Optical properties of semi-conductive MXene Sc₂CO_x, CsPbBr₃ nanoplatelets and quantum dots

Chen, Qiran

2021

Chen, Q. (2021). Optical properties of semi-conductive MXene Sc₂CO_x, CsPbBr₃ nanoplatelets and quantum dots. Doctoral thesis, Nanyang Technological University, Singapore. <https://hdl.handle.net/10356/152198>

<https://hdl.handle.net/10356/152198>

<https://doi.org/10.32657/10356/152198>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 09:16:04 SGT

Optical Properties of Semi-conductive MXene Sc_2CO_x , CsPbBr_3 Nanoplatelets and Quantum Dots

Qiran Chen

School of Electrical & Electronic Engineering

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

2021

Statement of Originality

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

23 Nov. 2020

.....

Date

CHEN Qiran

.....

Qiran Chen

Supervisor Declaration Statement

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

23 Nov. 2020

.....

Date

.....

Prof. Fan Weijun

Authorship Attribution Statement

Please select one of the following; *delete as appropriate:

*(A) This thesis does not contain any materials from papers published in peer-reviewed journals or from papers accepted at conferences in which I am listed as an author.

(B) This thesis contains material from [5] papers published in the following peer-reviewed journals / from papers accepted at conferences in which I am listed as an author.

Chapter 4 is published as Qiran Chen, Daohua Zhang, Jisheng Pan, Weijun Fan, *Optical properties of two dimensional semi-conductive MXene Sc_2CO_x produced by sputtering*, in *Optik*, Volume 219, 2020, 165046, ISSN 0030 4026

The contributions of the co-authors are as follows:

- Prof. Fan Weijun provided the initial project direction.
- I prepared the manuscript drafts. The manuscript was revised by Prof.Fan Weijun and Prof. Zhang Daohua.
- I performed all the laboratory work at the School of Electrical and Electronic Engineering. I also analyzed the data.
- Dr. Pan Jisheng assisted in the operation and interpretation of X-ray photo-electron spectroscopy (XPS).

Chapter 5 is submitted for review as Qiran Chen, Zhaojin Wang, Zhigang Song, Weijun Fan, Kai Wang, Munho Kim and Daohua Zhang, *Effect of thickness on the electronic structure and optical properties of quasi two-dimensional perovskite $CsPbBr_3$ nanoplatelets*

The contributions of the co-authors are as follows:

- Prof. Fan Weijun provided the initial project direction.
- I prepared the manuscript drafts. The manuscript was revised by Prof.Fan Weijun, Prof.Zhang Daohua, Prof.Wang Kai and Prof. Munho Kim.
- All simulations were conducted by me.
- Dr. Song Zhigang assisted in the establishment of $k \cdot p$ model.
- Mr. Wang Zhaojin performed the material synthesis, and collected X-ray diffraction patterns and photoluminescence spectrum.

Chapter 6 is published as Q. Chen, Z. Song, D. Zhang, H. Sun and W. Fan, *Effect of Size on the Electronic Structure and Optical Properties of Cubic CsPbBr₃ Quantum Dots*, in *IEEE Journal of Quantum Electronics*, vol. 56, no. 1, pp. 17, Feb. 2020, Art no. 7000207. doi: 10.1109/JQE.2019.2949 639

The contributions of the co-authors are as follows:

- Prof. Fan Weijun provided the initial project direction.
- I prepared the manuscript drafts. The manuscript was revised by Prof.Fan Weijun and Prof.Zhang Daohua.
- All simulations were conducted by me.
- Dr. Song Zhigang assisted in the establishment of $k \cdot p$ model.
- Prof.Handong Sun provided the initial project direction, too.

23 Nov. 2020

.....

Date

CHEN Qiran

.....

Qiran Chen

Acknowledgements

It is my honor to express my gratitude to all the people who have had immense contributions directly or indirectly, in the evolution of this thesis to its current form and shaping my doctoral career in general. First and foremost, I would like to express my deepest gratefulness to my supervisor, Prof.Fan Weijun. His patience allowed me to explore new areas and learn from my mistakes. His erudition guided me through countless difficulties and puzzles. And his trust supported me in my Ph.D. career. I am so fortunate to have Prof.Fan Weijun as my supervisor and I will always keep in mind his edification.

My co-supervisor, Prof.Zhang Daohua, has always been a good advisor and supporter. His expertise on semiconductor experiments prevented me from walking towards a dead end. And his support for the experiment systems and materials set up the solid foundation for my research. Beside of his concern for my study, Prof.Zhang also helped me out when I was in trouble, for which I am deeply grateful and I will never forget his kindness.

I would like to appreciate my seniors and colleagues, who are Dr. Tong Jingchao, Dr. Xu Zhengji, Dr. Li Huakai, Dr. Majie, Dr. Ye Yiyang, Dr. Zhang Jun, Mr. Liu Wenbo, Ms. Liu Lin, Dr. Aron David Mueller and Dr. Landobasa Yosef Mario Tobing. They offered me plenty of useful advice and assistance for my study and research. A special thank you to Dr. Qian Li and Dr. Song Zhigang, who shared their knowledge and experience on theory and experiments with me and helped me through a lot of detailed work with patience.

I would also like to thank all the technicians and staff who provided assistance to me in Nanophotonics Lab, Characterization Lab, Clean Room 2 and Clean Room 1.

Finally and most importantly, I would like to thank my parents, Mr. Chen Xuewen and Ms. Wang Xiuqin, and my girl friend, Ms. Huang Yao, for supporting my decisions and life. Thanks for tolerating my shortcoming.

Abstract

Semiconductors in the shape of nanostructures, including quantum dots (0-dimension) and nanoplatelets (2-dimension) demonstrate unique electronic and optoelectronic properties because of the quantum mechanism related to excitons confined in low dimensions. Such confinement can provide intriguing properties like high capability of photo-activated carriers, band gap tunability, splendid photoluminescence (PL) yield, narrow emission bandwidth, high absorption efficiency of light, fast fluorescence lifetime, etc. These properties attract great attention due to their high potential in applications like solar cells, light-emitting diodes (LEDs), lasers, photodetectors, catalysts, etc.

Novel semiconductors including MoS₂, MXene and perovskite have received increasing research interest in recent years. Unlike traditional semiconductor materials like Si, Ge, II-VI and III-V materials, the novel ones usually have low-dimensional form natively, which have emerged as very promising candidates for advanced electronic and optoelectronic devices.

Among the various novel semiconductor materials, this thesis focuses on two types of them, which are MXene Sc₂CO₂ and cesium lead halide perovskite CsPbBr₃. The two materials have some features in common. Both of them are direct band gap materials, which makes them available for optical applications. And they can be synthesized directly into two-dimensional structure, which offers the opportunity to learn the influence of one-dimensional confinement. To extend the study into another dimension, the quantum dots of CsPbBr₃ are also studied.

The first part of the thesis focuses on the study of Sc₂CO_x which is a type of semi-conductive MXene. The material is synthesized for the first time by using magnetron sputtering. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are performed to determine the composition of the sample. The

band gap of Sc_2CO_x sample is determined by ultraviolet-visible (UV-VIS) range absorption and photoluminescence (PL) spectrum. The Tauc plot indicates that Sc_2CO_x is a direct band gap material. The high sensitivity of scandium to oxygen makes the sample contain both scandium carbide and scandium oxide. Thermal annealing introduces more oxidation into the sample. The structure of MXene will be broken when the annealing temperature is higher than 600°C .

The second part of the thesis focuses on the study of perovskite CsPbBr_3 in forms of nanoplatelets and quantum dots. For CsPbBr_3 nanoplatelets, the effect of thickness of cesium lead halide perovskite CsPbBr_3 nanoplatelets (NPLs) on their electronic structure and optical properties are investigated using an 8-band $\mathbf{k} \cdot \mathbf{p}$ model which is based on effective-mass envelope function theory with exciton binding energy consideration. We first reported the CsPbBr_3 nanoplatelets' band structure and optical gain with exciton effect. As the thickness of NPLs decreases, their band gap increases and the band mixing is more obvious which influences the transition matrix element (TME). The optical gain of CsPbBr_3 nanoplatelets is calculated by taking into account of TME, Fermi factor, injected carrier density and thickness. A blue shift of peak position in optical gain can be observed as the thickness of NPLs decreases. For any given NPL with a certain thickness, there is a slight blue shift in peak position of optical gain as the carrier density increases because of band filling effect. The maximum optical gain of thinner NPLs need higher carrier density to reach saturation. To obtain high differential gain, the carrier density in thick NPLs has to maintain in a small range. Experimental work is carried out and the results agree with our theoretical results very well. For quantum dot, the size effect on the electronic structure and optical properties of cubic CsPbBr_3 perovskite quantum dots is investigated by using an 8-band $\mathbf{k} \cdot \mathbf{p}$ model which is also based on effective-mass envelope function theory with exciton binding energy consideration. Quantum dots with smaller sizes have larger band gaps due to quantum confinement. The transition matrix element (TME) is also influenced by the size. The optical gain of such material is calculated by considering TME, Fermi factor, injected carrier density, quantum dot size, and dephasing rate. Higher density of the injected carrier is needed for smaller quantum dots to get a positive optical gain. The peak of optical gain has a blue shift as the size of a quantum dot decreases. When the carrier density increases for a quantum dot with certain size,

a blue shift in emission peak position can be observed due to the band filling effect. Smaller quantum dots have higher differential optical gain at carrier densities within certain range.

In a word, two direct band gap semiconductor materials, Sc_2CO_x and CsPbBr_3 are studied via theoretical and experimental approaches. Their band-structure and optical properties are presented, followed by the analysis of their potential in applications.

Contents

Acknowledgements	ix
Abstract	xi
List of Figures	xvi
List of Tables	xix
Acronyms	xx
1 Introduction and Literature Review	1
1.1 History, Background and Motivation	1
1.2 Literature Review	6
1.2.1 MXenes	7
1.2.2 Cesium Lead Halide Perovskite Quantum Wells and Dots . .	8
1.3 Thesis Outline and Major Contributions	10
2 Optoelectronic Theory of Semiconductors	12
2.1 Theory of Electronic Bandstructures	12
2.2 Bloch's Theorem	13
2.3 $\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory	14
2.3.1 8-band $\mathbf{k} \cdot \mathbf{p}$ Model: First Basis Type For CsPbBr ₃ Nanoplatelets	15
2.3.2 8-band $\mathbf{k} \cdot \mathbf{p}$ Model: Second Basis Type For CsPbBr ₃ Quantum Dots	21
2.4 Optical Processes in Semiconductors	23
2.4.1 Optical Gain of CsPbBr ₃ Quantum Wells	24
2.4.2 Optical Gain of CsPbBr ₃ Quantum Dots	26
3 Fabrication and Characterization Methods of Low-Dimensional Materials	28
3.1 Introduction	28
3.2 Methods of MXenes Synthesis	29
3.2.1 Top-Down Approach: Chemical Exfoliation	29

3.2.2	Bottom-Up Approach: Magnetron Sputtering	32
3.3	Methods of Perovskite Synthesis	34
3.3.1	Solid-State Reactions	34
3.3.2	Gas Phase Preparations	34
3.3.3	Wet Chemical Methods	35
3.3.3.1	Hot Injection Method	35
3.3.3.2	Ligand-assisted Reprecipitation Method	37
3.4	Systems for Sample Characterization	38
3.4.1	X-ray Photoelectron Spectroscopy (XPS)	39
3.4.2	X-ray Diffraction (XRD)	39
3.4.3	Absorption Spectroscopy	40
3.4.4	Photoluminescence (PL)	40
3.4.5	Transmission Electron Microscope (TEM)	40
4	Sc₂CO_x: Synthesis, Characterization and Temperature Effect	42
4.1	Introduction	42
4.2	Method	43
4.3	Results and Discussion	44
4.4	Conclusion	50
5	CsPbBr₃ Nanoplatelet: Thickness Effect	51
5.1	Introduction	51
5.2	Theoretical Framework	51
5.3	Experiment Details	52
5.3.1	Materials	52
5.3.2	Preparation of Cesium-oleate Solution	52
5.3.3	Preparation of CsPbBr ₃ Nanoplatelets	53
5.3.4	Characterization	53
5.4	Results and Discussions	53
5.4.1	Theoretical Results	53
5.4.2	Experimental Results	61
5.5	Conclusions	61
6	CsPbBr₃ Quantum Dot: Size effect	63
6.1	Introduction	63
6.2	Theoretical Framework	63
6.3	Results and Discussions	65
6.4	Conclusion	73
7	Thesis Summary and Conclusions	74
7.1	Thesis Summary	74
7.2	Thesis Conclusion	75
	List of Author's Publications	77

List of Author's Publications	77
Bibliography	78

List of Figures

1.1	Density of states (DOS) in bulk and low-dimensional semiconductor nanostructures.	4
1.2	Brief indication of quantum well.	4
1.3	Splitting of energy levels in quantum dots as size changes. (sigmaaldrich.com)	5
2.1	The bandstructure of Ti_2CO_2	13
2.2	Schematic diagram of band structure of the bulk $CsPbBr_3$ near R-point.	16
3.1	Pathway to obtain MXene nanoflakes by chemical exfoliation processes. (A) Scanning Electron Microscope (SEM) micrograph of Ti_3AlC_2 . (B) SEM micrograph of $Ti_3C_2T_x$ particles. (C) Transmission electron microscope (TEM) of $Ti_3C_2T_x$ single layers.	30
3.2	Schematic of a magnetron sputtering system	33
3.3	(a) Brief indication of hot injection method used for synthesis of $CsPbX_3$ (X=Cl, Br, I) nanocrystals. (b) Transmission electron microscope (TEM) image of $CsPbBr_3$ nanocrystals fabricated by hot injection method. (c) $CsPbX_3$ (X=Cl, Br, I) nanocrystal colloidal solution under ultraviolet (UV) lamp with wavelength of 365nm.	36
3.4	Brief indication of Ligand-assisted reprecipitation method	37
4.1	XRD pattern of scandium carbide sample without annealing	44
4.2	Overview of XPS spectrum of scandium carbide sample without annealing	46
4.3	XPS spectrum of (a) scandium (b) carbon (c) oxygen and (d) argon in scandium carbide sample without annealing	46
4.4	XPS spectrum of (a) scandium (b) carbon (c) oxygen and (d) argon in scandium carbide sample with 600° annealing	47
4.5	PL spectrum of scandium carbide sample without annealing	47
4.6	Absorption coefficient vs. wavelength of scandium carbide samples with different temperature thermal annealing. The inset is the photo of samples.	48
4.7	Plot of $(\alpha h\nu)^2$ versus $h\nu$ of scandium carbide sample with different temperature annealing	49

