SiO₂, red trace) and bottom DBRs (TiO₂/SiO₂, black trace). (d) Typical PL spectrum (black trace) of QDs on the SiO₂/Si substrate and single-mode lasing emission (red trace) of the ODs embedded cavity. (e) Reflection spectrum (black trace) and lasing mode (red trace) of the CsPbBr₃ QDs embedded microcavity.*

4.3.3 Lasing characterization of CsPbBr₃ QDs VCSEL

To further explore the lasing characteristic of CsPbBr₃ QDs VCSEL, we employed a 488 nm CW laser as the pumping source for the detailed PL measurement. The demonstrative PL spectrum of CsPbBr₃ QDs VCSEL in Figure 4.2.d presents a sharp lasing emission (LE) peak locating at 536.1 nm, and a tolerably weak emission band resulting from leaked spontaneous emission (LSE). In particular, the steady-state PL spectra of this perovskite VCSEL sample pumped by low-excitation powers (i.e., ≤ 120 nW) are shown in Figure 4.3.a, with a narrow range from 534 to 539 nm. The emission band grows and narrows as excitation power increases. Compared with the LE peak, the ignorable LSE band indicates a small amount of loss. Figure 4.3.b shows the PL spectra at higher excitation powers in the broad spectral ranges. With the increase in excitation power, the evolution of the emission peak at 536.1 nm has been explored. Figure 4.3.c exhibits the integrated PL emission intensity as a function of excitation power, known as the light input-light output curve (L-L curve). When the excitation power overpasses a specific value, the dramatic increase of PL emission intensity can be identified, which suggests that the threshold is reached and lasing emission takes place in the sample. As shown in Figure 4.3.d, the L-L curve is plotted on a log-log scale with the intention of displaying the kink point more pronouncedly, which appears at around 100 nW. There are three regions assorted as spontaneous emission (SE), superlinear amplification (SLA), and lasing emission,

respectively. The SE data (in light blue) lays out a sublinear dependence, which can be likely attributed to the reabsorption induced by the DBR mirrors[148] and the quenching of exciton emission resulting from nonradiative recombination process such as exciton-exciton annihilation.[108] The SLA range (in orange) exhibits the superlinear characteristic, while the lasing range (in green) shows the nearly linear behavior. In brief, such a nonlinear characteristic in the L-L curve is a robust mark of lasing. It is noted that the transition features from sublinear to superlinear have also been observed in microcavity lasers based on organic single crystals[149] and 2D transition metal dichalcogenides[108], which are strongly correlated with the large excitonic systems being analogous to lead halide perovskites cases[148,150]. In the meantime, Figure 3e shows the evolution of allied peak widths under the various excitation powers. The emission peak narrows during the transition from spontaneous emission to superlinear amplification, and the width decreases from about 0.6 to 0.35 nm, reducing the ratio to 58.3%. The width of the emission peak is much smaller than those of previous CsPbBr₃ QDs VCSELs under the femtosecond pulse excitation. For example, the values of the LE width have been reported as 0.9 nm by Huang *et al.* [148] and 0.6 nm reported by Wang *et al.* [67], indicating the high Q-factor and strong light confinement of our VCSEL sample. Moreover, the bandwidth maintains almost steady at the higher excitation powers of the corresponding lasing emission region. The narrowing of the peak has commonly been observed in other perovskite lasers[67,148] and semiconductor VCSEL[108], which is another typical feature for the evolution from spontaneous emission to lasing emission. Combining the change of the intensity and the width with the increasing excitation power, the extracted lasing threshold is at about 100 nW, corresponding to 8.8 W cm^{-2} , which is much lower than the threshold of 15 W cm^{-2} reported by the latest CW pumped CsPbBr₃ QD laser[151]. In addition, the corresponding peak positions at different excitation powers are shown in Figure 4.3.f, indicating a slight blue-shift of about 0.06 nm over one order of magnitude range of excitation

power during the transition. Unlike the large blueshift up to several nanometres for the classic polariton lasing[150,152], this delicate blueshift of our sample may relate to self-heating of perovskite sample, which is considerable for continuous-wave operation at room temperature.[73,128,153] Even so, the 0.06 nm shift can be negligible, affirmed by the tremendously low excitation power for the realization of lasing.

Figure 4.3 Lasing characterization of CsPbBr₃ QDs VCSEL. (a) PL spectra of CsPbBr₃ QDs VCSEL under varied low excitation powers (≤ 120 nW). (b) PL spectra collected in the broad range under various high excitation powers (≥ 250 nW). (c) L-L curve presenting the emission intensity at lasing wavelength as a function of the excitation power. (d) Log-log plot of the emission intensity as a function of the excitation power. (e) The emission width as a function of the excitation power. The light blue, orange, and green regions represent spontaneous emission, superlinear amplification, and lasing, respectively. (f) The peak position of the emission as a function of the excitation power. The emission exhibits a slight blue-shift as power increases.

4.3.4 Spatial emission properties of CsPbBr₃ QDs VCSEL

To investigate the spatial distribution of lasing from the isolated CsPbBr₃ QDs embedded in a microcavity, we employed the *in-situ* PL spatial mapping measurement under the same 488 nm laser excitation above the threshold. As shown in Figure 4.4.a, even though QDs are invisible under the optical microscope, the fluorescence image can clearly identify their distribution. The PL mapping of the marked spot is shown in Figure 4.4.b, where the two-dimensional plot of the spatially resolved PL intensity of a CsPbBr₃ QDs VCSEL sample was taken at the excitation power of 8 μ W, and the integration range is from 535.0 to 537.5 nm, covering all the lasing spectrum range. The series of PL spectra plotted in Figure 4.4.c were collected from left to right along the dashed line in Figure 4.4.b, with a small step of 250 nm, which exhibits a constant single-mode lasing emission without apparent changes in FWHM and peak position. As shown in Figure 4.4.d, the FWHM of these spectra is about 0.32 ± 0.02 nm, and the peak position is 536.06 ± 0.02 nm. The integrated intensity of PL emission is presented as a function of distance in Figure 4.4.d. It can be fitted by a Gaussian distribution with a $1/e^2$ width of 1.0 μ m, which is typically used to describe the diameter of the Gaussian beam. Therefore, the size of the emission spot can be estimated as 1 μ m. Considering the size of the laser spot is about 1.2 μ m, the actual size of the embedded CsPbBr₃ QDs may be much smaller than the spot size in the mapping image, which could be isolated as an individual CsPbBr₃ QDs or aggregation of a few QDs.

For exploring the distribution of the isolated CsPbBr₃ QDs, their solution with the same contraction was spin-coated on the bare DBRs for AFM measurement. From the topography AFM image (Figure 4.5.a), the CsPbBr₃ QDs in such a dilute concentration show discrete distribution without prominent clusters. The topography image (Figure 4.5.b) of the selected area in Figure 4.5.a and its corresponding height profile (Figure 4.5.c) indicate that the thickness of the QDs is about 9.6 nm, which is consistent with the size measured from the TEM

image and demonstrates these QDs do not stack together. The density of the CsPbBr₃ QDs is about 1.3 dots/ μm^2 , which is sparse enough to ensure the isolation of QDs and the possible operation of individual CsPbBr₃ QDs in the full microcavity. Moreover, in comparison to the emission of a high-density ensemble of CsPbBr₃ QDs, the PL bandwidth of the isolated QD is considerably narrowed from 5 nm to 1.5 nm (Figure 4.6). Such narrowing of PL emission resulted from the reduction of inhomogeneous broadening is also an identifiable feature for isolated QDs.[154-156]

Figure 4.4 Spatial emission properties of as-fabricated CsPbBr₃ QD VCSEL. (a) Fluorescence image of fabricated CsPbBr₃ QDs embedded microcavity. Scale bar: 15 μm . (b) PL intensity mapping image of the microcavity sample, which is collected from the marked region in (a). Line profile analysis was put through along the labeled dash line in red. The excitation power is 8 μW . Scale bar: 1 μm . (c) PL spectra collected across the labeled line with a small step of 250 nm. The color traces from bottom to top stand for the spectra taken from left to right of the marked line in (a). (d)-(e) The line width, peak position, and intensity of PL emission across the labeled line from left to right, respectively. The solid line in (d) is a fit with a Gaussian function.