4.8	Plot of $(\alpha h\nu)^{0.5}$ versus $h\nu$ of scandium carbide sample with different temperature annealing	49
5.1	Band gaps of CsPbBr ₃ nanoplatelets with different thickness	54
5.2	The square of wavefunction of the first 5 conduction bands and first 3 valence bands of CsPbBr ₃ nanoplatelet with thickness of 3, 5, 7 and 9 unit-cell	55
5.3	Distribution of composition of CsPbBr ₃ nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell	55
5.4	Transverse electric (TE) mode transition matrix element (TME) for En-H1 transition of CsPbBr ₃ nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell	56
5.5	Transverse magnetic (TM) mode transition matrix element (TME) for En-H1 transition of CsPbBr ₃ nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell	57
5.6	Transverse electric (TE) mode transition matrix element (TME) at R-point for transitions between En and Hn (n=1,2,...,10) of CsPbBr ₃ nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell	58
5.7	Transverse magnetic (TM) mode transition matrix element (TME) at R-point for transitions between En and Hn (n=1,2,...,10) of CsPbBr ₃ nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell	58
5.8	The TE (a-d) and TM (e-h) mode optical gain spectrum of CsPbBr ₃ nanoplatelets with thickness of (a) (e) 3; (b) (f) 5; (c) (g) 7; and (d) (h) 9 unit-cell	59
5.9	The TE (a-d) and TM (e-h) mode maximum optical gain (MOG) and differential gain (dg/dn) spectrum of CsPbBr ₃ nanoplatelets with thickness of (a) (e) 3; (b) (f) 5; (c) (g) 7; and (d) (h) 9 unit-cell	60
5.10	The (a) photoluminescence (PL) spectrum and (b) transmission electron microscopy (TEM) image of CsPbBr ₃ nanoplatelets with thickness of 4.1 nm.	62
6.1	Three-dimensional atom-by-atom model of typical CsPbBr ₃ quantum dots.	64
6.2	Band gaps of cubic CsPbBr ₃ quantum dots with different sizes.	66
6.3	The square of wavefunction of the first 3 conduction bands and valence bands of 4nm cubic CsPbBr ₃ quantum dot.	67
6.4	TE mode of transition matrix element of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr ₃ quantum dot.	68
6.5	TM mode of transition matrix element of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr ₃ quantum dot.	68
6.6	The difference of Fermi distribution between conduction band and valence band $f_c - f_v$ of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr ₃ quantum dot.	69

6.7	The product of TE mode transition matrix element and the difference of Fermi distribution between conduction band and valence band $f_c - f_v$ of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr ₃ quantum dot.	70
6.8	The product of TM mode transition matrix element and the difference of Fermi distribution between conduction band and valence band $f_c - f_v$ of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr ₃ quantum dot.	70
6.9	The optical gain spectrum of (a) 4nm, (b) 6nm, (c) 8nm and (d) 10nm CsPbBr ₃ quantum dot. n is the carrier density with unit of 10^{18}cm^{-3}	72
6.10	The maximum optical gain (MOG) and differential gain(dg/dn) spectrum of (a) 4nm, (b) 6nm, (c) 8nm and (d) 10nm CsPbBr ₃ quantum dot.	72

List of Tables

2.1	Material Parameters	19
3.1	Summary of MXenes synthesized by chemical exfoliation	31
4.1	Sputtering conditions for scandium carbide synthesis.	43

Acronyms

0D, 1D, 2D, 3D	Zero-, One-, Two-, Three-dimensional
A.U. (a.u.)	Arbitrary unit
AE	Atomic Elasticity
BAC	Band anticrossing
CB	Conduction band
CE	Continuum Elasticity
CVD	Chemical vapor deposition
DC	direct-current
DOS	Density of states
FWHM	Full width at half maximum
GOST	Giant oscillator strength transition
GUI	Graphical user interface
IC	Integrated circuit
K	Kelvin
LE	Heavy electron
LED	Light-emitting diode
LH	Heavy hole
ML	Monolayer
NPL	Nanoplatelet
ODE	Octadecene
PL	Photoluminescence
PVD	Physical vapor deposition
QCL	Quantum cascade laser
QD	Quantum dot
QR	Quantum ring
QW	Quantum well
RF	Radio-frequency

RT	Room Temperature
SO	Spin-orbit / Split-off
TE	Transverse electric
TEM	Transmission electron microscopy
TM	Transverse magnetic
TME	Transition matrix element
TRPL	Time-resolved photoluminescence
VB	Valence band
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZB	Zinc-blende

Chapter 1

Introduction and Literature Review

1.1 History, Background and Motivation

Semiconductors refer to materials with electrical conductivity falling between that of an electrical conductor and an insulator. The history of semiconductors can trace back to the late 18th and early 19th centuries when "unusual" properties of material were observed. The concept of semiconductor was first introduced by Alessandro Volta in his report to the Royal Society of London in 1782 [1]. In 1821, Thomas Johann Seebeck noticed some materials, which are known as semiconductors today, have much stronger "thermomagnetism" in contact with copper during his famous thermoelectrical experiments [2]. In 1833, Michael Faraday reported his finding of reverse resistance change of silver sulfide when they are heated [3]. Later more discoveries were reported, which requires a unified theory to explain. In 1878, Edwin Herbert Hall published his observation about flowing charge carriers influenced by magnetic field, which is known as Hall effect [4]. In 1897, J.J. Thomson suggested a kind of fundamental unit much smaller than an atom, which is now known as an electron [5]. The positive charge carrier, known as holes today, was suggested by Karl Baedeker [6]. Based on these findings, Johan Koenigsberger put forward the idea to category solid materials as metals, insulators and "variable conductors" in 1914 [1]. Hereafter, the area of semiconductor began to enter people's vision and more mechanism was revealed. In 1928, Felix Bloch described

electrons' movement in atomic lattices in his doctoral thesis, which helps the establishment of quantum theory of solids [7]. In 1930, B.Gudden introduced the idea that the influence of impurities in semiconductors could be crucial to their conductivity [7]. In the same year, Kronig and Penney defined a theoretical model for semiconductor lattice analysis. By 1931, Alan Herries Wilson had put up the band theory and introduced the concept of band gap [7].

The application of semiconductors began with Walter H. Schottky and Nevill Francis Mott, who built a metal-semiconductor junction model in 1938 and theoretically anticipated the potential barriers between the two kinds of contact[8]. In 1880, Alexander Graham Bell and his assistant Charles Sumner Tainter transmitted sound on a beam of light using a piece of selenium. In 1883, Charles Fritts built the first working solar cell with selenium and gold [7]. In 1904, Jagadish Chandra Bose used sulfide to design a point-contact microwave detector. The optoelectronic potential of semiconductors was also revealed. In 1906, H.J. Round observed the phenomenon that electric current passing through silicon carbide can cause light emission, which makes him the pioneer of light-emitting diodes. Because of the great influence of impurities, more experimental breakthrough of semiconductors was achieved until 1920s when commercially pure semiconductor materials were available. The potential barrier in a metal-semiconductor junction described by Walter Schottky in 1938 also promoted more banausic applications of semiconductors. In 1945, William Shockley designed the first semiconductor amplifier. Two years later, the first point-contact transistor based on germanium was built by Shockley, John Bardeen and Walter Brattain in the Bell Laboratory, which won the Nobel Prize in Physics for them in 1956 [9]. The invention of transistors promotes the comprehension of charge particles moving in semiconductors and further facilitated related researches. In 1955, Carl Frosch and Lincoln Derick realized that silicon dioxide deposited on silicon can help prevent electron diffusion [10]. In 1958, Jack Kilby and Robert Noyce came up with the idea of integrated circuit (IC) at Texas Instruments. In 1961, James Biard and Gary Pittman made the idea of electrical current transferring into light beam come true by building the first light-emitting diode (LED). A year later, Robert Hall from General Electric and Marshall Nathan from IBM invented the first semiconductor laser diode. Such studies were later classified into the field named optoelectronics, which concentrates on

electronic devices and systems that source, detect and control photons. The foundation of optoelectronics includes the quantum mechanical effects of photons on electronic materials, especially semiconductors, or electric field and the movement of charge carriers in the crystal lattice. With further studies, researchers have dug into nanometer (10^{-9}m) scale where Rayleigh criterion has no longer applicable. To better understand the world in the deep sub-wavelength range, more theoretical results were revealed during the 20th century. Researchers including Werner Heisenberg, Albert Einstein, Erwin Schrödinger, Paul Dirac, Enrico Fermi, Wolfgang Pauli, David Hilbert, Satyendra Nath Bose and others contributed a lot to semiconductor physics and quantum mechanics. Their effort allow us to explore new emergent phenomenon when semiconductors have at least one dimension smaller than 100 nanometers. We usually call such materials nanocrystals or nanostructures. When bulk materials usually keep constant physical properties regardless of size, semiconductor nanostructures show various size-dependent properties. Size can change the surface to volume ratio, the movement of charge carriers and introduce quantum mechanical effects such as the density of states (DOS). DOS refers to the number of states available per unit energy at each energy level which allows charge carriers to occupy. Charge carriers can exist at any given energy level in bulk materials, while only discrete levels are available when the dimension of materials shrink to nanometer scales. Nanostructures can be further divided into quantum wells (QW) which have one direction bound to the nanometer scale (2D), quantum wires which are confined along two directions (1D) and quantum dots (QD) which are confined along with three directions (0D). The DOS of a bulk material, a quantum well, a wire and a dot are shown in Fig. 1.1.

The quantum well structure of semiconductors was first developed in 1970 by Esaki and Tse, who put up the idea to form a heterostructure with alternating thin layers of semiconductors with different band-gaps [11]. The fabrication of quantum well structures is highly related with the quality of semiconductor materials. So the advancements in crystal growth techniques contribute a lot to the development of quantum well devices. In 2000, Zhores and Herbert won the Nobel Prize in Physics for their great effort in the development of the semiconductor heterojunction for optoelectronics. For traditional semiconductors, quantum wells can be formed by having a material with a relatively small band gap, like gallium arsenide, sandwiched between two layers of another semiconductor material with a wider band

FIGURE 1.1: Density of states (DOS) in bulk and low-dimensional semiconductor nanostructures.

gap, like gallium aluminum arsenides. Fig. 1.2 briefly indicates the structure of a basic quantum well [12, 13]. The electrons in conduction band and holes in valence band can be trapped in the potential wells formed by the difference of band gaps when their energy is low. From Fig. 1.1 we can see the distinct steps of DOS in quantum wells which differs from bulk material. Additionally, the effective mass of holes in valence band is closer to that of electrons in conduction band due to the quantum confinement. These properties of quantum wells make them a good candidate for optoelectronic applications like laser diodes including infra-red lasers and blue lasers. Quantum wells can also be used for low-noise electronics like high electron mobility transistors and infrared imaging.

FIGURE 1.2: Brief indication of quantum well.

The discovery of quantum dot was in 1980s by Alexey Ekimov and Louis Brus in a glass matrix and colloidal solutions, respectively [14, 15]. As mentioned above, quantum dots are considered to be a zero-dimensional structure which has absolute discrete density of states as shown in Fig. 1.1. The space between scattered states increases as the size of quantum dots decreases which causes the broaden of band

gap as shown in Fig. 1.3. The surface-to-volume ratio of quantum dots is also higher than other structure. These properties of quantum dots bring the possibility of band structure engineering and single electron based devices. By tuning the size of quantum dots, different needs can be fulfilled. The sharper DOS of quantum dots bring them superior transport and optical properties, which can help improve the performance of laser diodes, amplifiers and sensors. Some quantum dots have been proven to be efficient triplet photosensitizers [16]. Other applications like photodynamic therapy, photovoltaic devices, molecular electronics and catalysis are also developed based on quantum dots.

FIGURE 1.3: Splitting of energy levels in quantum dots as size changes. (sig-maaldrich.com)

As the advancement of material science, more novel semiconductors rises people's interest. The synthesis of graphene in 2004 by Andre Geim and his student Konstantin Novoselov brought a lot of attention to the naturally low-dimensional materials [17]. Later, materials like transition metal dichalcogenide, MXenes, and perovskites were synthesized and studied. These materials have proven to be useful in applications like photovoltaics, semiconductors, electrodes and water purification.

Nowadays, over 700 kinds of low-dimensional materials have been theoretically predicted to be stable, although many of them lack further study [18]. And the needs for these materials are growing everyday. It is predicted that the global market for low-dimensional materials could exceed US\$390 million by 2025 [19].

The novel semiconductor materials can be classified into two-dimensional, one-dimensional and zero-dimensional materials according to their atom-alignment, or into direct band gap and indirect band gap semiconductors according to their band-structure. Materials of the same type share some common features and are sometimes aiming for similar applications. Besides, the approaches studying these materials are similar, which offers enough space for comparison among them. For the study of a certain material with different structures, on the other hand, brings more understanding of how the space confinement affects the properties of materials.

From the above-mentioned importance and ideas of engineering semiconductor nanostructures, we draw the motivation of the work done and presented in this thesis. Among the various types of materials, we focus on two specific materials that have shown their great potential in optoelectronic applications. The first one is scandium based MXene Sc_2CO_x , which is a two-dimensional direct band gap semiconductor. And the second one is cesium lead halide perovskite CsPbBr_3 , which is also a direct band gap semiconductor and can be in forms of nanoplatelets or quantum dots. In the sections to follow, we explain the originality, definition and methods to the understanding of this research domain, and also identify the contributions extended through this thesis.

1.2 Literature Review

Here we review the relevant literature reported in this paper, and briefly introduce the latest practices of related research aspects, which is roughly divided into two categories: (i) research status of MXenes which spans Chapters ; and (ii) quantum dots and quantum wells of cesium lead halide perovskite which spans Chapters

1.2.1 MXenes

In 2011, Gogotsi and Barsoum discovered a new type of two-dimensional material which consists of transition metal carbide or nitride [20]. Their research indicated that HF can etch away the aluminum layer in one of the MAX type materials Ti_3AlC_2 and form layered material $\text{Ti}_3\text{C}_2\text{X}$ [20]. Later the same method is applied to synthesis materials with similar structure but different transition metals [21–28]. To emphasize the new material’s two-dimensional structure like graphene and their synthesis process of selective etching the A element away from MAX material, the new material is named as MXene [20].

MXenes can potentially form a very large family. They have formula as M_{n+1}X_n or $\text{M}_{n+1}\text{X}_n\text{T}_x$ for pristine MXene and functionalized MXene, respectively. Here M represents early transition metal, X represents carbon or nitrogen, and T_x indicates terminals like -OH, -O and -F [29, 30]. These terminals are known as functional groups because they can change the properties of MXenes [31–34].

MXenes draw people’s attention because of their fascinating properties and potential in various applications. The combination of good conductivity and hydrophilicity of MXenes opens people’s minds [20]. What is more important, the properties of MXene can be tuned by changing the functional groups according to different needs. Applications of MXenes have reached areas including electrochemical energy storage materials, sensors, electronic device materials, catalysts in the chemical industry, and conductive reinforcement additives to polymers [35–41]. Among the different types of MXenes, semiconductor-like MXenes are rare and valuable. Studies of semi-conductive MXenes can broaden the applications of MXenes to fields like photonics and electronic devices. Theoretical calculations have indicated that some functionalized MXenes are very likely to be semiconductors [42, 43]. Such MXenes can form all heterostructure types with the same base material, which can contribute to new devices in fields like photonics, electronics and optoelectronics[44]. Scandium based MXenes are even more attractive because they have both appropriate band gap and high capability of photo-activated carriers, which leads to better photocatalytic performance [45]. Yet few researches have been concentrated on semiconducting MXenes on experiments aspects. Also, the MXene family is so big that a lot of members are still waiting to be revealed

including scandium based MXenes. The widely used method to synthesize MXene nowadays is using HF or other etchants to remove the 'A' layer away from MAX phase. However, the lack of a stable corresponding MAX phase makes it not suitable for scandium based MXenes. This article is concentrating on semiconducting MXene Sc_2CO_x . Sputtering is applied to synthesize Sc_2CO_x for the first time. The optical properties of the sample are determined by light absorption spectrum and photoluminescence (PL).

1.2.2 Cesium Lead Halide Perovskite Quantum Wells and Dots

Perovskite Quantum Wells

Perovskite is believed to be originated from the discovery of CaTiO_3 by a Russian mineralogist Perovski in 1839[46]. It is now known as a large family of materials with a form of ABX_3 , where A and B are cations and X is the anion. When A is an organic group like Methylammonium(MA), B is an inorganic element like Plumbum(Pb) and X is a halide element like Chlorine(Cl), such organic-inorganic hybrid perovskites can be direct band gap materials with intriguing optoelectronic properties and high potential in applications such as solar cells [47–56]. Since the stability is currently limiting the application of such material, all-inorganic perovskites, where cesium replaces the organic cation, are studied to yield higher stability and an extended range of materials. [57].

Like hybrid perovskites, cesium lead halide perovskites possess attractive optoelectronic properties such as high quantum yield, narrow photoluminescence emission bandwidth, high absorption efficiency of light [58–62]. They are proved to be promising candidates in several optoelectronic devices, such as solar cells, light-emitting diodes, photodetectors and lasers[63–67]. A more interesting property of cesium lead halide perovskites is their tunable band structure which leads to various optoelectronic properties. It has been proven that both the composition of material and thickness of perovskite nanoplatelets have great influence on the photoluminescence emission peaks[68, 69]. Since such all-inorganic perovskites are

usually synthesized in the form of nanoplatelet(NPL) or nanocrystal, their optoelectronic properties are strongly geometry dependent. The low-dimensional structure limits the freedom of movement of carriers, thus influence the density-of-states and wavefunction distribution [70]. The modified optical transition energy between states and the carrier confinement enhances the optical transition matrix, which leads to improved performances in optoelectronic devices [71]. The significance of geometry encourages a lot of experimental studies which claim that cesium lead halide perovskites emit at discrete wavelength depending on atomic-layer thickness [72–77]. Unlike nanocrystals who offer 3-dimensional confinement to the excitons, nanoplatelets have strong 1-dimensional confinement due to their small thickness compared with the Bohr radius [78]. The lateral sizes of nanoplatelets often vary among the observations and are commonly neglected, which leaves thickness the most important factor. In Chapter 4, we build an electronic structure model with accessibility and reliability based on $\mathbf{k} \cdot \mathbf{p}$ method to better understand the working principle behind the tunable optoelectronic properties of CsPbBr₃ nanoplatelets(NPLs). The effect of thickness of NPLs on energy band structure and optoelectronic properties is studied based on this model. The results learned from the model are compared with experiments. The model is also applicable for other all-inorganic halide perovskite NPLs with similar structure when proper parameters are applied.

Perovskite Quantum Dots

Cesium lead halide perovskite (CsPbX₃, X=Cl, Br, I, Cl/Br, and Br/I) in form of quantum dots attracts people's interest due to their advantageous optical properties and great potential for optoelectronic applications [79]. CsPbX₃ is known as a direct band gap semiconductor with a significant photoconductivity response [80]. It can present different nanostructures including spherical quantum dots, nanocubes, nanorods, and nanoplatelets [81]. CsPbX₃ quantum dots have been studied for various applications including solar cells [82, 83], light-emitting diodes [84, 85], lasers [86], photodetectors [87, 88], and high energy radiation detectors [89]. The advantages of such material include splendid photoluminescence (PL) yield reaching 90% [90, 91], adjustable band gaps covering the whole visible range [92], relatively higher stability compared with organic-inorganic hybrid perovskites [93–95], versatile surface architecture with various functional ligands [96], narrow emission bandwidth reaching 86meV [97], reduced fluorescence blinking [98] and

low threshold lasing capability [99].

The properties of CsPbBr₃ quantum dots and the mechanism behind them can be better studied with the help of an accessible and reliable electronic structure model. Since halide perovskites are found to have a “reverse” band structure from direct band gap zincblende phase semiconductors, the methods for studying conventional semiconductors can also be performed on these materials. In Chapter 5, we develop an effective-mass model of CsPbBr₃ cubic perovskite quantum dots based on $\mathbf{k} \cdot \mathbf{p}$ method and information available in the literature. It is also applicable for other halide perovskite quantum dot with similar structure when proper parameters are applied. Based on this model, we studied the size effect on energy band and optical properties of cubic CsPbBr₃ perovskite quantum dot.

1.3 Thesis Outline and Major Contributions

Chapter 1 introduces the history, background and motivation of the work done and reported in this thesis. Relevant literature is reviewed to give a general account of the current state-of-the-art researches, which is broadly categorized into: (i) research status of MXenes which covers Chapter 4; and (ii) quantum nanoplatelets and quantum dots of cesium lead halide perovskite which spans Chapters 5 and 6.

Chapter 2 briefly introduces the various optoelectronic processes in semiconductors. We give a mathematical account of the $\mathbf{k} \cdot \mathbf{p}$ perturbation theory and multi-band related theory which are used for calculating the band structure of semiconductors. The process of photon generation and the effect of exciton interaction are also introduced in this chapter.

Chapter 3 introduces the widely used techniques and methods for the fabrication and characterization of low-dimensional materials, especially of MXenes and perovskites. The systems for synthesizing scandium based MXene and cesium lead halide perovskite are listed and introduced in details. This is followed by the introduction of equipment for the determination of chemical composition, crystal structure and optoelectronic properties. The mechanism of each system is explained.

Chapter 4 introduces the synthesis process of Sc_2CO_x by magnetron sputtering. The introduction focuses on the material related procedures. This is followed by characterization processes of Sc_2CO_x samples including X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) for the determination of the chemical composition, and ultraviolet-visible (UV-VIS) range absorption and photoluminescence (PL) spectrum for the determination of optoelectronic properties. The effect of temperature on Sc_2CO_x samples is also discussed in this chapter.

Chapter 5 discusses the effect of thickness on the electronic bandstructure and optical properties of CsPbBr_3 nanoplatelets using theoretical modeling and experimental measurements. Theoretically, we use a variant of the 8-band $\mathbf{k} \cdot \mathbf{p}$ model to investigate the influence of thickness. Experimentally, we fabricated CsPbBr_3 nanoplatelets with a certain thickness and measured their optoelectronic properties. The introduction of experiment process concentrates on the materials instead of the equipment. Results from theoretical modeling and experiments are compared to verify our conclusion.

Chapter 6 studies the influence of size on CsPbBr_3 quantum dots with the help of an 8-band $\mathbf{k} \cdot \mathbf{p}$ model. The contents of this chapter are pure theoretical results. The electronic bandstructure and optical properties of CsPbBr_3 quantum dots with different sizes are investigated. Experimental studies from literature validate the results from our model. From the literature, we can also notice the sizes of CsPbBr_3 quantum dots often vary among observations, which necessitates the need for such work.

Chapter 7 gives a brief thesis summary including the motivation, scope, methodologies and results of the presented work. The major findings of each chapter are listed.

Chapter 2

Optoelectronic Theory of Semiconductors

2.1 Theory of Electronic Bandstructures

In solid-state physics, bandstructures are diagrams representing the allowed electronic energy levels of solid crystals. Bandstructures is usually described by E- $\mathbf{k}$ diagram, also known as the dispersion curve, from which we can distinguish whether a material is metal, semiconductor, or insulator. For a semiconductor, bandstructure can reveal whether it has a direct or indirect band gap as well as the magnitude of the gap. We can also analyze the carrier mobility based on the curvature of the bands in the E- $\mathbf{k}$ diagram. Fig. 2.1 shows the bandstructure of Ti_2CO_2 , as an example.

The highest point of the valence band is usually set as the ($k_x = 0, k_y = 0, k_z = 0$) point in the $\mathbf{k}$ -space, which is known as Γ -point. In some semiconductors, if the lowest point of conduction band is not at Γ -point, which means the minimum of conduction band and maximum of valence band do not occur at the same point in $\mathbf{k}$ -space, such materials are known as indirect-gap semiconductors. However, if the lowest point of conduction band is at Γ -point, materials with such bandstructure are called direct-gap semiconductors. Silicon is a typical indirect-gap semiconductor, so is another commonly seen semiconductor germanium. Examples of direct-gap semiconductors include InAs, GaAs, etc. Γ -point is essential for the comprehension of the electronic and optic behaviors in direct-gap semiconductors. So studies of a

FIGURE 2.1: The bandstructure of Ti_2CO_2

small portion of the bandstructure near the Γ -point is of great importance. One of the commonly used methods for such need is $\mathbf{k} \cdot \mathbf{p}$ perturbation theory. To have a better understanding of $\mathbf{k} \cdot \mathbf{p}$ theory, we may begin with a brief introduction of Bloch's theorem.

2.2 Bloch's Theorem

Bloch's theorem was named after Swiss physicist Felix Bloch, which is applicable to the wave function of electrons inside solid-state materials. Since the Coulomb potential in the crystalline solid is periodic, we have the potential energy function $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R}_n)$ in the time-independent Schrödinger's equation (Eq. 2.1), where $\mathbf{r}$ is the position vector, $\psi(\mathbf{r})$ is the wave function, E is the energy of photons, $\hbar$ is Planck constant and m is the mass of an electron. $\mathbf{R}_n$ stands for the arbitrary translation vector of the crystallographic lattice and is expressed as $\mathbf{R}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$, ($\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the unit lattice vectors). The electrons in such a periodic lattice are named as Bloch electrons.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (2.1)$$

Based on Bloch's theorem, we can get the solutions to such equation as [100]

$$\psi(\mathbf{r}) = u(\mathbf{r})e^{i\mathbf{k}\mathbf{r}} \quad (2.2)$$

where $\mathbf{k}$ is the crystal wavevector, and $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{R}_n)$. We can also write it in a different form:

$$\psi(\mathbf{r} + \mathbf{R}_n) = \psi(\mathbf{r})e^{i\mathbf{k}\mathbf{R}_n} \quad (2.3)$$

2.3 $\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory

As we mentioned above, the charge behaviors at band extrema are crucial for the understanding and explanation of the electronic and optic properties of direct band gap semiconductors. In this regard, $\mathbf{k} \cdot \mathbf{p}$ perturbation theory is often used to analyze the bandstructure near a particular point, Γ point for instance, in the $\mathbf{k}$ -space. The concept of $\mathbf{k} \cdot \mathbf{p}$ theory is first introduced by Bardeen [101] and Seitz [102]. Later Kittel [103] and Kane [104, 105] made further development and introduced spin-orbit interaction calculations. In 1955, Luttinger and Kohn improved the theory by introducing degenerate bands, invariants and symmetry arguments [106]. After generations of evolution, $\mathbf{k} \cdot \mathbf{p}$ perturbation theory has become an empirical band-structure method with a basis of band states. It has been widely used to calculate band edges analyzing electronic and optic properties of semiconductors, especially of nanostructures [107–109].