Figure 4.5 The spatial distribution of CsPbBr₃ QDs. (a) AFM topography image of CsPbBr₃ QDs spin-coated on DBRs. The CsPbBr₃ QDs were in the same concentration as that of QDs embedded in a microcavity, which has been diluted enough to be isolated. Scale bar: 1 μm . (b) Zoom-in image of the marked region in (a), scale bar: 50 nm. (c) Height profiles corresponding to the labeled line in (b), indicating that the thickness of the QDs is about 9.6 nm. After spin-coating with a spin rate of 4000 rpm, the CsPbBr₃ QDs were dispersed sufficiently with a density of 1.3 dots/ μm^2 .

Figure 4.6. PL measurement at 80 K. (a) PL spectrum of the isolated CsPbBr₃ QDs, which is diluted to the same concentration used for CsPbBr₃ VCSEL. (b) PL spectrum of CsPbBr₃ QDs, which is 10 times of the concentration of the CsPbBr₃ QDs in (a).

In addition, the distinct lasing characteristic of the CsPbBr₃ QD VCSEL was identified *via* the confocal system along the direction orthogonal to the sample plane, which was defined as Z-direction. In the confocal microscopic system, only the optical signals around the focal plane were probed while the out-of-focus signals are eliminated efficiently. Therefore, unlike the classical wide-field microscope, it offers a method to explore the optical response of the sample layer by layer in depth. The location of isolated CsPbBr₃ QDs as the gain material is regarded as a reference plane. As the focal plane scans from the bottom ($Z = -9 \mu\text{m}$) to top ($Z = 9 \mu\text{m}$), the extraordinary evolution of the PL spectrum comes out as shown in Figure 4.7.a, where the maximum intensities of LE and LSE are located at different planes, i.e., $Z_{\text{maxLE}} = -1.2 \pm 0.1 \mu\text{m}$ and $Z_{\text{maxLSE}} = -0.3 \pm 0.1 \mu\text{m}$, respectively. The distance between their maxima is properly accordant with the evaluated thickness of top DBRs ($1.5 \pm 0.1 \mu\text{m}$) obtained from the cross-sectional SEM image (Figure 4.2.b). In such a situation, the plane of the maximum of LSE is the exact location of CsPbBr₃ QDs near the top DBRs, while the plane of the maximum of LSE is located at the surface of the microcavity. In contrast to the emission range of LSE, the range of LE is much more extensive along Z-direction, indicating less diffusion and more

steadiness in the spatial, which is a critical fingerprint for the spatially coherent beam. As shown in Figure 4.7.b, the contour map is enlarged for better recognizing the behavior of LE with an asymmetric intensity profile (in red). It is reasonable that the LE has a preference to emit towards outside vertically from the cavity surface, because a tremendous number of photons are trapped inside the cavity in the effect of strong optical confinement. The trapped photons form the standing wave and oscillate inside the cavity, so they cannot be directly probed by the confocal microscopic system. This spatial-intensity asymmetry of the LE reveals its directional preference, i.e., tending to propagate out of the low-reflective top DBRs as expected. If the light diffused randomly and was in lack of directionality, no asymmetry of intensity would come out. Such a distinctively directional feature is the most significant fingerprint for VCSEL[157,158]. The PL spectra taken at the QDs' plane (black curve) and the surface (red curve) are plotted in Figure 4.7.c, where the maxima of LSE and LE emerge, respectively. The PL spectrum taken at $Z = 2.5 \mu\text{m}$ is also plotted for comparison, which locates above the surface of VCSEL. As the scanning objective rises from the QDs' plane, the LSE decreases remarkably while the LE becomes more and more prominent. In order to evaluate the evolution of the LE proportion in the overall emission output, we calculated it as a function of Z-position, in the range from $Z = -2$ to $2 \mu\text{m}$ (Figure 4.7.d). The ratio of LE intensities is defined as:

$$\frac{I_{\text{LE}}}{I_{\text{LE}} + I_{\text{LSE}}}$$

Where I_{LE} denotes the intensities of LE and I_{LSE} denotes the intensities of LSE, respectively. With the lifting in the Z-direction, the ratio of LE intensities increases from 0.19 to 0.65, which is comparable to the previous VCSEL study.[108] Besides, we estimate the relative external efficiency η_{re} to describe the quantitative characteristic of the QDs VCSEL, which is defined as:

$$\eta_{re} = \frac{I_{\max LE}}{I_{\max LE} + I_{\max LSE}}$$

where $I_{\max LE}$ stands for the maximum integrated intensity of LE and $I_{\max LSE}$ stands for the same term of LSE. In our CsPbBr₃ QDs VCSEL, the derivative η_{re} is 41.6%.

Figure 4.7 Photoluminescence characterization of as-fabricated CsPbBr₃ QD VCSEL across Z-direction. Z-direction is defended as being perpendicular to the sample surface. (a) The contour map of the Z-position dependent PL intensity. The excitation power is 8 μW. (b) The zoom-in contour map of the marked region in (a) with an asymmetric profile. (c) Normalized PL spectra taken at the QDs' plane (black), surface (red), and Z = 2.5 μm (blue), respectively.

(d) The intensities ratio of LE to the complete emission as a function of Z-position. I_{LE} : the intensities of LE, I_{LSE} : the intensities of LSE. The inset illustrates the schematic of LE and LSE.

4.3.5 Stability of CsPbBr₃ QDs VCSEL

The stability under constant pumping is of crucial concern to evaluate the performance of a laser and its practical application. To study the stability of our device, we monitored the lasing behavior *via* confocal PL measurement over time. As shown in Figure 4.8.a, the as-fabricated CsPbBr₃ QDs VCSEL was continuously excited by a 488 nm laser with a power of 12 μ W for 300 s, and the emission spectra collected on a single exciting spot were plotted as the contour map of the time-dependent PL intensity. The lasing spectrum exhibits a single narrow peak constantly, where no boarding or shifting was observed. The integrated emission intensity of the lasing emission as a function of pumping time is presented in Figure 4.8.b, in which the lasing sustained for 300 s without any reduction in intensity. In the previously reported organic-inorganic perovskite VCSELs[66], the RT lasing emission of which totally can be sustained about 220 mins under sub-ns pumping. However, under nanosecond pulse pumping, the output intensity decreases rapidly to 10% of its initial value after 50 min. Therefore, it is acceptable that the obtained CW lasing was sustaining 300 s (5 min) without any obvious decrease under CW pumping. Such outstandingly stable CW lasing is owing to the efficient protection of PMMA from moisture and oxygen.