To understand the basic principle of $\mathbf{k} \cdot \mathbf{p}$, we can derive the Schrödinger's equation based on Eq. 2.1 for an electron wavefunction $\psi_{n\mathbf{k}}$ in the m^{th} band with wavevector $\mathbf{k}$ as

$$\hat{H}\psi_{n\mathbf{k}}(\mathbf{r}) = \left(\frac{p^2}{2m_0} + U(\mathbf{r})\right)\psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k})\psi_{n\mathbf{k}}(\mathbf{r}) \quad (2.4)$$

Combining with Bloch function $u_{n\mathbf{k}}(\mathbf{r})$, we have

$$\hat{H}\psi_{n\mathbf{k}}(\mathbf{r}) = \left(\frac{p^2}{2m_0} + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} + U(\mathbf{r}) \right) u_{n\mathbf{k}}(\mathbf{r}) = \left(E_n(\mathbf{k}) - \frac{\hbar^2 k^2}{2m_0} \right) u_{n\mathbf{k}}(\mathbf{r}) \quad (2.5)$$

For a certain point in the $\mathbf{k}$ -space, Eq.2.5 can be further expanded. For instance, at Γ -point, we have

$$\hat{H}\psi_{n\mathbf{k}}(\mathbf{r}) = \left(H_0 + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} \right) u_{n\mathbf{k}}(\mathbf{r}) = \left(E_n(\mathbf{k}) - \frac{\hbar^2 k^2}{2m_0} \right) u_{n\mathbf{k}}(\mathbf{r}) \quad (2.6)$$

where $H_0 = \frac{p^2}{2m_0} + U(\mathbf{r})$ and $H_0 u_{n\mathbf{k}}(\mathbf{r}) = E_n(0) u_{n\mathbf{k}}(\mathbf{r})$. The H_0 here is usually called Hamiltonian. By solving the Hamiltonian we can get the eigenvalue $E_n(\mathbf{k})$.

$\mathbf{k} \cdot \mathbf{p}$ theory can be further classified into one-, four-, six-, eight- and higher band calculations, which is used for various situations[110]. In this thesis, we will focus on the 8-band model to study perovskite CsPbBr₃ nanoplatelets and quantum dots, as will be explained in the following sections. The software for our modeling and simulation is our in-house software package platform called *KdotPsoft*. The platform has integrated various $\mathbf{k} \cdot \mathbf{p}$ models for different semiconductor materials including InAs, GaAs, perovskite, GeSn, CdSe, CdS, etc. With a friendly graphical interface, users may collect useful bandstructure information with proper input of parameters.

2.3.1 8-band $\mathbf{k} \cdot \mathbf{p}$ Model: First Basis Type

For CsPbBr₃ Nanoplatelets

As a direct band gap material, CsPbBr₃ shows a band structure that looks like a 'reverse version' of zincblende-phase semiconductors as shown in Fig. 2.1 [111]. Unlike traditional semiconductors, the band extremes in CsPbBr₃ perovskite lies on the R-point in the $\mathbf{k}$ -space [112]. The bandstructure near R-point can be obtained by solving the Hamiltonian and getting the eigenvalue in the R-point vicinity of the Brillouin zone.

FIGURE 2.2: Schematic diagram of band structure of the bulk CsPbBr_3 near R-point.

The 8-band $\mathbf{k} \cdot \mathbf{p}$ model can have two different forms depending on the basis used in the model. Both types use an effective mass envelope function theory approach to explain the nonparabolicity of the coupled conduction band (CB) and valence band (VB) simultaneously while the orbit-splitting bands are also considered. Here we lay down the mathematical framework of our first 8-band $\mathbf{k} \cdot \mathbf{p}$ model, which is suited to study the electronic bandstructure of CsPbBr_3 nanoplatelets. The basis function is taken as

$$\begin{aligned}
\varphi_V(+) &= |S \uparrow\rangle \\
\varphi_V(-) &= |S \downarrow\rangle \\
\varphi_C\left(\frac{3}{2}, \frac{3}{2}\right) &= -\frac{i}{\sqrt{2}}|(X + iY) \uparrow\rangle \\
\varphi_C\left(\frac{3}{2}, -\frac{3}{2}\right) &= \frac{i}{\sqrt{2}}|(X - iY) \downarrow\rangle \\
\varphi_C\left(\frac{3}{2}, \frac{1}{2}\right) &= -\frac{i}{\sqrt{6}}|[(X + iY) \downarrow - 2Z \uparrow]\rangle \\
\varphi_C\left(\frac{3}{2}, -\frac{1}{2}\right) &= \frac{i}{\sqrt{6}}|[(X - iY) \uparrow + 2Z \downarrow]\rangle \\
\varphi_C\left(\frac{1}{2}, \frac{1}{2}\right) &= \frac{i}{\sqrt{3}}|[(X + iY) \downarrow + Z \uparrow]\rangle \\
\varphi_C\left(\frac{1}{2}, -\frac{1}{2}\right) &= \frac{i}{\sqrt{3}}|[(X - iY) \uparrow - Z \downarrow]\rangle
\end{aligned} \tag{2.7}$$

The 8-band Hamiltonian is expressed as follows.

$$H = \begin{pmatrix}
VB & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\
0 & VB & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\
\frac{1}{\sqrt{2}}P_- & 0 & CH & c.c. & c.c. & c.c. & c.c. & c.c. \\
-\sqrt{\frac{2}{3}}P_z & \frac{1}{\sqrt{6}}P_- & S^* & CL & c.c. & c.c. & c.c. & c.c. \\
-\frac{1}{\sqrt{6}}P_+ & -\sqrt{\frac{2}{3}}P_z & -R^* & 0 & CL & c.c. & c.c. & c.c. \\
0 & -\frac{1}{\sqrt{2}}P_+ & 0 & -R^* & -S^* & CH & c.c. & c.c. \\
-\frac{1}{\sqrt{3}}P_z & -\frac{1}{\sqrt{3}}P_- & \frac{S^*}{\sqrt{2}} & -D & -\sqrt{\frac{3}{2}}S & \sqrt{2}R & CS & c.c. \\
-\frac{1}{\sqrt{3}}P_+ & \frac{1}{\sqrt{3}}P_z & -\sqrt{2}R^* & -\sqrt{\frac{3}{2}}S^* & D & \frac{S}{\sqrt{2}} & 0 & CS
\end{pmatrix}$$

The main diagonal terms VB, CH, CL, CS represent energy levels on valence band (VB), heavy electron (CH), light electron (CL) and spin-orbit electron (CS) in conduction band, respectively. All the terms are expressed as follows [109, 113].

$$P_{\pm} = P(k_x \pm ik_y) \tag{2.8a}$$

$$P_z = Pk_z + i\Delta z \tag{2.8b}$$

$$VB = E_G + \frac{\hbar^2}{2m_0}\gamma_V(k_x^2 + k_y^2 + k_z^2) \tag{2.8c}$$

$$\gamma_V = \frac{1}{m_V^*} - \frac{E_P}{3} \left(\frac{2}{E_G} + \frac{1}{E_G + \Delta} \right) \quad (2.8d)$$

$$CH = -\frac{\hbar^2}{2m_0} [(\gamma_1 + \gamma_2)(k_x^2 + k_y^2) + (\gamma_1 - 2\gamma_2)k_z^2] \quad (2.8e)$$

$$CL = -\frac{\hbar^2}{2m_0} [(\gamma_1 - \gamma_2)(k_x^2 + k_y^2) + (\gamma_1 + 2\gamma_2)k_z^2] \quad (2.8f)$$

$$CS = -\frac{\hbar^2}{2m_0} [\gamma_1(k_x^2 + k_y^2 + k_z^2)] - \Delta so \quad (2.8g)$$

$$S = -\frac{\hbar^2}{2m_0} 2\sqrt{3}\gamma_3(-k_x + ik_y)k_z \quad (2.8h)$$

$$R = -\frac{\hbar^2}{2m_0} \sqrt{3} [\gamma_2(k_x^2 - k_y^2) - 2\gamma_3 ik_x k_y] \quad (2.8i)$$

$$D = -\frac{\hbar^2}{2m_0} \sqrt{2}\gamma_2(k_x^2 + k_y^2 - 2k_z^2) \quad (2.8j)$$

E_G is the band gap of bulk CsPbBr₃. Δso is the spin-orbit splitting energy. P is the Kane matrix element and is normally expressed in term of energy units as:

$$E_P = \frac{2m_0}{\hbar^2} P^2 = \frac{2}{m_0} P_0^2 \quad (2.9)$$

The effective mass is calculated by first-principle and enlisted in Table. 2.1. Based on the data, The Luttinger effective mass parameters γ_1^L , γ_2^L and γ_3^L are derived. The normalized Luttinger parameters can be calculated by

$$\gamma_1 = \gamma_1^L - \frac{1}{3} \frac{E_P}{E_G} \quad (2.10a)$$

$$\gamma_2 = \gamma_2^L - \frac{1}{6} \frac{E_P}{E_G} \quad (2.10b)$$

$$\gamma_3 = \gamma_3^L - \frac{1}{6} \frac{E_P}{E_G} \quad (2.10c)$$

We can expand the eight dimensional hole and electron envelope wave function as follows.

$$\Phi_m = \{\Phi_m^j\} (j = 1, 2, \dots, 8) \quad (2.11a)$$

Parameter	Symbol(unit)	Value for CsPbBr ₃
Lattice constant[114]	a(Å)	5.865
Bulk band gap[115]	E _g (eV)	2.36
Effective electron mass[116]	m _e (m ₀)	0.134
Effective hole mass[116]	m _h (m ₀)	0.128
Effective heavy electron mass	m _{he} (m ₀)	0.90709
Effective light electron mass	m _{le} (m ₀)	0.09186
Spin-orbit splitting energy[117]	Δ _{so} (eV)	-1.1
Kane matrix element[116]	E _p (eV)	39.9
Dielectric constant[116]	ε	4.8
Luttinger parameters	γ ₁ ^L	5.994
	γ ₂ ^L	2.446
	γ ₃ ^L	0.528

TABLE 2.1: Material Parameters

$$\Phi_m^j = \exp[i(k_x x + k_y y)] \sum_m a_{n,m}^j \frac{1}{\sqrt{L}} \exp\left[i\left(k_z + m\frac{2\pi}{L}\right)z\right] \quad (2.11b)$$

where L is the quantum well period and we have $L = l + d$, where l is the width of quantum well and d is the width of the barrier. k_i ($i = x, y, z$) is the wavevector, $a_{n,m}^j$ is the expansion coefficient while n is the energy subband index [118].

The exciton binding energy of quantum well can be calculated based on the data listed in Table. 2.1. As mentioned above, the band structure of CsPbBr₃ looks like a 'reverse version' of zincblende-phase semiconductors, so here we use SO electrons, light electrons and heavy electrons to distinguish the different electron states in conduction band. And we have

$$E_{bwellso} = \frac{E_{bso}}{1 - \frac{1}{2}e^{-L_W/2a_{so}}} \quad (2.12a)$$

$$E_{bwellle} = \frac{E_{ble}}{1 - \frac{1}{2}e^{-L_W/2a_{le}}} \quad (2.12b)$$

$$E_{bwellhe} = \frac{E_{bhe}}{1 - \frac{1}{2}e^{-L_W/2a_{he}}} \quad (2.12c)$$

where $E_{bwellso}$, $E_{bwelllh}$ and $E_{bwellhh}$ are binding energy of SO electrons, light electrons and heavy electrons in CsPbBr₃ quantum wells, respectively. L_W is the width of quantum wells, i.e., the thickness of nanoplatelets. E_{bso} , E_{ble} and E_{bhe} are binding energy of SO electrons, light electrons and heavy electrons in bulk CsPbBr₃, respectively, and can be calculated by

$$E_{bso} = \frac{R_y m_{rso}}{\epsilon^2} \quad (2.13a)$$

$$E_{ble} = \frac{R_y m_{rle}}{\epsilon^2} \quad (2.13b)$$

$$E_{bhe} = \frac{R_y m_{rhe}}{\epsilon^2} \quad (2.13c)$$

where R_y is the Rydberg constant, ϵ is the dielectric constant. m_{rso} , m_{rle} and m_{rhe} can be calculated by

$$m_{rso} = \frac{1}{\frac{1}{m_e} + \frac{1}{m_h}} \quad (2.14a)$$

$$m_{rle} = \frac{1}{\frac{1}{m_{le}} + \frac{1}{m_h}} \quad (2.14b)$$

$$m_{rhe} = \frac{1}{\frac{1}{m_{he}} + \frac{1}{m_h}} \quad (2.14c)$$

where m_e , m_h , m_{le} and m_{he} can be found in Table. 2.1. a_{so} , a_{le} and a_{he} in Eq. 2.12 are the exciton Bohr radius of SO electrons, light electrons and heavy electrons of CsPbBr₃ quantum well, respectively, and they can be calculated by

$$a_{so} = \frac{\epsilon a^H}{m_{rso}} \quad (2.15a)$$

$$a_{le} = \frac{\epsilon a^H}{m_{rle}} \quad (2.15b)$$

$$a_{he} = \frac{\epsilon a^H}{m_{rhe}} \quad (2.15c)$$

where a^H is the Bohr radius of hydrogen.

As we can see from Eq. 2.12, the binding energy of quantum wells/nanoplatelets of CsPbBr₃ depends on the thickness of nanoplatelets.

2.3.2 8-band $\mathbf{k} \cdot \mathbf{p}$ Model: Second Basis Type For CsPbBr₃ Quantum Dots

The second type of 8-band $\mathbf{k} \cdot \mathbf{p}$ model shares the same theory background with the first type, but applies a different set of basis and Hamiltonian. The basis Bloch functions are taken as $|s\rangle \uparrow, |11\rangle \uparrow, |10\rangle \uparrow, |1-1\rangle \uparrow, |s\rangle \downarrow, |11\rangle \downarrow, |10\rangle \downarrow, |1-1\rangle \downarrow$.

Using the basis functions above, we create the 8-band Hamiltonian as follows.

$$H = \begin{pmatrix} H_{int} & 0 \\ 0 & H_{int} \end{pmatrix} + H_{so} + V_0 \quad (2.16)$$

where H_{so} presents the spin-orbit coupling, V_0 is the nanocrystal confining potential from environment, and H_{int} contains all the $\mathbf{k}$ -independent, $\mathbf{k}$ -linear, and $\mathbf{k}$ -quadratic terms and is expressed as

$$H_{int} = \begin{pmatrix} h_{11} & \frac{ip_0(k'_x + ik'_y)}{\sqrt{2}} & ip_0k'_z + \Delta z & \frac{ip_0(k'_x - ik'_y)}{\sqrt{2}} \\ \frac{-ip_0(k'_x + ik'_y)}{\sqrt{2}} & h_{22} & h_{23} & h_{24} \\ -ip_0k'_z + \Delta z & h_{23}^* & h_{33} & h_{34} \\ \frac{-ip_0(k'_x - ik'_y)}{\sqrt{2}} & h_{24}^* & h_{34}^* & h_{44} \end{pmatrix} \quad (2.17)$$

where $p_0 = \hbar\sqrt{E_p/2m_e}$ and E_p is the matrix element of Kane's theory. The Hamiltonian elements h_{ij} are as follows.

$$h_{11} = E_g + \frac{\hbar^2}{2m_0} \gamma_c (k_x^2 + k_y^2 + k_z^2) - \Delta_{so} \quad (2.18a)$$

$$h_{22} = h_{44} = -\frac{\hbar^2}{2m_0} \left[\frac{L' + M'}{2} (k_x^2 + k_y^2) + M' k_z^2 \right] \quad (2.18b)$$

$$h_{33} = -\frac{\hbar^2}{2m_0} [M' (k_x^2 + k_y^2) + L' k_z^2] \quad (2.18c)$$

$$h_{23} = h_{34} = -\frac{\hbar^2}{2m_0} \left[\frac{N' (k_x - i k_y) k_z}{\sqrt{2}} \right] \quad (2.18d)$$

$$h_{24} = -\frac{\hbar^2}{2m_0} \left[\frac{L' - M'}{2} (k_x^2 - k_y^2) - i N' k_x k_y \right] \quad (2.18e)$$

$$\gamma_c = \frac{m_0}{m_e^*} - \frac{E_p}{3} \left[\frac{3E_g + 2\Delta_{so}}{E_g (E_g + \Delta_{so})} \right] \quad (2.18f)$$

where E_g is the band gap of bulk CsPbBr₃. The strain tensor is not considered for quantum dot. We apply modified Luttinger parameters which are calculated by

$$L' = L - E_p/E_g = \gamma_1 + 4\gamma_2 + 1 \quad (2.19a)$$

$$M' = M = \gamma_1 - 2\gamma_2 + 1 \quad (2.19b)$$

$$N' = N - E_p/E_g = 6\gamma_3 \quad (2.19c)$$

The applied L-K effective mass parameters γ_1 , γ_2 and γ_3 are calculated by Eq. 2.10.

The colloidal solution where quantum dots are synthesized makes them periodically arranged in three dimensions. So we expand the basis using plane waves as:

$$\Phi_m = \{ \Phi_m^j \} (j = 1, 2, \dots, 8) \quad (2.20a)$$

with,

$$\Phi_m^j = \frac{1}{\sqrt{V}} \sum_{n_x, n_y, n_z} a_{m, n_x, n_y, n_z}^j \exp [i (k_{nx}x + k_{ny}y + k_{nz}z)] \quad (2.20b)$$

where $V = L_x L_y L_z$, $k_{nx} = 2\pi n_x / L_x$, $k_{ny} = 2\pi n_y / L_y$, $k_{nz} = 2\pi n_z / L_z$. n_x, n_y, n_z are the plane wave numbers set in the range of ± 3 . j and m are the basis and energy subband indices, respectively.

2.4 Optical Processes in Semiconductors

As mentioned in Chap. 1, semiconductors in forms of nanostructure have quantized energy levels due to the spatial confinement. The probability of chargers occupying a certain band E_{nc} in conduction band or E_{nv} in valence band can be calculated by

$$f_c = \frac{1}{1 + e^{(E_1 - E_{fc})/k_B T}} \quad (2.21a)$$

$$f_v = \frac{1}{1 + e^{(E_2 - E_{fv})/k_B T}} \quad (2.21b)$$

where f_c and f_v is called quasi-Fermi distribution functions for conduction band and valence band, respectively. E_{fc} and E_{fv} are the quasi-Fermi energy level for conduction band and valence band, respectively. E_1 is a given energy level in conduction band and E_2 is a given energy level in valence band. ΔF is the quasi-Fermi energy separation and we have $\Delta F = E_{fc} - E_{fv}$. k_B is the Boltzmann's constant and T is the absolute temperature in Kelvin. And the energy levels depend on the injection carrier density. From Eq. 2.21 we can see the maximum optical gain can be reached when $f_c - f_v = 1$, i.e. $f_c = 1$ and $f_v = 0$, which means that the conduction band is fully occupied by electrons and the valence band is fully occupied by holes. If $f_c = 0$ and $f_v = 1$, the maximum absorption will be reached. The stimulated emission is proportional to $f_c(1 - f_v)$ while the band-to-band absorption is proportional to $f_v(1 - f_c)$ [119]. So optical gain is proportional

to $(f_c - f_v)$ which is called Fermi factor. As photon energy increases to the quasi-Fermi energy separation ΔF , the Fermi factor decreases to 0. When photon energy is larger than ΔF , gain becomes negative, which means absorption dominates. So Fermi factor is a quantifiable parameter that is essential for the gain process, and we have a limitation of $E_g < \hbar\omega < \Delta F$ if a positive gain is required.

2.4.1 Optical Gain of CsPbBr₃ Quantum Wells

The definition of optical gain is the growth ratio of light intensity per unit length of light propagation with a unit of $1/cm$. When a semiconductor media encounters a photon with a certain energy, the photon may be absorbed or create gain depending on the energy of photon and the bandstructure of the semiconductor. If the photon is absorbed, energy will allow an electron to transit to a higher energy band, which creates an electron-hole pair. The photon may also stimulate the recombination of an electron and a hole, which generate optical gain as a new photon is created. Such process is called stimulated emission, in which the new photon shows the same phase and wavelength as the original photon. Stimulated emission can self-repeat and continuously generate more photons. However, the photons generated by stimulated emission are also absorbed in the meantime. To have strong light amplification, the emission process needs to be stronger than the absorption process. And to achieve this goal, the density of electrons should be larger in the higher energy level [119].

We also need to consider the influence of excitonic interactions in the optical process. Excitonic interaction happens between electrons and holes and can affect the bound excitons in both energy-gap region and continuum region [120], especially in quantum-well structures. Compared with bulk material, the thickness quantization energy in quantum-wells is much larger, which results in a great increase of exciton binding energy [121, 122]. So the excitonic effect should be considered when calculating the optical gain.

The squared optical transition matrix element (TME) of CsPbBr₃ quantum wells is calculated by

$$Q_i^{n,n_v} = \frac{2}{m_0} |\langle \Psi_{n_c} | \hat{\epsilon} \cdot p_i | \Psi_{n_v} \rangle|^2, i = x, y, z, \quad (2.22)$$

where $\hat{\epsilon}$ is the unit vector in the direction of the electric field, p_i is the momentum operator for three directions, and Ψ_{n_v} and Ψ_{n_c} are the real electron and hole wave functions, respectively. The real wave function is the product of the Bloch wave functions and envelope wave functions. TME of transverse electric (TE) mode is the average of Q_x and Q_y , while the transverse magnetic (TM) mode is Q_z . TME indicates the strength of the transitions between the electron and hole subbands.

Based on TME, we can calculate the density matrix equation which helps us study the optical gain of CsPbBr₃ NPLs. Theoretically, we have emission energy of NPL as $E_G^{NPL} = E_G + E_{conf} + E_{bi} + \Delta E_{bi} + E_{self}$, where E_G is the band gap of bulk material, E_{conf} is the energy increase due to quantum confinement, E_{bi} is the excitonic binding energy of NPL, ΔE_{bi} is the increment in binding energy due to dielectric ligand environment and E_{self} is the energy due to self-interaction of electron and holes. ΔE_{bi} and E_{self} are conflicting contributions and almost exactly cancel off [123]. So $E_G^{NPL} \approx E_G + E_{conf} + E_{bi}$ is applied in our calculation. And we have the equation of optical gain as a sum of contributions from band-to-band continuum-states with Sommerfeld enhancement (G^{bb}) and that from the excitonic bound states (G^{ex}).

The band to band gain with Sommerfeld enhancement is

$$G^{bb}(E) = \frac{\pi e^2 \hbar}{2Enm_0 \varepsilon_0 c} \sum_{n_c, n_v} \iint \frac{Q_{tot}^{n_c, n_v}}{4\pi^2 l} C_s \frac{\tau}{n_c n_v \hbar} \sec h[(E_{eh} - E) / (n_c n_v \hbar / \tau)] (f_c + f_v - 1) dk_x dk_y, \quad (2.23)$$

where

$$Q_{tot}^{n_c, n_v} = \frac{2 |p^{cv}|^2}{m_0} \quad (2.24)$$

is derived from Eq. 2.17. Here p^{cv} is the optical transition momentum matrix elements, E is the photon energy, E_{eh} is the interband transition energy, ε_0 is the

free-space dielectric constant, n is the refractive index, c is the speed of light in free space, τ is the intraband relaxation time and C_s is the Sommerfeld enhancement factor. The exciton absorption is given by

$$G^{ex}(E) = \frac{\pi e^2 \hbar}{2Enm_0\varepsilon_0 c L_z} \sum_{n_c, n_v} Q_{tot}^{n_c, n_v}(0) |I_{nm}|^2 |\varphi_{ns}(0)|^2 \frac{\tau_{ex}}{n_c n_v \hbar} \sec h[(E_{eh} - E_{nb} - E) / (n_c n_v \hbar / \tau_{ex})] (f_c + f_v - 1), \quad (2.25)$$

where τ_{ex} is the intraband relaxation time for exciton and I_{nm} is the free electron and free hole wavefunction overlap integration. E_{nb} is the absolute value of exciton binding energy, which is given in by

$$E_{nb} = \frac{E_b^{3D}}{(n - 1/2)^2}, \quad (2.26)$$

where E_b^{3D} is the exaction binding energy for bulk material.

$$|\varphi_{ns}(0)|^2 = \frac{1}{\pi(a_B^{3D})^2(n - 1/2)^3}, \quad (2.27)$$

where a_B^{3D} is the exciton Bohr radius for bulk material.

2.4.2 Optical Gain of CsPbBr₃ Quantum Dots

The linear optical gain of cubic CsPbBr₃ quantum dot is given by [124]

$$G(E) = \frac{\pi e^2 \hbar}{m_0^2 \varepsilon_0 n_r c E} \sum_{n_c, n_v} \frac{1}{V} |\mathcal{P}_{cv}|^2 [f_c - f_v] \times \frac{1}{\pi} \times \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-(E - E_{cv})^2 / (2\sigma^2)\right] \quad (2.28)$$

where $e, \hbar, c, n_r, \varepsilon_0, m_e, E$ are standard physical parameters, σ is Gaussian smearing, V is the volume of a quantum dot, E_{cv} is the center of the energy distribution function of each interband transition, and $|\mathcal{P}_{cv}|^2$ stands for optical transition matrix element (TME). f_c and f_v are electron and hole Fermi distribution functions

which are described in Eq. 2.17.

TME along the x , y , and z directions can be calculated by

$$\begin{aligned} \mathcal{P}_{cv,x} = & \frac{p_0}{\sqrt{2}} \sum_{n_x, n_y, n_z} \left[\left(a_{v,n_x, n_y, n_z}^2 + a_{v,n_x, n_y, n_z}^4 \right) a_{c,n_x, n_y, n_z}^{1*} \right. \\ & + \left(a_{v,n_x, n_y, n_z}^7 + a_{v,n_x, n_y, n_z}^{6*} \right) a_{c,n_x, n_y, n_z}^{6*} \\ & + \left(a_{c,n_x, n_y, n_z}^{2*} + a_{c,n_x, n_y, n_z}^1 \right) a_{v,n_x, n_y, n_z}^1 \\ & \left. + \left(a_{c,n_x, n_y, n_z}^{7*} + a_{c,n_x, n_y, n_z}^9 \right) a_{v,n_x, n_y, n_z}^6 \right] \end{aligned} \quad (2.29a)$$

$$\begin{aligned} \mathcal{P}_{cv,y} = & \frac{ip_0}{\sqrt{2}} \sum_{n_x, n_y, n_z} \left[\left(a_{v,n_x, n_y, n_z}^4 - a_{v,n_x, n_y, n_z}^4 \right) a_{c,n_x, n_y, n_z}^{1*} \right. \\ & + \left(a_{v,n_x, n_y, n_z}^7 - a_{v,n_x, n_y, n_z}^{6*} \right) a_{c,n_x, n_y, n_z}^{6*} \\ & + \left(a_{c,n_x, n_y, n_z}^{4*} - a_{c,n_x, n_y, n_z}^1 \right) a_{v,n_x, n_y, n_z}^1 \\ & \left. + \left(a_{c,n_x, n_y, n_z}^{7*} - a_{c,n_x, n_y, n_z}^9 \right) a_{v,n_x, n_y, n_z}^6 \right] \end{aligned} \quad (2.29b)$$

$$\begin{aligned} \mathcal{P}_{cv,z} = & p_0 \sum_{n_x, n_y, n_z} \left[a_{v,n_x, n_y, n_z}^3 a_{c,n_x, n_y, n_z}^{1*} \right. \\ & + a_{v,n_x, n_y, n_z}^{8*} a_{c,n_x, n_y, n_z}^{6*} + a_{c,n_x, n_y, n_z}^{3*} a_{v,n_x, n_y, n_z}^1 \\ & \left. + a_{c,n_x, n_y, n_z}^{8*} a_{v,n_x, n_y, n_z}^6 \right] \end{aligned} \quad (2.29c)$$

where $p_0 = \langle S | p_x | X \rangle = \langle S | p_y | Y \rangle = \langle S | p_z | Z \rangle$, The average of $P_{cv,x}$ and $P_{cv,y}$ indicates the transition element matrix of transverse electric (TE) mode, while $P_{cv,z}$ stands for transverse magnetic (TM) mode.