Figure 4.8 *Stability of as-fabricated CsPbBr₃ QDs VCSEL under continuous illumination. (a) The contour map of the time-dependent PL intensity. (b) The integrated emission intensity of the lasing emission as a function of pumping time under the 488 nm CW laser excitation at room temperature in the ambient atmosphere. The excitation power is 12 μ W.*

It is significant to point out that, the stability of the device in the operating environment is another vital consideration for the practical application. Many efforts have been made to improve the environmental stability of perovskites via surface passivation[159] or encapsulation[160,161]. However, preservation is still challenging for over one year. Herein, the robustness and repeatability were explored in our CsPbBr₃ QDs VCSEL. The parallel PL measurement was conducted on the identical VCSEL device, which was only stored in an ambient atmosphere over one year. As shown in Figure 4.9.a, the PL spectra of CsPbBr₃ QDs exhibit a single narrow emission peak, whose intensity rises with the increase in pumping power. Figure 4.9.b displays the PL spectra under higher pumping power in a broad range for the exploration of lasing behavior. LE located at 536.2 nm is predominant while LSE is extremely low, indicating that the lasing fraction is dominating. As shown in Figure 4.9.c, the L-L curve exhibits the kink point pronouncedly, which appears around 200 nW. The regions of SE, SLA, and LE can be identified clearly. Figure 4.9.d presents a similar evolution of the line width of the emission peak, which decreases from around 0.74 nm to 0.45 nm at 200 nW. Therefore, a single-mode lasing with a threshold of 200 nW (17.6 W cm^{-2}) and a Q factor of 1191 have been demonstrated explicitly for our one-year preserved CsPbBr₃ QDs VCSEL. The increase in threshold and the decrease in Q factor is possibly related to the deterioration of PMMA, which can affect the quality of the cavity and reduce the optical confinement. At the same time, the change of PMMA would influence the cavity length. As a result, the peak of LE has a slight shift. Even though the performance of our one-year preserved VCSEL is not well

as a fresh one, such threshold and Q factor can be well acceptable compared with the existing CW pumped laser as well as its single-mode operation[128,151].

Figure 4.9 Lasing characterization of CsPbBr₃ QDs VCSEL after one-year preservation. (a) PL spectra collected at the small range under a variety of low excitation powers (≤ 300 nW). (b) PL spectra collected at the extensive range under a variety of excitation powers (≥ 400 nW). The intensity (c) and line width (d) of PL emission as a function of the excitation power. The light blue, orange, and green regions represent spontaneous emission, superlinear amplification, and lasing, respectively.

4.4 Discussion

Even though the PL quantum yield of CsPbBr₃ QDs is rarely high, the emission of a single quantum emitter is usually weak. In order to overcome the relatively weak emission of the

isolated CsPbBr₃ QDs at room temperature, DBRs with high reflectivity is an excellent choice for enhancing the emission, where the selection of wavelength is the most vital consideration to design a microcavity. By carefully tuning the reflectivity wavelength of the DBRs, the PL emission of QDs on DBRs can be enhanced. Hence the fluorescence of CsPbBr₃ QDs spin-coated on DBRs becomes much stronger (Figures 4.10.a and b). In comparison to the PL intensity of CsPbBr₃ QDs on a SiO₂ substrate, the PL intensity of QDs on DBRs has increased by 6.7 times (Figure 4.10.c).

Figure 4.10 Comparison between PL intensity of CsPbBr₃ QDs on DBR and SiO₂ substrate. (a) Fluorescence image of CsPbBr₃ QDs on DBR. (b) Fluorescence image of CsPbBr₃ QDs on the SiO₂ substrate. (c) PL spectra of QDs on DBR (black trace) and SiO₂ substrate (red trace), respectively.

In addition, the wavelength of cavity photon should be designed to locate at the lower energy side of the emission range, considering the higher absorption at the higher energy side. In general, the effective wavelength of the optical confinement should cover all the range of PL emission of CsPbBr₃ QDs to reduce optical loss. Especially, the wavelength of the cavity mode is highly dependent on the cavity thickness. As theoretically calculated with the finite-difference time-domain method (FDTD), the simulated reflection spectrum of our designed cavity structure with the perpendicular incidence shows two dips, locating at 558 nm and 465.6 nm, respectively (Figure 4.11.a). The cavity length was set to 400 nm constructed by PMMA. Thus, it is understandable that there are two dips in the spectrum. In contrast to the simulated result, the measured perpendicular reflection spectrum of the CsPbBr₃ QDs embedded microcavity shows only one dip with a slight shift in position (536.1 nm on the upper panel, Figure 4.2.e). The undiscovered dip at 465.6 nm is possibly due to the comparatively large absorption of CsPbBr₃ at the short-wavelength range. Besides, the tender shift of the cavity mode is mainly due to the insertion of CsPbBr₃ and unavoidable limitations of the fabrication process such as the slight thickness fluctuation of the DBR layer and the rough surface of the spin-coated PMMA, which would lead to the change of dielectric environment inside the cavity. From the cross-sectional electric field distribution of the simulated cavity mode at 558.0 nm ((Figure 4.11.b), it is clear that the electromagnetic field is strongly confined in the cavity (the position of the PMMA layer). There are three strong regions locating at the top, center, and bottom of the PMMA layer. In other words, the emission of the isolated CsPbBr₃ CDs located near the top DBRs can be confined and enhanced significantly. This agrees well with the PL

scanning measurement along the Z-direction. Moreover, unlike the existing lasers based on CsPbBr₃ QDs thin film[67] or the high-density ensemble[151], which usually exhibit the multi-mode operation, our VCSEL based on isolated CsPbBr₃ QDs shows the outstanding single-mode emission. Owing to the small dimensions of the microcavity and limited size of isolated CsPbBr₃ QDs, the inhomogeneity of gain saturation has been significantly reduced. Hence, the VCSEL with homogeneous optical resonance is in favor of single-mode lasing[162]. In addition, compared with other morphologies such as the thin film or single crystal, the QDs have higher exciton binding energy owing to their quantum confinement nature, which normally results in a high fluorescence quantum yield[163,164]. Such higher binding energy of the CsPbBr₃ QDs ensures the high stability of exciton even at room temperature, which could provide an excellent experimental platform to further study the fascinating quantum physics frontiers such as exciton-polariton coupling, Bose-Einstein condensates, superfluidity, and single-photon emission. [150,152].

Figure 4.11 FDTD simulation for the bare microcavity. (a) Simulated reflection spectrum with the perpendicular incidence. (b) Spatial electric field distribution of the calculated cavity mode ($\lambda = 558.0$ nm) inside the cavity along the vertical direction. The reference plane ($Z = 0$) is defined at the bottom surface of the first layer TiO_2 . The electric field is tightly confined in the region of the PMMA layer.

4.5 Conclusion

High-quality CsPbBr_3 QDs have been successfully synthesized by a modified hot injection solution method, which exhibits outstanding light-emitting performance at room temperature. The as-synthesized CsPbBr_3 QDs solution was diluted 1000 times to ensure their sparse dispersion on the substrate. The as-synthesized CsPbBr_3 QDs was employed as the gain medium and sandwiched by two sets of high-reflectivity DBRs to form a high Q-factor VCSEL. The single-mode CW lasing with an ultra-low threshold of 8.8 W cm^{-2} has been observed at room temperature, verified by the intensity kink of the light input-output curve, the linewidth narrowing, and the spatially asymmetric emission. The dispersion of QDs was also explored by low-temperature PL measurement and AFM, which is different from the high-density ensemble. Such gain media are promising for achieving single dot coherent light sources and high-resolution displays. The developed VCSEL device is stable and robust, which can sustain more than 5 mins and conserve the lasing characteristic after one-year preservation. Our strategy to design and fabricate perovskite-based VCSELs can be easily generalized to other lead halide perovskites with different emission wavelengths. This work sheds light on the realization of ultralow threshold laser based on lead halide perovskites with electrical pumping and truly pushes the frontier of practical coherent light applications based on the emerging gain media of lead halide perovskites.