Chapter 3

Fabrication and Characterization Methods of Low-Dimensional Materials

3.1 Introduction

While low-dimensional materials continuously attract the reward of scientists globally, its fast development is inseparable from the advancement of synthetic techniques. The synthetic strategies are growing everyday to be more distinct, powerful and widely applicable to enable more nova materials into innovative applications. To make the synthetic processes more effective, different systems and methods are applied for different kinds of materials. And the properties of produced samples require specific systems to characterize. This thesis focuses on two types of materials - scandium based MXene and cesium lead halid perovskite. The following sections will introduce the widely used methods of synthesis and characterization systems for these two types of materials. This chapter concentrates on the systems and equipment. The working principle of each systems are presented in detail. Material related process is covered in Chapter 4 and 5.

3.2 Methods of MXenes Synthesis

Generally speaking, two-dimensional materials like MXenes are usually synthesized by two approaches: top-down approach and bottom-up approach. Top-down approaches refer to the exfoliation of layered bulk target materials, which includes mechanical and chemical exfoliation. Mechanical exfoliation has been proven to be effective to separate graphene layers [17], it is, however, not applicable to MAX phases which is the precursor of MXenes because the bond between M and A elements of MAX phases are usually metallic or strong covalent, which is much stronger than the bonds between graphene layers. So top-down approaches for MXenes usually refer to chemical exfoliation. Bottom-up approaches involve the deposition of target materials on a substrate, which includes chemical vapor deposition (CVD), sputtering, epitaxy, etc. The following subsections will briefly introduce the two approaches.

3.2.1 Top-Down Approach: Chemical Exfoliation

Since the discovery of MXenes, chemical exfoliation has been the most commonly used approach to synthesize different types of MXenes. The basic idea of chemical exfoliation is to weaken the bonds between interlayers so that the 2D structure can be exfoliated from its original 3D bulk material. To achieve this goal, the combination of solvent and intercalant which is used to separate the layers, should be carefully chosen for different materials. The process of chemical exfoliation usually happens in liquid and there are four basic types: (i) oxidizing and dispersing by using sulfuric acid and permanganate potassium as the oxidizers and water as the solvent [125]; (ii) concomitant swelling to increase the space between layers so that the bond is weakened [126]; (iii) replacing the intrinsic cations with larger ones to bring vigorous stirring which separates the layers [127, 128]; (iv) preventing the reaggregation of layers by using ultrasonic waves in liquid [129]. As for MXenes, the precursors used in chemical exfoliation are usually MAX phases, which requires the removal of the A element as the first step. Since the bond between M and A are usually metallic or covalent bonds, chemical etchant like hydrofluoric acid (HF) is usually applied. A brief indication of the exfoliation process for synthesizing MXene monolayers is shown in Fig. 3.1 [130].

FIGURE 3.1: Pathway to obtain MXene nanoflakes by chemical exfoliation processes. (A) Scanning Electron Microscope (SEM) micrograph of Ti_3AlC_2 . (B) SEM micrograph of $Ti_3C_2T_x$ particles. (C) Transmission electron microscope (TEM) of $Ti_3C_2T_x$ single layers.

Around thirty different types of MXenes have been successfully synthesized by chemical exfoliation to date, whose precursors and etching methods are listed in Table 3.1. Most precursors are MAX phases with $P6_3/mmc$ space group [131]. Although there are more than 130 different types of MAX phases, only a handful of them are proven to be applicable for the synthesis of MXenes. From Table 3.1 we may notice that MAX phases with aluminum as A element are more preferred as precursors. This is because the bond between Al and M is usually weaker than that between M and X, which allows the etchant to selectively remove the Al layer without breaking the M-X bond. From an environmental perspective, we would like to use less etchant like hydrogen fluoride (HF) which can penetrate through skin, muscle and bones and cause severe corrosive damage. It is also troublesome to deal with the chemical waste containing HF. So substitute like fluoride salts with hydrochloric acid (HCl) are studied [132]. However, HF still plays an important role in the chemical exfoliation process of MXenes because there is no other etchant applicable for certain types of MXenes.

The products after etching are still in the form of multi-layer crystals, which requires further steps to exfoliate them and get monolayer flakes. Two methods are usually used for the exfoliation: (i) sonication [20] and (ii) swelling of the interlayer

MXene type	Precursor type	Precursor Composition	Etching Method	MXenes	Highlights	Refs.	
$M_{1.33}XT_x$	i-(M, M') ₂ AX 211	($Mo_{2/3}Sc_{1/3}$) ₂ AlC	HF	$Mo_{4/3}CT_x$	Ordered divacancies	[133]	
		($Mo_{2/3}Y_{1/3}$) ₂ AlC	HCl			[134]	
		($W_{2/3}Sc_{1/3}$) ₂ AlC	+ HF	$W_{4/3}CT_x$		[135]	
		($W_{2/3}Y_{1/3}$) ₂ AlC				[135]	
	(M, M') ₂ AX 211	($Nb_{2/3}Sc_{1/3}$) ₂ AlC	HF	$Nb_{4/3}CT_x$		[136]	
M_2XT_X	M_2AX 211	Ti_2AlC	HF			[21]	
			HCl + LiF			[137]	
			HCl + (Na, K or NH_4F)	Ti_2CT_z		[138]	
		HCl - electrochemical		Fluorine free MXenes	[139]		
		$ZnCl_2$	Fully chlorinated MXenes	[140]			
		V_2AlC	HF	V_2CT_z	Nitration 600°C	[23]	
	Nb_2AlC Ti_2AlN	HCl+ NaF	Nb_2CT_z		[141]		
		HF	Nb_2CT_z		[23]		
		HCl +KF	Ti_2NT_z		[142]		
	i-(M, M') ₂ AX 211	($Mo_{2/3}Y_{1/3}$) ₂ AlC	HF	($Mo_{2/3}Y_{1/3}$) ₂ CT _x	In-plane ordered MXenes	[134]	
	(M, M') ₂ AX 211	($Ti_{1/2}V_{1/2}$) ₂ AlC	HF	($Ti_{1/2}V_{1/2}$) ₂ CT _x		[143]	
		($Ti_{1/2}Nb_{1/2}$) ₂ AlC		($Ti_{1/2}Nb_{1/2}$) ₂ CT _x		[21]	
Non MAX	Mo_2Ga_2C	HF HCl + LiF	Mo_2CT_x	Gallium etching	[144] [144]		
$M_3X_2T_x$	M_3AX_2 312	Ti_3AlC_2	HF		First synthesis of MXenes	[20]	
			HCl + LiF		In-situ HF, day behavior	[145]	
			HCl + (Na, K or NH_4F)	$Ti_3C_2T_x$		[138]	
			NH_4HF_2			[35, 146]	
			NaOH + hydrothermal		Fluorine free Mxenes	[147]	
			$NH_4Cl/TMAOH$ -electrochemical			[148]	
	$M_3X_2T_x$	Ti_3SiC_2 Ti_3AlCN	$ZnCl_2$		Fully chlorinated MXenes	[140]	
			H_2O_2 +HF		Silicon etching	[149]	
			HF	Ti_3CNT_x		[21]	
		(M, M') ₃ AX ₂ 312	($Ti_{1/2}V_{1/2}$) ₃ AlC ₂	HF	($Ti_{1/2}V_{1/2}$) ₃ C ₂ T _x		[143]
			($Cr_{1/2}V_{1/2}$) ₃ AlC ₂		($Cr_{1/2}V_{1/2}$) ₃ C ₂ T _x		[21]
		o-(M, M') ₃ AX ₂ 312	($Cr_{2/3}Ti_{1/3}$) ₃ AlC ₂	HCl + LiF	($Cr_{2/3}Ti_{1/3}$) ₃ C ₂ T _x	Out of plane ordered MXenes	[150]
($Mo_{2/3}Ti_{1/3}$) ₃ AlC ₂	HF		($Mo_{2/3}Ti_{1/3}$) ₃ C ₂ T _x	[150]			
($Mo_{2/3}Sc_{1/3}$) ₃ AlC ₂			($Mo_{2/3}Sc_{1/3}$) ₃ C ₂ T _x	[133]			
Non MAX	$Zr_3Al_3C_5$ $Hf_3(Al, Si)_4C_6$	HF	$Zr_3C_2T_x$ $Hf_3C_2T_x$		[151] [152]		
$M_4X_3T_x$	M_4AX_3 413	Ti_4AlN_3	LiF, NaF, KF molten salts	$Ti_4N_3T_x$	First nitride MXene	[153]	
		V_4AlC_3		$V_4C_3T_x$		[154]	
		Nb_4AlC_3	HF	$Nb_4C_3T_x$		[25]	
		Ta_4AlC_3		$Ta_4C_3T_x$		[21]	
	(M, M') ₄ AX ₃ 413	($Nb_{4/5}Ti_{1/5}$) ₄ AlC ₃	HF	($Nb_{4/5}Ti_{1/5}$) ₄ C ₃ T _x		[155]	
		($Nb_{4/5}Zr_{1/5}$) ₄ AlC ₃	HCl + LiF	($Nb_{4/5}Zr_{1/5}$) ₄ C ₃ T _x		[155]	
o-(M, M') ₄ AX ₃ 413	($Mo_{1/2}Ti_{1/2}$) ₄ AlC ₃	HF	($Mo_{1/2}Ti_{1/2}$) ₄ C ₃ T _x		[150]		

TABLE 3.1: Summary of MXenes synthesized by chemical exfoliation

space by introducing proper molecules [156–158]. The molecules serving as the intercalants are various depending on the types of MXenes and their etchant. The polar organic molecule dimethyl sulfoxide (DMSO), for instance, has been proven to be a proper intercalant to exfoliate Ti₃C₂T_x [158] and (Mo_{2/3}Ti_{1/3})₃C₂T_x [150], but it is not applicable to other MXenes.

The major drawbacks of MXenes produced by chemical exfoliation are mainly

about controlling the defects, flake size, and variety of surface terminations. Not surprisingly, the exfoliated samples are usually in the form of small, irregular flakes with metal adatoms and vacancies [146, 159]. Decreasing the concentration of etchant can help reduce the number of defects, but the efficiency of transforming MAX phases to MXenes is greatly lowered in same time [144]. There is no report of a defect-free monolayer of MXene up to date.

3.2.2 Bottom-Up Approach: Magnetron Sputtering

To find solutions to the problems met in the chemical exfoliation method, several bottom-up synthesis methods are developed including chemical vapor deposition (CVD) [160–162], template method [163–165], and plasma enhanced pulsed laser deposition (PEPLD) [166, 167]. As a widely used physical vapor deposition method, magnetron sputtering also has the potential to be applicable for the synthesis of MXenes.

Magnetron sputtering consists of three main components: target, medium and substrate, which are placed in a high-vacuum chamber as shown in Fig. 3.2 [168]. Targets contain the desired materials we would like to deposit on the substrate. Argon gas is usually used as the medium which is introduced into the chamber after a high-vacuum level is reached. A high voltage is placed between the target and substrate, which has enough power to ionize Argon atoms and creates plasma carrying positive charges. The positive ions in plasma are accelerated in the strong electric field and bombard the target with high kinetic energy. Such collision ejects the atoms on the surface of the target, which travel to the substrate and settle. In the mean time, electrons released during the ionization of Argon are also accelerated in the electric field and generate more ions by colliding in the chamber, which cycles the process [169].

There are two ways to offer the strong electric field in magnetron sputtering: direct current (DC) and radio frequency (RF) power supply. DC sputtering is a cost-effective method to deposit materials with good conductivity like metal while it is not applicable to semiconductors or insulators. Charges tend to accumulate on the targets with low conductivity and decrease the speed of ions bombard on

FIGURE 3.2: Schematic of a magnetron sputtering system

the surface of targets. Finally the hole process is stopped as the amount of charges on the target is too high. RF sputtering can solve such problem by exchanging the direction of electric field periodically, which removes the accumulated charges from the target. So RF sputtering is widely used for the deposition of semiconductors and insulators.

The history of sputtering can trace back to the early 1800s when preferential sputtering of alloys, liquids, and multitarget sputtering was reported [170]. In 1930, the idea of magnetron sputtering was realized by Frans Penning, which greatly increased the efficiency of sputtering by enhancing the ion current [171]. Sputtering is widely used for the production of computer hard disks and other semiconductor fabrication process because of its advantages of low substrate temperature and universality. As a kind of physical vapor deposition, sputtering is applicable to materials with a very high melting point. The difference of element mass greatly affects the spreading rate of different materials, but such influence is usually constant, which does not influence the stability and reliability of sputtering. Compared with films deposited by thermal evaporation, sputtered films typically stick tighter to the substrate. Such is favorable to process like layer coating.

In our experiment, we apply dual-target magnetron sputtering which allows scandium and carbon deposit at the same time. DC and RF power supply are applied

to scandium target and carbon target separately. By controlling the voltages of the two power sources, we are able to control the composition of sputtered films on the substrate.

3.3 Methods of Perovskite Synthesis

The synthesizing methods for perovskite usually take the physical and chemical properties of the target material into consideration. The commonly used methods include solid-state reactions, gas phase preparations, wet chemical method, etc. The following subsections will briefly introduce these methods and will concentrate more on wet chemical method, which is used in our work.

3.3.1 Solid-State Reactions

Solid-state reactions are applicable when the raw materials and the final products are in solid-state and are commonly used for carbonates, nitrates, oxides, etc. [172]. The product is in the form of bulk material. If the target perovskite material has a formula of ABO_3 where A and B are metal elements, raw materials containing A- and B- ions will be ball milling in appropriate media like acetone or isopropanol [173, 174]. The obtained powder will be dried and calcined in the air for a period of time. The calcined sample will be well ground and sieved, after which a higher temperature calcining process is needed to confirm the formation of a single phase of perovskite [173, 175]. Another round of grinding and sieving will be carried out before the sample is ready. Solid-state reactions have been proven to be available for the synthesis of $BaCe_{0.95}Yb_{0.05}O_{3-\delta}$ [176].

3.3.2 Gas Phase Preparations

Gas phase preparations include laser ablation [177], molecular beam epitaxy [178], sputtering [179, 180], electron beam evaporation [181], and thermal evaporation [182]. These techniques can deposit perovskite in a form of thin films (could be bulk materials or nanostructures). The atmosphere and temperature conditions are crucial to control the final products. According to the conditions, gas phase

preparations can be classified into three types: (i) deposition at room temperature with post-annealing at high temperature to form crystal; (ii) deposition at high temperature with post-annealing for crystal perfection; (iii) deposition at very high temperature to form crystal directly. $YBa_2Cu_3O_7$ is an example synthesized by gas phase preparation, which needs Y, Cu and BaF_2 as raw materials and co-evaporation in O_2 with water vapor [182].

3.3.3 Wet Chemical Methods

Wet chemical methods refer to preparations in solution where the product can natively form nanostructures due to the reaction environment. Since the discovery of quantum-size effects was discovered in nanometer-sized semiconductors, the need for synthesizing high quality nanocrystals with controllable size is increasing [183, 184]. While solid-state reactions and gas phase preparations usually produce bulk materials, the liquid-phase chemical reactions have been proven to be the best approach to fabricate well-defined colloidal nanocrystals, especially for metal halide perovskite [185, 186]. There are two commonly used liquid-phase methods for the synthesis of colloidal metal halide perovskites: the hot injection method and the ligand-assisted reprecipitation method [187, 188]. Generally speaking, The hot injection method is performed in a high temperature environment while the ligand-assisted reprecipitation can be done in room temperature, which makes the latter one more cost-effective [189, 190].

3.3.3.1 Hot Injection Method

Hot injection method was first used for the synthesis of cadmium chalcogenide (CdE) nanocrystals in 1993 by Murray et al. [191]. The working principle of hot injection method is to rapidly inject a precursor into a hot solution containing other precursors and ligands, after which a rapid nucleation burst will occur and form small nuclei. The nuclei will continuously grow and become nanocrystals until there are no more monomers available in the solution [192]. Ideally, the formation of nuclei only happens at the first stage, which enables the produced nanocrystals to have a uniform size [190]. Size control of nanocrystals in hot injection method can be realized by (i) tuning the ratio of the surfactants to the precursors; (ii) adjusting the environment temperature for reaction; (iii) changing

reaction time; and (iv) modulating the concentration of the precursors. Hot injection method has been proven to be applicable to synthesize cesium lead halide perovskite $CsPbX_3$, $X = Cl, Br, and I$ by Protesescu et al. in 2015 [91]. In their study, the raw materials are PbX_2 which was dissolved in hot octadecene (ODE), carboxylic acids and primary amines, and Cs-oleate which was injected into the solution. The size control in this study was accomplished by adjusting the reaction time along. Fig. 3.3 shows the sketch of hot injection method used in Protesescu's study and part of their results [193]. A similar method can also be applied to synthesize $MAPbX_3$ with methylamine solution as the injected precursor instead of Cs-oleate [194].

FIGURE 3.3: (a) Brief indication of hot injection method used for synthesis of $CsPbX_3$ ($X=Cl, Br, I$) nanocrystals. (b) Transmission electron microscope (TEM) image of $CsPbBr_3$ nanocrystals fabricated by hot injection method. (c) $CsPbX_3$ ($X=Cl, Br, I$) nanocrystal colloidal solution under ultraviolet (UV) lamp with wavelength of 365nm.

3.3.3.2 Ligand-assisted Reciprecipitation Method

The working principle of ligand-assisted reprecipitation method is based on the supersaturated recrystallization which was first used to extract salt in South Poland in 3500BC [195]. In supersaturated recrystallization, desired ions are continuously dissolved in a solvent until the equilibrium concentration is reached, after which the solution will be moved to a supersaturated non-equilibrium state by means like changing temperature, evaporating solution or adding miscible co-solvent in which the desired ions has low solubility. Processes of precipitation and crystallization happen spontaneously under the non-equilibrium state and produce the requested crystal. Ligand-assisted reprecipitation improves the supersaturated recrystallization by adding ligand to help control the size of crystals down to the nanoscale. The sketch of ligand-assisted reprecipitation is shown in Fig. 3.4 [193].

FIGURE 3.4: Brief indication of Ligand-assisted reprecipitation method

When ligand-assisted reprecipitation is applied to the synthesis of perovskite, the raw materials are precursor salts containing desired ions, ligands, good polar solvent such as dimethylformamide (DMF), dimethylsulfoxide (DMSO), etc., and poor solvent such as toluene and hexane. Depending on the target material, the salts can be MX_2 where $M = \text{Pb, Sn, etc.}$, or CsX , MAX and FAX where $X = \text{Cl}$,

Br, and I. The solubility difference of the precursor salts between the good and poor solvent facilitate the nucleation and crystal growth of perovskite. Unlike hot injection method, the nucleation and crystal growth happens at the same time in ligand-assisted reprecipitation [196], which allows the produced crystal to scale up to gram scale [197–199].

Ligand-assisted reprecipitation method applied on halide perovskite was first reported by Papavassiliou et al. in 2012 who used bulk $MAPbX_3$ as precursor salts, DMF and toluene as a solvent to produce $MAPbX_3$ nanocrystals [200]. Later in 2015, Zhang et al. synthesized $MAPbX_3$ nanocrystals by using $PbBr_2$ and $MABr_2$ as precursor salt which was dissolved in alkyl amines, carboxylic acids and DMF and put into toluene for crystal growth at room temperature [201]. As for all-inorganic cesium lead halide perovskite, hot inject method was commonly used until 2016 when Li et al. synthesized $CsPbX_3$ nanocrystals ($X = Cl, Br, I$) with ligand-assisted reprecipitation method at room temperature [202]. They applied CsX and PbX_2 as precursor salts, DMF together with OLA and OA as good solvent and toluene as poor solvent. Based on their research, the control over the morphology of $CsPbBr_3$ nanocrystals was discovered later by Seth et al. who used ethyl acetate as the poor solvent instead of toluene [203]. The ligands difference in the two kinds of solvent enables formation of quasi-cubic quantum dots, nanoplatelets and nanobars in ethyl acetate, while the growth of nanocubes, nanorods, and nanowires are more encouraged in toluene [203]. The effect of ligands is crucial to the phenomenon. In ethyl acetate which is more polar than toluene, part of the OLA molecules is less likely to attach themselves on the surface of the growing nuclei and allows the crystal to grow more freely. In toluene, on the other hand, the surfaces of nanocrystals are more protected by OLA molecules and the nanocrystals are forced to form cubic structure when the concentration of OLA is high, or wire structure when the concentration of OLA is low.

3.4 Systems for Sample Characterization

To determine the chemical composition, crystal phases and properties of synthesized samples, various systems are applied. The following subsections briefly introduce the tools and methods used in this thesis.

3.4.1 X-ray Photoelectron Spectroscopy (XPS)

XPS is an advanced analysis technique in the microanalysis of materials and micro-devices. It provides information on elemental composition and content, molecular structure, chemical states and bonds of various compounds. Since the X-ray beam incident on the surface of the sample is a photon beam, it has very little damage to the sample. The working principle of XPS is injecting X-rays to the surface of the sample and analyzing the kinetic energies of emitted electrons. The electron binding energy of emitted electrons can be calculated by:

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi) \quad (3.1)$$

where $E_{binding}$ is the binding energy of the electron in the measured material, E_{photon} is the energy of X-ray photons, $E_{kinetic}$ is the kinetic energy of the emitted electron and ϕ is the work function for the specific surface of the material. Since E_{photon} is known and ϕ is a constant, by measuring $E_{kinetic}$ we can learn the binding energy and further analyze the component and structure status of samples.

3.4.2 X-ray Diffraction (XRD)

XRD is usually used in the analysis of crystal structure. When X-ray is incident on the crystal, it produces a periodically changing electromagnetic field. The field causes the electrons and atomic nucleus in the atom to vibrate, which is negligible because of the large mass of the atomic nucleus. The vibrating electron is the wave source of the secondary X-ray, whose wavelength and phase are the same as the incident light. Based on the periodicity of the crystal structure, the scattered waves of each electron in the crystal interfere with each other and form diffraction. The direction in which the scattering wave cycles are consistent and mutually reinforcing is called the diffraction direction, along which lies the diffraction lines. The diffraction intensity of X-rays for crystals is determined by the type, number and arrangement of atoms in the crystal unit cell. So XRD can be used to determine whether a sample is a crystal, if yes it can further determine its crystalline, crystal form and stress of the material structure.

3.4.3 Absorption Spectroscopy

Absorption spectroscopy refers to spectroscopic techniques that measure the spectrum produced by matter absorbing photons and transitioning from a low energy level to a high energy level. The absorption spectrum can be a line spectrum or an absorption band. By studying absorption spectrum we can understand the structure and motion state of atoms, molecules and many other substances, as well as their interaction with electromagnetic fields or particles. The experimental approaches of absorption spectroscopy can be classified according to the light source, sample arrangement and detection techniques. The frequency range of detection varies from X-ray to infrared light.

3.4.4 Photoluminescence (PL)

Photoluminescence (PL) is the light emission from any form of matter under the excitation of photons. It has three main stages including light absorption, energy transfer and light emission. When a material is exposed to light, electrons in the material receive the energy from photons and jump up to higher energy levels and leave holes. The re-combination of electrons and holes creates new photons, and observation of luminescence can be viewed with energy associated with the transition energy.

For semiconductors, PL usually happens when the energy of injected photons is larger than the band gap of semiconductors. The measurement of PL can be used to study the types of recombination, fundamental radiative characteristics, energy transfer rate and doping concentration in semiconductors.

3.4.5 Transmission Electron Microscope (TEM)

Transmission electron microscope is a microscopy technique in which an accelerated and concentrated electron beam is projected onto a very thin sample to form an image. The electrons collide with atoms in the sample and change direction, thereby generating solid angle scattering. The size of the scattering angle is related to the density and thickness of the sample, so images with different brightness and

darkness can be formed. The images will be displayed on imaging devices (such as phosphor screens, films, and photosensitive coupling components) after zooming in and focusing. Because the De Broglie wavelength of electrons is very short, the resolution of transmission electron microscopes is much higher than that of optical microscopes, which can reach 0.1-0.2nm, and the magnification is tens of thousands to millions of times. TEM can be used to observe the fine structure of the sample.

Chapter 4

Sc₂CO_x: Synthesis, Characterization and Temperature Effect

4.1 Introduction

Theoretical result indicates that scandium based MXenes including Sc₂CO₂, Sc₂CF₂ and Sc₂C(OH)₂ are semiconductor with great potential in application [43, 204]. Yet no scandium based MXenes have ever been successfully synthesized. As mentioned earlier, the widely used method to synthesize MXenes is applying hydrofluoric acid (HF) or other liquid etchants like solution of lithium fluoride (LiF) and hydrochloric acid (HCl) to selectively etch away the ‘A’ layer from MAX phases. This method suffers from the limited size of MXene sheets, severe structural defects and uncertain termination groups [20, 21, 23]. Besides, the etchants are usually chemicals containing HF, which is harmful to both humans and environment. What is more important is that selectively etching may not be applicable for all MXenes. The attempt of synthesizing scandium based MXenes using selectively etching has been proven to be difficult due to the lack of a stable corresponding MAX phase [205, 206]. To produce MXenes with better quality in a safer way, other methods are being explored. Mo₂C has been synthesized by chemical vapour deposition (CVD) [160], which proves that selective etching in aqueous acid is not the only way to fabricate MXene. Ti₃AlC₂ has been fabricated by sputtering [35], it may

suggest sputtering is another possible way of MXene synthesis. So here we apply magnetron sputtering to synthesize scandium based MXene. The procedure of synthesis and characterization concentrate on the material instead of equipment.

4.2 Method

The sputtering system applied here is dual-target magnetron sputtering which is customized from Nanofilm Technologies International PTE LTD. The process conditions are set as shown in Table 4.1. Both silicon and sapphire are used as substrates. Substrates are cleaned in the order of Acetone, IPA and DI water with ultrasonic cleaning. The thickness of sample is around 200 nm determined by surface profiler.

Target	Base pressure	Process pressure	Power	Ar ₂ flow
C	6×10^{-4} mTorr	5 mTorr	200 w	24 sccm
Sc	6×10^{-4} mTorr	5 mTorr	29 w	24 sccm
Target	Time	Deposition rate	Substrate temperature	Substrate size
C	2 hrs	30 nm/hr	room temperature	1 cm ²
Sc	2 hrs	60 nm/hr	room temperature	1 cm ²

TABLE 4.1: Sputtering conditions for scandium carbide synthesis.

To determine the properties of the sample, several characterization methods are applied including X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) for chemical composition determination; UV-VIS spectrometer for light transmission and absorption detection; and photoluminescence (PL) for light emission. Thermal annealing was applied to invest the influence of temperature to the sample and was processed in MRL Alloy Furnace under N₂ atmosphere. XRD measurements were carried out on an X-ray diffractometer (Bruker Advance D8 Ew, Germany) with Cu K α radiation ($\gamma=1.54178$ Å) and Bragg-Brentano geometry. The operation voltage and current were 45 kV and 200 mA, respectively. The 2θ range was from 10° to 60° in steps of 0.02°. For XPS, we use AXIS Supra+ XPS surface analysis instrument from Kratos Analytical, which provides 500 mm Rowland circle monochromated Al K α X-ray source, a 165 mm mean radius hemispherical

analyzer and spherical mirror analyzer. Photoluminescence(PL) spectrum was obtained by using Cary eclipse spectrophotometer with the selected light of 190 nm wavelength from xenon flash lamp under room temperature. Absorption spectrum was recorded by using a UV-Vis spectrophotometer from Perkin Elmer Lambda 950.

4.3 Results and Discussion

The comparison among the XRD plots of silicon substrate, scandium carbide, scandium oxide and our sample without annealing is shown in Fig. 4.1. Beside of the peaks corresponding to the (220), (311), (400) and (331) crystal planes of silicon substrate, the peaks at 67° and 61° can be assigned to the (220) plane of scandium carbide and (622) plane of scandium oxide, respectively[207, 208].