Chapter 5

Continuous-wave lasing from 2D layered organic-inorganic hybrid perovskites embedded microcavity

5.1 Introduction

Organic-inorganic metal halide perovskites have developed a fantastic family of semiconducting materials on account of their extraordinary optoelectronic performances in photovoltaics[165,166], photodetector[167-169], and light-emitting devices[170,171]. Recently, 2D layered organic-inorganic perovskites have aroused much attention owing to their outstanding environmental stability. The general chemical formula for the 2D organic-inorganic perovskites is $R_2A_{n-1}Pb_nX_{3n+1}$, where R represents long organic chains such as phenylethylammonium (PEA^+), 1-naphthylmethylamine (NMA^+) and n-butylammonium (BA^+), A means the organic/inorganic cation, including methylammonium (MA^+), formamidinium (FA^+), and cesium (Cs^+), and X can be halide anion like iodide (I^-), bromide (Br^-) or chloride (Cl^-)[172]. For $n > 1$, multilayered small cations (A) forms quasi-2D perovskites, and for $n = 1$, two long-chain layers and one inorganic $[PbX_6]^{4-}$ form a molecularly thin 2D structure[173]. The variations of n values affect the bandgaps and binding energies of the materials due to different quantum confinement effects of self-built multiple quantum-well structures. In particular, the exciton in 2D organic-inorganic perovskites owns a robust electrostatic Coulomb coupling and small Bohr radius, leading to their distinct properties, such as large exciton binding energy, effective quantum yield, and efficient radiative recombination[174]. Thanks to these brilliant properties, 2D layer organic-inorganic perovskites are supreme candidates for realizing the practical lasing applications in the integrated optical circuit, quantum communication, and quantum computing.

Recently, the amplified spontaneous emission (ASE) and lasing emissions of 2D organic-inorganic perovskites have been intensively studied[175-181]. For example, Fu *et al.* have reported the tunable ASE in hybrid $(\text{NMA})_2(\text{FA})\text{Pb}_2\text{Br}_y\text{I}_{7-y}$ thin films[182]. Using NMA-based 2D perovskite films as gain media, Leyden *et al.* reported distributed feedback lasers and LEDs at room temperature[183]. By fabricating micro-ring arrays based on 2D $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{Br}_{3n+1}$ perovskite thin film, high Q-factor whispering gallery mode lasers have been realized[184]. However, the lasing was mainly observed from solution-processed thin films, consisting of a mixture of domains having components with different n values, which leads to different bandgaps, and the energy funneling from small n domains (high bandgaps) to large n domains (low bandgaps) contributes to the build-up of population inversion. The investigation of pure phase 2D organic-inorganic perovskites is necessary for further understanding of inherent lasing mechanisms. Besides, achieving continuous-wave (CW) pumped lasing from 2D perovskites is still challenging, which is regarded as a precondition towards the electrically pumped laser[185,186]. Indeed, restricted trials have been done. Chen *et al.* reported the random lasing from the millimeter-sized homologous $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$ ($n = 1, 2, \text{ and } 3$) single crystals at room temperature, attribute to the multiple scatterings from the resonant feedback formed by gain media[187]. Zhang *et al.* demonstrated broadly tunable lasing from exfoliated single-crystalline BA-based 2D perovskite thin flakes at the cryogenic temperature[188]. Due to the weak van der Waals interactions among the organic layers, the 2D perovskites are appropriately exfoliated and transferred to the substrates without counting the lattice match, which is easy for the device fabrication. Unlike cavity-free perovskite lasers, Adachi *et al.* recently demonstrated CW lasing from 2D PEABr-based and NMABr-based perovskite thin-film spin-coated on distributed feedback gratings[105]. Due to low defect densities of single-crystalline 2D perovskites and their self-built quantum well structures, 2D perovskites embedded microcavities with the

matched resonance between the spontaneous emission and the cavity mode are the promising device architectures to achieve CW lasing with low threshold and high stability at room temperature.

In this chapter, we have realized CW lasing from a single-crystalline $(\text{PEA})_2\text{PbI}_4$ flake embedded microcavity at room temperature. Owing to the high quality of the $(\text{PEA})_2\text{PbI}_4$ crystal and the ultrathin cavity, a single-mode lasing emission has been observed at an ultra-low threshold of 65 nW, which is comprehensively lower than the lasing threshold values reported in existing 2D perovskite lasers[105]. The apparent features of spectral narrowing and nonlinear evolution of the emission intensity reveal the occurrence of lasing emission. The fabricated $(\text{PEA})_2\text{PbI}_4$ VCSEL exhibits environmental and optical stability. Our results not only advance the development of 2D single-crystalline perovskite planar VCSELs, but also shed light on the next-generation of on-chip integrated photonics.

5.2 Experimental details

5.2.1 Synthesis of $(\text{PEA})_2\text{PbI}_4$ single crystals

lead iodide (PbI_2 , 98%), phenethylammonium iodide (PEAI , $\geq 98\%$), and hydroiodic acid (wt. 57%) are ordered from Sigma Aldrich. The reagents and solvent were directly utilized as gotten without any further refinement. As shown in Figure 5.1.a, PbI_2 and PEAI (1:2 molar ratio) were added into the hydroiodic acid solution at 90 °C under vigorous stirring for 15 min. After all solids were dissolved, one molar solution containing $(\text{PEA})_2\text{PbI}_4$ was obtained, which was quickly transferred in vials and kept in an oven at 90°C for 30 min. Some tiny crystals were attained, and one of them was picked out and added into the vial containing a flesh $(\text{PEA})_2\text{PbI}_4$ solution as a crystal seed for further growth. Subsequently, the solution was slowly cooled down from 90 °C to room temperature with a rate of 1°C /hour, and the millimeter-sized

PEA₂PbI₄ crystal was obtained after around one week (Figure 5.1.b). All the growth processes were carried out under the ambient condition.

5.2.2 Exfoliation of (PEA)₂PbI₄ flakes

The PEA₂PbI₄ flakes were mechanically exfoliated from the bulk single crystal. In detail, a small piece of the PEA₂PbI₄ single crystal was firstly put on the Scotch tape, and the tape was folded several times to thin down the flakes subsequently. Secondly, another fresh Scotch tape was carefully attached to the original one and then detached promptly to make further the flakes thinner as demanded. Moreover, the origin tape with PEA₂PbI₄ thin flakes was carefully put on the substrate (SiO₂ or DBR) for 10 min, and the bubbles should be avoided during this process. After that, the tape was removed rapidly, and then the PEA₂PbI₄ flakes were deposited on the substrate.

5.2.3 Fabrication of (PEA)₂PbI₄ VCSEL

The 0.5 mm silicon wafer with a 300 nm silica capping layer was used as the substrate to construct the devices. An e-beam evaporator (Cello, Ohmiker-50B) with a high vacuum ($\sim 10^{-6}$ torr) was employed to deposit oxide sources (SiO₂, TiO₂, and Ta₂O₅, 99.9%). Firstly, 12 pairs of 97.6 nm SiO₂ and 52.3 nm TiO₂ were deposited to fabricate the bottom DBR, followed by transferring the PEA₂PbI₄ flakes via the Scotch tape method. Then, PMMA was spin-coated on the surface with a spin rate of 8000 rpm. Finally, 11 pairs of 88.3 nm SiO₂ and 59.8 nm Ta₂O₅ were deposited as the top DBR.

5.2.4 Morphological and optical characterization

The XRD pattern was collected by a Bruker D8 Discover thin-film X-ray diffractometer ($\lambda = 0.71073 \text{ \AA}$).

Thermal stability was measured on the bulk crystal by a thermal gravimetric analysis (TGA)

Q500 V6.7 Build 203 facility with a rate of 10 K min^{-1} under the ambient condition.

Scanning electron microscopy (SEM) images were obtained from a Zeiss Auriga Dual-Beam FIB/SEM system. Atomic force microscopy (AFM) images were acquired from an Asylum Research Cypher ES Scanning Probe Microscope. Optical images were collected from an Olympus BX51 system with the coordinate axis for locating the sample.

PL and Raman measurements were performed by a WITec Alpha300 Series confocal microscope system with a 600 g/m grating. A 488 nm excitation laser was used for PL measurements, while a 633 nm excitation laser was used for Raman measurements. A $50\times$ objective of $\text{NA} = 0.55$ and $\text{WD} = 10.1\text{ mm}$ was used to focus the laser beam, with a spot size of $1.2\text{ }\mu\text{m}$ on the sample surface. The reflectivity spectra were collected from the backscattering configuration of the confocal microscope system, in which a white-light source was used to irradiate the sample perpendicularly with a $20\times$ objective lens of $\text{NA} = 0.4$ and $\text{WD} = 3.1\text{ mm}$.

5.2.5 Theoretically simulation

The simulated reflection spectrum was calculated with Lumerical FDTD Solutions.

Figure 5.1 Synthetic strategy of $(\text{PEA})_2\text{PbI}_4$ single crystal. (a) Schematic diagram of the growth process of $(\text{PEA})_2\text{PbI}_4$ single crystal via crystallization method. (b) images of the as-grown millimeter-sized $(\text{PEA})_2\text{PbI}_4$ single crystal.

5.3 Result and discussion

5.3.1 Basic characterizations of the (PEA)₂PbI₄ bulk and thin crystals

2D layer (PEA)₂PbI₄ ((C₆H₅C₂H₄NH₃)₂PbI₄) single crystal was fabricated in a modified seed-growth approach[70,189], which includes two typical crystallization procedures of nucleation and growth. In particular, unlike the previous growth process using γ -butyrolactone (GBL) as the dissolving solvent, which usually requires a step of heating up to 110 °C[190], the operation of the seed-growth approach is simpler and safer with a comparable gentle condition (90 °C). Structurally, the inorganic layer of (PEA)₂PbI₄ is formed by the arrangement of [PbI₆]⁴⁻ octahedra, which share corners in their orthogonal directions. This inorganic lead-halide layer is separated from each other by two organic layers formed by long-chain PEA⁺ cations, as shown in Figure 5.2.a. The connection between the organic layer and the inorganic layer is attributed to the H_N···I hydrogen bond, while the interaction between two adjacent organic layers is owing to the weak van der Waals force[191]. Therefore, such a structure is a two-dimensional layered hybrid perovskite, which allows to mechanically exfoliate the bulk crystal to the thin flake.

The thermal stability of this crystal is studied by the TGA system. As shown in Fig. 5.2.b, this material gets no weight to lose until ~190 °C, which means (PEA)₂PbI₄ single crystal has excellent stability at room temperature. X-ray diffraction (XRD) is a useful instrument to get vision into the crystal structure of crystalline materials. We performed the XRD examination of an as-prepared (PEA)₂PbI₄ single crystal with the (00n) crystal direction perpendicular to the measurement stage. The observed positions of these fingerprinting peaks show the right consistency with the previous studies[192,193], and the sharp shape of each peak indicates good crystal quality of (PEA)₂PbI₄. The strongest peak locating at $2\theta = 5.38^\circ$ is corresponding to the (002) plane, suggesting an interplanar distance of 1.65 nm. Thus, the thickness of a single

layer $(\text{PEA})_2\text{PbI}_4$ can be estimated[194].

Figure 5.2 Crystal structure and thermal stability characterization of the as-grown $(\text{PEA})_2\text{PbI}_4$ single crystal. (a) Schematic illustration of the optimized crystal structure of 2D layered $(\text{PEA})_2\text{PbI}_4$ crystals along the C axis, where the purple octahedra represent the inorganic $[\text{PbI}_6]^{4-}$ compounds, and the inorganic layers are separated from each other by two organic layers formed by long-chain PEA ligands. (b) Thermal gravimetric analysis of the $(\text{PEA})_2\text{PbI}_4$ single crystal. (c) The XRD patterns of the $(\text{PEA})_2\text{PbI}_4$ bulk crystal recorded from the (001) plane.

The representative optical image of exfoliated $(\text{PEA})_2\text{PbI}_4$ flakes is presented in Figure 5.3.a, with a relatively large size of several micrometers. In particular, the optical contrast of the

(PEA)₂PbI₄ can estimate its thickness, which originates from the interference between the sample and substrate[195]. The region in purple represents thinner samples, while the area in yellow represents a much thicker location (i.e., hundreds of nanometre). The AFM and corresponding height profile are shown in Figure 5.3.b and e, respectively, where the thickness of the thin region is 175 nm. The Raman spectrum excited by a 633 nm CW laser is shown in Figure 5.3.d, where the dominant peak is located at 106 cm⁻¹. Coincident with the previous studies, this peak is ascribed to the $\pi - \pi$ vibration of PEA rings.[196,197] The modes of in-plane Pb — I stretching, out-of-plane I — Pb — I rocking, and octahedral rotation, which were demonstrated locating at the frequency smaller than 60 cm⁻¹[198], are not recorded here due to the cut-off of Rayleigh scattering by our long-pass filter. In addition, under the excitation of a 488 nm CW laser at room temperature, the (PEA)₂PbI₄ flake exhibits the PL emission with a narrow linewidth of 13.5 nm at 527.1 nm (Figure 5.3.e), which is corresponding to an excitonic emission at 2.36 eV and indicates the high quality of the crystals[167]. Due to such a robust excitonic emission, the (PEA)₂PbI₄ flake can be unambiguously employed as an optical gain medium for further lasing investigation.

Figure 5.3 Morphological and optical characterization of the exfoliated $(\text{PEA})_2\text{PbI}_4$ flake. (a) Optical image and (b) Atomic Force Microscope (AFM) image of the exfoliated $(\text{PEA})_2\text{PbI}_4$ flake on the SiO_2 substrate. (c) The corresponding height profile of the selected zone in (b). Scale bar: $10\ \mu\text{m}$ for (a) and $5\ \mu\text{m}$ for (b). (d) Raman spectrum of the exfoliated $(\text{PEA})_2\text{PbI}_4$ flake at room temperature, and the arrow denotes the Raman peaks at $106\ \text{cm}^{-1}$. (e) PL spectrum of the exfoliated $(\text{PEA})_2\text{PbI}_4$ flake at room temperature. The emission peak is at $527.1\ \text{nm}$.

5.3.2 Structure and characterization of the microcavity

To realize efficient lasing emission, fulfilling the harsh requirements of sufficient optical gain and affordable losses is the most important consideration for the design of the cavity. In general, high reflectivity DBRs are the prerequisite to realize in a vertical-cavity surface-emitting laser. As illustrated in Figure 5.4.a, the bottom DBRs is constructed by 12 pairs of dielectrics $\text{SiO}_2/\text{TiO}_2$ layers with a thickness of quarter optical-wavelength-thick to guarantee

the outstanding reflectivity. Notably, in order to reduce the possible strain effect arising from the SiO₂/Si substrate, one layer of SiO₂ was deposited in advance. After the deposition of the bottom DBR, the exfoliated (PEA)₂PbI₄ flakes were transferred onto the surface via the Scotch tape method. Subsequently, about 200 nm-thick PMMA was spin-coated on the exfoliated (PEA)₂PbI₄ flake for covering the fragile perovskites, preserving their intrinsically optical quality, and merged with the perovskite layer to support Fabry-Pérot oscillation. After that, 11 pairs of SiO₂/Ta₂O₅ layers were deposited on the PMMA as the top DBR. Replacing TiO₂ with Ta₂O₅ here is vital because Ta₂O₅ has a low melting point. Thus, the operating temperature of the e-beam evaporation could keep low, which prevents the damage of the delicate gain media. The cross-sectional scanning electron microscope (SEM) image of the as-fabricated bare cavity is presented in Figure 5.4.b, in which the solid dielectrics layers can be clearly distinguished, and their interfaces are evident for the alternating structures of the microcavity. As shown in Figure 5.4.c, the normalized reflection spectra ranging from 500 to 570 nm of the bottom and top DBRs exhibit their minimum reflectivity of 99.8% and 97.4%, respectively. Such a broad high-reflectivity region of the stopband covers the complete spontaneous emission of the (PEA)₂PbI₄ perovskite and is beneficial to strong optical confinement. In consideration of the incidence of 488 nm excitation laser and the output emission from top DBR, its reflectivity is designed to be slightly smaller than that of the bottom one. Figure 5.4.d shows the emission of the (PEA)₂PbI₄ perovskite embedded cavity. Compared with the spontaneous emission band (i.e., located at 527.1 nm with a width of 13.5 nm) of the (PEA)₂PbI₄ perovskite on the SiO₂ substrate (Figure 5.3.e), the emission spectrum of the perovskite embedded in the microcavity narrows down to 0.45 nm and redshifts to 537.4 nm, owing to the strong optical confinement of the microcavity. The quality factor Q is estimated by

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

where $\Delta\lambda$ and λ represent the width of cavity mode and the emission wavelength, respectively, in our case, the derivative Q is about 1194. PL spectrum shows other three peaks besides the dominant lasing peak in Figure 5.4.d. The peaks locating at 515 and 550 nm originate from noise during the measurement, as our PL measurement Witec alpha 300 use ultra-high throughput spectrometers based on CCD detector, which owns quick response with a slight poor signal-to-noise ratio. For the peak at 532 nm, it could be attributed to the roughness surface of the exfoliated flake, which would change the cavity length and further change the cavity mode. The more specific discussion has been illustrated in Figure 5.7 and Figure 5.8.

Figure 5.4 Construction and characterization of the microcavity. (a) Schematic of the $(\text{PEA})_2\text{PbI}_4$ VCSEL, green block: SiO_2 layer, orange block: $(\text{PEA})_2\text{PbI}_4$, grey block: PMMA, purple block: Ta_2O_5 , blue block: TiO_2 . (b) Classic cross-sectional scanning electron microscope (SEM) image of the microcavity. Scale bar: $1\mu\text{m}$. PMMA locates at the center with a thickness of about 200 nm. (c) Reflectivity spectrum of top DBRs ($\text{Ta}_2\text{O}_5/\text{SiO}_2$, red trace) and bottom DBRs ($\text{TiO}_2/\text{SiO}_2$, black trace). (d) Lasing mode of the $(\text{PEA})_2\text{PbI}_4$ embedded microcavity.

5.3.3 Lasing characterization of $(\text{PEA})_2\text{PbI}_4$ VCSEL

The lasing characteristic of $(\text{PEA})_2\text{PbI}_4$ VCSEL is explored by using a 488 nm CW laser as the pumping source and collecting the emission from the backscattering at room temperature. As presented in Figure 5.4.d, a strong lasing emission (LE) peak at 537.4 nm and a weak broad emission band resulting from leaked spontaneous emission (LSE) emerge in the PL spectrum of $(\text{PEA})_2\text{PbI}_4$ VCSEL. Figure 5.5.a presents the evolution of the steady-state PL spectra of this perovskite VCSEL sample pumped by various low-excitation powers, ranging from 535 to 540 nm. The emission band raises in intensity and becomes narrower with the increase in excitation power. Figure 5.5.b shows the evolution of PL spectra under different high excitation powers in the broad spectral ranges covering all the emission range, where the LSE band is ignorable compared with the LE peak, implying the low loss of the VCSEL device. Furthermore, the evolution of the emission peak at 537.4 nm has been explored in detail as the excitation power increases. As shown in Figure 5.5.c, the integrated PL emission intensity is plotted as a function of excitation power, which also is called L-L curve. As the excitation power exceeds a specific value, the PL emission intensity increases remarkably, where such a value is called threshold[199]. Subsequently, lasing emission takes place from the device. From the L-L curve, it is evident that there are two kink points, which divide the curve into three regions categorized as spontaneous emission (SE), superlinear amplification (SLA), and lasing emission,

respectively. The SE data (in green) displays a sublinear dependence, owing to the reabsorption caused by the reflection of the DBR mirrors and the quenching of exciton emission originating from nonradiative recombination[105,108,184]. The SLA range (in yellow) displays the superlinear feature, while the lasing range (in red) presents the nearly linear behaviour. Concisely, this nonlinear characteristic in the L-L curve is a tangible evidence of lasing. A similar transition from sublinear to superlinear has been broadly observed in microcavity lasers based on other large excitonic systems such as 2D transition metal dichalcogenides and organic solid-state crystals[108,200]. Meanwhile, the evolution of the emission peak width under the excitation with various powers is present in Figure 5.5.d, where it narrows from 0.67 nm to 0.42 nm during the transition from SE to SLA, with a reducing ratio of 38 %. The emission peak is much narrower compared with existing 2D perovskite VCSELs under the pulsed laser pumping, for example, the width of which is 0.8 nm reported by Zhai *et al.*[179], suggesting a high Q-factor and efficiently optical confinement of our VCSEL device. This narrowing of the lasing peak has generally been detected in other 2D perovskite lasers[179,188,201], which is another suggestive evidence for the evolution from SE to LE. From the change of the intensity and the width with the increasing excitation power, the lasing threshold is extracted at about 65 nW, equivalent to 5.7 W cm^{-2} , which is one order of magnitude lower than the threshold of the recently reported 2D perovskites CW laser[105]. Such a value is reasonable because perovskites with preferred crystal orientation usually exhibit a lower threshold[180,202]. For example, a threshold of VCSEL based on the single-crystalline 3D MAPbBr₃ perovskite thin film is lately reported as 34 mW cm^{-2} [203]. This ultra-low threshold is ascribed to the high quality of the crystalline gain medium and cavity. The spin-coated 2D perovskite thin-film usually contains multiple Ruddlesden–Popper perovskite components, which is easy to form bound excitons and bi-excitons under high-density pumping. In addition, the scattering and the nonradiative recombination at the boundary of the polycrystalline domain could induce optical

loss, which hinders the occurrence of lasing. On the contrary, a single crystal with high crystallinity can reduce defect density efficiently. On the other hand, unlike cavity-free configurations such as nanowire[176], the designed VCSEL configuration is a useful strategy to promote optical gain. During the fabrication process, the use of PMMA is in favor of smoother surface and waveguiding effects. Unlike merely covering the top DBR, which is hard to control the thickness and probably induces an air gap, directly depositing the top DBR help for close contact, resulting in better optical confinement. In contrast, existing CW DFB lasers[105,128] rely on the growth of perovskites as the submicron periodic construction, which produces large scattering loss and leads to larger thresholds.

Figure 5.5 Lasing characterization of (PEA)₂PbI₄ VCSEL. (a) PL spectra collected at the zoom-in range under varied low excitation powers (≤ 120 nW). (b) PL spectra collected at the extensive range under various high excitation powers (≥ 160 nW). (c) L-L curve presenting the emission intensity at lasing wavelength as a function of the excitation power. (d) The full width at half maximum (FWHM) of the emission as a function of the excitation power. The green, yellow, and red regions represent spontaneous emission, superlinear amplification, and lasing, respectively.

The stability of emission with continuous excitation is of critical concern for the practical application of a laser device. In order to evaluate the stability of our device, the lasing behavior was monitored *via* confocal PL measurement along with time. As shown in Figure 5.6.a, the as-fabricated (PEA)₂PbI₄ VCSEL is under constantly pumping by a 488 nm CW laser with an intensive power of 20 μ W for 300 s, and the emission spectra probed from a single pumping spot are illustrated as the contour map of the *in-situ* time-dependent PL intensity. A single narrow peak was observed from the spectra without any boarding or shifting but decreased in intensity over. Figure 5.6.b shows the integrated emission intensity of lasing emission as a function of pump time, where the lasing intensity decrease to 75% of its original value over 300 s. In the previously reported organic-inorganic MAPbI₃ perovskite CW laser, the RT lasing emission of which totally vanished after 250 s continuously pumping with the excitation power of near the threshold. By contrast, our (PEA)₂PbI₄ VCSEL is more stable, owing to the protection afforded by the long-chain PEA cations and surface passivation effects of PMMA[167,204].

Figure 5.6 Stability of as-fabricated $(\text{PEA})_2\text{PbI}_4$ VCSEL under constant excitation. (a) The contour map of the time-dependent PL intensity. (b) The integrated emission intensity of lasing emission as a function of pumping time at room temperature, ambient atmosphere. The excitation is the 488 nm CW laser with a power of 12 μW .

It is worth mentioning, the variation of $(\text{PEA})_2\text{PbI}_4$ perovskite layer thickness, unintentionally induced from the exfoliation process, is possible to cause changes of the cavity length, which may lead to multi-mode emission. As shown in Figure 5.7.a, the PL spectra of $(\text{PEA})_2\text{PbI}_4$ VCSEL in a broad range exhibit two narrow emission peaks locating at 538.3 and 539.8 nm, denoted as mode 1 and mode 2, respectively. Both modes rise with the increase in pumping power. LSE is relatively low, indicating the lasing fraction is dominating. The mode

spacing between modes 1 and 2 is 1.5 nm. If we assume this 1.5 nm spacing is free spectral range of a Fabry–Pérot resonator, which is defined as:

$$\Delta\lambda_{FSR} = \frac{\lambda^2}{2nL}$$

Where λ represents the wavelength of the resonated optical wave in vacuum, n denotes the group refractive index, and L stands for the length of the cavity. In our designed cavity, $\Delta\lambda_{FSR}$ can be deviated as:

$$\Delta\lambda_{FSR} = \frac{\lambda^2}{2n_{\text{Pero}}L_{\text{Pero}} + 2n_{\text{PMMA}}L_{\text{PMMA}}}$$

Where n_{Pero} and n_{PMMA} denote the refractive index of (PEA)₂PbI₄ perovskite and PMMA, as well as L_{Pero} and L_{PMMA} stands for the thickness of (PEA)₂PbI₄ perovskite and PMMA, respectively.

If we take:

$$\Delta\lambda_{FSR} = 1.5 \text{ nm}$$

The thickness of (PEA)₂PbI₄ perovskite can be calculated as:

$$L_{\text{Pero}} = 44 \text{ }\mu\text{m}$$

Which is two orders of magnitude larger than our designed thickness, even much larger than the lateral size. Therefore, we assigned these two modes to the emission originated from perovskite flakes with slightly various thicknesses. The power-dependent PL measurement has been conducted for detailed studies. As shown in Figure 5.7.b, the L-L curve of mode 1 exhibits the kink point pronouncedly, which appears around 307 nW. The regions of SE, SLA, and LE can be identified clearly. Figure 5.7.c presents a similar evolution of mode 2, but the extracted threshold is at 110 nW. The different thresholds of these two modes indicate that they are originated from perovskite flakes with different thicknesses, i.e., the cavity length is changed. Thus, the thresholds are different due to the change of the dielectric environment.

Figure 5.7 Lasing characterization of as-fabricated $(\text{PEA})_2\text{PbI}_4$ VCSEL with two lasing modes. (a) PL spectra collected under a variety of excitation powers. (b)-(c) The intensity of PL emission of 2 modes as a function of the excitation power. The green, yellow, and red regions represent spontaneous emission, superlinear amplification, and lasing, respectively.

The wavelength of the cavity mode is greatly dependent on the cavity length. In order to explore the relation between the thickness of the $(\text{PEA})_2\text{PbI}_4$ flake and the position of the cavity mode, the simulated reflection spectrum of our designed cavity structure with the perpendicular incidence was theoretically calculated with the FDTD method. The ideal cavity was set to consists of over 200 nm $(\text{PEA})_2\text{PbI}_4$ layer and 200 nm PMMA. Thus, it is understandable that there are two modes in the spectrum (Figure 5.8). However, only the mode at the long

wavelength side will be observed from PL spectra because the mode located at about 460 nm is out of the emission range of (PEA)₂PbI₄. As the thickness of the (PEA)₂PbI₄ layer slightly increases, the cavity mode redshifts synchronously. The modes at the long-wavelength side of the cavities with 243, 245, and 248 nm (PEA)₂PbI₄ layer are 536.1, 538.8, and 541.5 nm, respectively. Obviously, the step of the redshift with an increase of 3 nm in thickness is 2.7 nm. Therefore, considering the mode spacing between modes 1 and 2 in is Figure 5.7.a is 1.5 nm, which can be attributed to the roughness of the exfoliated (PEA)₂PbI₄ flakes surface, leading to the difference in thickness as well as the change in cavity length.

Figure 5.8 Simulated reflection spectrum of as-designed VCSEL with various thickness of (PEA)₂PbI₄ flakes,

5.4 Conclusion

In summary, millimeter-sized high-quality 2D layered (PEA)₂PbI₄ single crystals have been successfully synthesized by a modified two-step seed-growth method, the mechanically exfoliated thin flakes of which exhibit high crystallization, excellent thermal stability, and outstanding optical properties. The exfoliated (PEA)₂PbI₄ flakes were utilized as the superior gain materials and embedded in two sets of high-reflectivity DBRs to form a high Q-factor

VCSEL. The single-mode CW lasing with an ultra-low threshold of 65 nW has been observed at room temperature, which is demonstrated by the intensity kink of the L-L curve and the linewidth narrowing. The as-fabricated laser displays improved photostability with a working duration of over 300 s, which is much more stable compared with the relevant 3D perovskite laser[128]. The multi-mode emission has been synchronously explored, attributed to the roughness induced unintentionally during the exfoliation process. This work is not only beneficial to the development of electrically driven laser based on 2D lead halide perovskites, but also truly pushes the field of practical coherent light sources and on-chip integrated optics.

Chapter 6

Conclusion and outlook

6.1 Conclusion

In this thesis, my studies begin with the fabrication of high-quality lead halide perovskites, which prepares the ground for the later investigation in the development of CW laser based on perovskite embedded in the microcavity. In essence, our contributions to the perovskites research community are concluded generally in three respects (Chapter 3-5). In the first part, we explore lasing emission from MAPbBr₃ nanoplates sandwiched in microcavity at low temperature, demonstrating CW pumping is able to produce lasing from perovskites. In the following part, we use all-inorganic CsPbBr₃ QDs as the active gain media to fabricate VCSEL, by which the CW lasing operation can be realized at room temperature. In the third part, we study the lasing emission from 2D layered (PEA)₂PbI₄ thin crystal, which shows an ultra-low threshold, indicating the potential of planar lasers based on 2D perovskites. The strategy for the design and fabrication of VCSELs to be generalized to other lead halide perovskite analog.

Part I: CW lasing in MAPbBr₃ nanoplates embedded in microcavities

In Chapter 3, the phase transition of the solution-grown single-crystalline MAPbBr₃ nanoplates was systematically studied by temperature-dependent Raman scattering. In consideration of the outstanding PL performance at low temperature, MAPbBr₃ nanoplates were employed as the gain medium, which was embedded in microcavity to form a high Q-factor VCSEL. CW lasing with a threshold of 55.2 W cm⁻² and a high Q-factor of 1140 has been observed at 80 K, which is verified by the intensity kink of the L-L curve, FWHM narrowing, and the linear polarization.

Part II: CW lasing in all-inorganic CsPbBr₃ QDs embedded microcavities at room temperature

In Chapter 4, the hot-injection synthesized CsPbBr₃ QDs were sparsely dispersed inside the microcavity as gain materials. CW lasing with the single-mode operation and an ultra-low threshold of 8.8 W cm⁻² was demonstrated at room temperature, exhibiting apparent features such as the intensity kink of the light input-output curve, linewidth narrowing, and spatially asymmetric emission. The developed VCSEL held excellent environmental stability, which can sustain more than 5 min and conserve the lasing characteristic after one-year preservation. This sparsely dispersed QDs based VCSEL is promising for achieving single dot coherent light sources and high-resolution displays.

Part III: CW lasing in 2D layered organic-inorganic hybrid perovskites embedded in microcavities

In Chapter 5, millimeter-sized (PEA)₂PbI₄ single crystal was obtained from a two-step seed-growth method, showing high crystallization, excellent thermal stability, and outstanding optical properties. The exfoliated (PEA)₂PbI₄ flakes were utilized as gain media and sandwiched between two sets of DBRs to construct a VCSEL, displaying the single-mode CW lasing operation with an ultra-low threshold of 5.7 W cm⁻² at room temperature. The multi-mode emission was also discussed, ascribed to the roughness induced unintentionally during the fabrication.

In summary, three kinds of perovskites, including the single-crystalline MAPbBr₃ nanoplates, inorganic CsPbBr₃ quantum dots (QDs), and 2D layered (PEA)₂PbI₄ perovskites, were studied in this thesis. Among these perovskites, the VCSEL based on CsPbBr₃ QDs exhibited the best optical performance, considering the high Q factor, low threshold, and outstanding operational stability. However, limited by the QDs' morphological nature, it is challenging to fabricate

large-area uniform planar lasers by using CsPbBr₃ QDs. The VCSEL based on 2D layered (PEA)₂PbI₄ single-crystalline thin flakes showed CW operation at room temperature with ultra-low thresholds, owing to the self-built quantum well structure and high binding energy. The 2D layer structure also benefits the vertical integration of VCSELs. From our studies, it seems that our single-crystalline MAPbBr₃ nanoplates showed the worst lasing performance. However, it is caused by our early poor outstanding of perovskites and experimental technique. For example, the nanoplates were not protected by PMMA and the temperature of the evaporating chamber might be too high to damage the samples. The performance of MAPbBr₃ should be improved by optimizing the fabrication process. In addition, electrical transport is another important factor for electrically driven lasers in the future. According to the study from K. Sim *et al.*, 3D perovskites have smaller exciton binding energy and better charge transport properties, while 2D perovskites are the opposite, representing the trade-off between binding energy and transport ability[205]. However, the electrical properties can be improved through material engineering. Most recently, Jiang *et al.* demonstrated 2D perovskite LEDs with peak external quantum efficiency (EQE) of 20.36% and luminance of 82480 cd m⁻² by using a polar molecule, p-fluorophenethylammonium, to reduce the exciton binding energy of quasi-2D perovskites and suppress Auger recombination. [206] In addition, Kong *et al.* reported high efficient 2D perovskite-based LEDs reaching EQE of 20.5% and current efficiency of 63 cd A⁻¹. [207] The performance of 2D perovskite-based LEDs is comparable to the most recently reported 3D perovskite LED with EQE of 23.4% [208]. Therefore, more efforts are demanded to find out the best candidate for practical perovskite-based VCSELs.

6.2 Outlook

6.2.1 Electrically driven laser based on perovskite embedded microcavity

Nowadays, although optically excited lasers have been developed from various perovskite systems, we still have a long way to go in terms of the realization of electrically driven lasing, which is regarded as the cornerstone for integrated photonics. The development of polariton lasers is a promising direction to achieve this objective, whose thresholds are usually orders-of-magnitude lower than those of photonic lasers, suggesting less requirement of carriers density and current injection[209-211]. The existing electrically driven lasers based on III-V semiconductors mainly depend on cutting edge epitaxy techniques. For example, Schneider *et al.* demonstrated electrically driven polariton lasing from InGaAs quantum wells, which is grown by molecular beam epitaxy (MBE) method[212]. Later, Bhattacharya *et al.* developed the electrically injected polariton laser based on MBE-grown GaN microcavity with room temperature operation[213]. Further progress on electrically driven lasers requires simplification of fabrication and optimization of light-emitting performance. The emerging lead halide perovskites are such bright candidates to achieve these targets. Considering the realization of perovskite-based light-emitting diodes (LED) with efficiency over 20% [208,214-216], and the demonstration of the room temperature polariton laser[150], lead halide perovskites promisingly hold the key to achieve electrically driven lasers. More endeavors are demanded to introduce conductive optical cavities, optimize the transport of charge carriers, and improve the quantum efficiency of devices.

The stability of the device is another vital consideration for practical application. In the early stage, perovskite polycrystalline thin films showed poor stability[128,217], which limited their application. In the past few years, many efforts have been made to improve the stability of perovskites. For example, Zhang *et al.* demonstrated a 2D Ruddlesden–Popper perovskite laser

array with an artificial light-harvesting system, which can sustain stable lasing emission for 6 hours without a significant decrease in intensity[176]. Encapsulated by a dense Al_2O_3 layer, a waterproof perovskite laser was demonstrated[218]. In addition, the Al_2O_3 layer can effectively protect perovskites and conserve their excellent optical and lasing stability[219]. More recently, Li *et al.* reported efficient perovskite LED with excellent operational stability over 300 hours and EQE of 17.8%, which benefits from the improvement of crystal phase quality. Therefore, electrically driven perovskite-based lasers are promising in future real-life applications, with constant efforts for the improvement of stability.

6.2.2 Manipulation of strong-coupling at room temperature

Semiconductor based cavities with an embedded individual quantum dot (QD) are promising in upcoming applications such as photonic integrated systems and quantum-information scheme[220-222]. In such semiconductor microcavity systems, fascinating phenomena like vacuum Rabi splitting in the strong-coupling regime[223-226] and effective lasing in the weak-coupling regime[227-231] have been reported thus far. The laser oscillation in semiconductor microcavity systems interacting with only one single quantum dot (SQD) is substantially desirable to reveal the underlying physics of cavity quantum electrodynamics effects. However, in the microcavity systems containing hundreds of QDs, the interference arises from a bunch of QDs, which obstructs the understanding of the intrinsic properties of an SQD-cavity system. Employing a small cavity with a highly sparse distribution of QDs can minimize this interference. For example, a photonic crystal cavity laser solely driven by only one SQD is successfully developed, with high SQD purity and gain contribution[232]. Besides, the coexistence of vacuum Rabi oscillation and laser oscillation appears to be contradictory in nature due to the lack of a reversible process. Nevertheless, with the effects of an extremely

high Q-factor cavity and strong field coupling, the strong-coupling effect could be sustained in laser oscillation. Nomura *et al.* demonstrated the direct transition from a strong-coupling regime to a lasing regime in an SQD embedded cavity at liquid helium (LHe) temperature, while the delicate coherent exchange of quanta between the SQD and cavity is sustained[233]. Owing to the relatively high exciton binding energy of perovskites, the strong coupling and formation of exciton-polariton have been demonstrated by incorporating perovskites with microcavities[152,234-236]. Therefore, the perovskite SQD embedded microcavity could be a testbed for manipulating strong-coupling of photons and matter at room temperature.

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