FIGURE 4.1: XRD pattern of scandium carbide sample without annealing

More details of the composition of sample is determined by XPS measurement shown in Fig. 4.2. Clearly only scandium, carbon, oxygen and a tiny bit of argon exist in the sample. Argon is introduced during the removal of surface layer in

XPS measurement. Since scandium is very sensitive to oxygen, it is hard to eliminate its influence. The detailed XPS spectrum of scandium, carbon, oxygen and argon are shown in Fig. 4.3. Because argon is stable and hardly reacts with other chemicals, it is used as a reference for the position calibration of other elements as shown in Fig. 4.3(d). The 2p peak of Argon is at 242 eV which is typical for Argon in Silicon[209]. The number and position of peaks can provide information of the chemical components and the bonds in the sample. The scandium XPS spectrum in Fig. 4.3(a) shows two separate sets of peaks (each set contains a 2p_{3/2} peak and a 2p_{1/2} peak), which indicates that scandium has two types of bonds. According to the position of the peaks, the 401 eV peak represents the bond between scandium and oxygen while the 399 eV peak indicates the bond between scandium and carbon[209]. Such bonding suggests the existence of scandium carbide and scandium oxide. The conclusion is supported and further completed by spectrum of oxygen and carbon. Fig. 4.3(b) shows that carbon has two peaks, the 281 eV peak of which indicates the bond between scandium and carbon while the 284 eV peak suggests the existence of C-Sc-O bond[209]. It means that part of the pristine MXene Sc_2C are functionalized by O- terminals. Fig. 4.3(c) gives two bonds of oxygen. The 529 eV peak supports the presence of scandium oxide while the 531 eV peak proves the existence of C-Sc-O bond[209]. It is reasonable as Sc in pristine MXene has dangling bond which attract ions like F-, OH- and O- to become functional groups[20]. So once the sample contact with air, O- will combine with scandium and form O- terminated MXene. In general, the sample consists of Sc_2C , Sc_2CO_x and scandium oxide. The XPS spectrum of sample after 600° thermal annealing is shown in Fig. 4.4. Most of the bond between scandium and carbon has been destroyed as shown in Fig. 4.4(a) and Fig. 4.4(b). The sample mainly consists of scandium oxide after annealing. The XRD and XPS spectrum are the same for samples on both silicon and sapphire substrate beside of the substrate peak. Since sapphire is transparent, the color change of sample before and after annealing is more obvious as shown in the inset of Fig. 4.6.

The optical properties of the sample can be characterized by PL and light absorption measurement. The PL signal of sample without annealing in UV range at around 290 nm was observed under 190 nm laser (Fig. 4.5). The small peak at around 245 nm may be introduced by scandium oxide whose band gap is around 5-6 eV[210]. The absorption coefficient spectrum of sample without annealing agrees

FIGURE 4.2: Overview of XPS spectrum of scandium carbide sample without annealing

FIGURE 4.3: XPS spectrum of (a) scandium (b) carbon (c) oxygen and (d) argon in scandium carbide sample without annealing

FIGURE 4.4: XPS spectrum of (a) scandium (b) carbon (c) oxygen and (d) argon in scandium carbide sample with 600° annealing

with the PL signal as the absorption edge appears at around 290 nm (indicated by the tangential line in Fig. 4.6).

FIGURE 4.5: PL spectrum of scandium carbide sample without annealing

To investigate the influence of temperature on the sample, light absorption coefficient spectrum of samples with different temperature thermal annealing is shown

in Fig. 4.6. The absorption coefficient edge becomes smaller after annealing. And the higher annealing temperature is, the smaller absorption edge will become. The phenomenon is easy to understand as higher temperature encourages more oxygen terminals to attach to scandium carbide. After the temperature becomes higher than 600°C, the remaining scandium carbide in the sample is rapidly oxidized. The whole sample shows a light absorption spectrum similar to scandium oxide (6 eV band gap) which indicates that most of the scandium carbide structure in sample has broken and become scandium oxide. Such conclusion agrees with the XPS spectrum shown in Fig. 4.4. The sample becomes more transparent as the annealing temperature increases because of the change of band gap as indicated in the inset of Fig. 4.6.

FIGURE 4.6: Absorption coefficient vs. wavelength of scandium carbide samples with different temperature thermal annealing. The inset is the photo of samples.

The optical transition can be described in the following equation: $\alpha h\nu = A(h\nu - E_g)^m$, where A is a constant, E_g is the band gap, m equals to 1/2, 2 or 3/2 for direct, indirect and forbidden materials, respectively[211]. The plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus $h\nu$, also known as Tauc plot, are shown in Fig. 4.7 and Fig. 4.8, respectively. We can find straight lines in the $(\alpha h\nu)^2$ curve, which indicates the presence of direct optical transition. Such lines cannot be seen in the $(\alpha h\nu)^{1/2}$ curve, which suggests no obvious indirect optical transitions can be detected[212]. The Tauc plot indicates the scandium carbide samples are direct band gap material.

By continuing the linear part of $(\alpha h\nu)^2$ curve until intersection with the energy axis, band gap can be found. The trend of more oxidation with temperature increasing can also be observed in Tauc plot.

FIGURE 4.7: Plot of $(\alpha h\nu)^2$ versus $h\nu$ of scandium carbide sample with different temperature annealing

FIGURE 4.8: Plot of $(\alpha h\nu)^{0.5}$ versus $h\nu$ of scandium carbide sample with different temperature annealing

4.4 Conclusion

Magnetron sputtering is performed to synthesize scandium based MXene for the first time. The existence of scandium carbide is confirmed by XRD and XPS spectrum. The oxygen sensitivity of scandium makes the sample a mixture of Sc_2C , Sc_2CO_x and scandium oxide which is supported by the XPS spectrum. Photoluminescence measurement indicates that the sample can illuminate light at 290 nm under 190 nm laser excitation which agrees with UV-VIS absorptance measurement. The oxidation of sample becomes more severe as annealing temperature increases. After the temperature goes above 600°C , the MXene structure begins to break and scandium oxide becomes the majority of the sample.

Chapter 5

CsPbBr₃ Nanoplatelet: Thickness Effect

5.1 Introduction

Cesium lead halide perovskites are known for their high quantum yield, narrow photoluminescence emission bandwidth, high absorption efficiency of light [58–62]. The form of nanoplatelets further allows them to adapt to various applications by changing the thickness [69]. In this chapter, we are going to study the effect of thickness on the optoelectronic properties of *CsPbBr₃* by building a $\mathbf{k} \cdot \mathbf{p}$ model. *CsPbBr₃* nanoplatelets with a certain thickness are synthesized and measured to verify the results from theoretical analysis. The details of experiment lie more on the material related process.

5.2 Theoretical Framework

As mentioned above, CsPbBr₃ shows a band structure which looks like a 'reverse version' of zincblende-phase semiconductors as shown in Fig. 2.1 [111]. So the methods used for conventional semiconductors are also applicable for CsPbBr₃. $\mathbf{k} \cdot \mathbf{p}$ method is one of the commonly used theoretical methods for semiconductors, especially for direct band gap semiconductors where the physically relevant states are those close to the band extremes. In this study, we applied an effective mass

envelope function theory approach based on the 8-band $\mathbf{k} \cdot \mathbf{p}$ method in the neighborhood of R-point of the Brillouin zone, where the band extremes of CsPbBr₃ lies[112]. The $\mathbf{k}$ in $\mathbf{k} \cdot \mathbf{p}$ indicates the wave vector away from the R-point while $\mathbf{p}$ is the quantum-mechanical momentum operator. Nonparabolicity of the coupled conduction band (CB) and valence band (VB) including the orbit-splitting bands are considered in our method to solve the eigenenergy and obtain the electronic structure.

Halid perovskite usually has different phases of structure at different temperatures [213]. CsPbBr₃ crystal transforms from orthorhombic $\mathbf{D}_{2h}^{16} - Pmbn$ to tetragonal $\mathbf{D}_{4h}^5 - P4/mbm$ at 88°C and further to cubic $\mathbf{O}_h^1 - Pm3m$ structure at 133 °C as temperature increases [214]. The study in this article focuses on a higher temperature case and applies a modified cubic structure with a parameter $\Delta z = 500meV$ added on the z-axis as band split which describes the inversion asymmetry. The binding energy is also considered.

The basis function and 8-band Hamiltonian are represented in Sec. 2.3.1. The calculation of TME and optical gain are listed in Sec. 2.4.1.

5.3 Experiment Details

5.3.1 Materials

Cesium carbonate (Cs₂CO₃, 99.998%), lead bromide (PbBr₂, 99.999%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), Oleylamine (OAm, 70%), Hexane (99%), Eethyl acetate (99.8%) were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

5.3.2 Preparation of Cesium-oleate Solution

0.2 g Cs₂CO₃, 0.6 mL OA and 8 mL ODE were loaded into a 25 mL three neck flask, dried for 30 min at 120 °C under vacuum, and then heated to 150 °C under

N_2 until all Cs_2CO_3 reacted with OA to form cesium-oleate (Cs-oleate) solution. Then the solution was cooled down to 120 °C.

5.3.3 Preparation of CsPbBr_3 Nanoplatelets

In a typical process, 0.5 mL OAm, 0.5 mL OA, 5 mL ODE and PbBr_2 (0.069 g) were loaded into a 25 mL three neck flask and dried under vacuum for 1.5h at 120 °C. After complete dissolving of PbBr_2 , hot Cs-oleate solution (0.4 mL, prepared as described above) was added at 100 °C, then the reaction mixture was immediately terminated by an ice-water bath. The nanoplatelets were extracted from the crude solution by centrifuging at 10000 rpm for 5 min. After centrifugation, the supernatant was discarded and the precipitate was re-dispersed in hexane, and then centrifuged at 3000 rpm for 3 min to obtain high quality nanoplatelets.

5.3.4 Characterization

Photoluminescence spectrum was obtained from Hamamatsu Quantaurus-QY (model no. C11347) under 365 nm Xenon lamp pulsed. The transmission electron microscopy (TEM) image was obtained from FEI Tecnai G2 F30 at 300 kV.

5.4 Results and Discussions

5.4.1 Theoretical Results

The thickness of CsPbBr_3 nanoplatelets is varied from 2 to 18 unit cells (1.17nm to 10.2nm) for the investigation of its effect on the electronic band structure. Fig. 5.1 shows the band gap between the bottom of conduction band (E1) and top of valence band (H1) (i.e., E1-H1) versus thickness of nanoplatelets. The black dots are band gaps calculated based on our model while the other dots are experiment results from both our experiment and literature. We can observe an increase of band gap as the nanoplatelets become thinner. Such change is more obvious when the thickness of nanoplatelets is less than 6 nm (around 10 unit cell). So we will focus on CsPbBr_3 nanoplatelets with thickness of 3, 5, 7 and 9 unit cell (1.75 nm,

2.93 nm, 4.1 nm and 5.28 nm, respectively) and study their electronic and optical properties.

FIGURE 5.1: Band gaps of CsPbBr₃ nanoplatelets with different thickness

Fig. 5.2 shows the spatial charge densities (square of the wavefunction) of the first five electron states (E1, E2, E3, E4 and E5) and the first three hole states (H1, H2 and H3) of the CsPbBr₃ nanoplatelets with thickness of 3, 5, 7 and 9 unit cell at the R-point. The band offset is fixed at 3eV. We can see that E1 and H1 states for all four types of nanoplatelets are s-like, E2 and H2 states are p-like, while the shape of other states is thickness dependent.

As mentioned above, cesium lead halide perovskites have a 'reverse' band structure compared with direct band gap zincblende-phase semiconductors which have heavy holes, light holes and spin-orbit holes (SO holes). Here we use heavy electrons (HE), light electrons (LE) and SO electrons (SE) to distinguish the electron states in conduction band of CsPbBr₃ nanoplatelets. The distribution of components of the eight levels (E1 to E5 and H1 to H3), also known as the probability in band mixing between conduction electrons and valence holes, for CsPbBr₃ nanoplatelets with thickness of 3, 5, 7 and 9 unit-cell at the R-point is shown in Fig. 5.3. The electron levels are SE dominant in 9 unit-cell nanoplatelet, while HE and LE contribution increases as the thickness of nanoplatelets decreases. The varying extend of coupling between valence holes and conduction HE, LE and SE determine the band-mixing probabilities which are related to the aggregate electron and hole wavefunction and associated charge densities.

FIGURE 5.2: The square of wavefunction of the first 5 conduction bands and first 3 valence bands of CsPbBr₃ nanoplatelet with thickness of 3, 5, 7 and 9 unit-cell

FIGURE 5.3: Distribution of composition of CsPbBr₃ nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell

The TE and TM mode of TME for En-H1 ($n=1, 2, 3, 4$ and 5) transition in the four types of CsPbBr₃ nanoplatelets near R-point is shown in Fig. 5.4 and Fig. 5.5, respectively. The TME in [100] and [110] directions are symmetrical in our model so we only plot TME in [110] direction. From Fig. 5.4 and Fig. 5.5 we can see more types of states participate in the transition process as the thickness of NPLs decreases. For TM mode of TME at R-point, the transition process is dominated by SE1-H1 transition in 5, 7 and 9 unit-cell NPLs while SE2-H1 transition becomes the major one in 3 unit-cell case. The TE mode seems to be influenced by thickness even more as SE1-H1 is no longer the dominant transition for 3, 5, and 7 unit-cell NPLs.

FIGURE 5.4: Transverse electric (TE) mode transition matrix element (TME) for En-H1 transition of CsPbBr₃ nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell

The TE and TM mode of TME for a transition process between En and Hn (n is the subband index, $n = 1, 2, \dots, 10$) at R-point of the four types CsPbBr₃ NPLs are shown in Fig. 5.6 and Fig. 5.7, respectively. The strength of each transition process is indicated by the depth of color. As the thickness of the NPLs decreases, higher strength of transition is less likely to stay on the En-Hn diagonal, which means the optical transition rule of $\delta n = 0$ does not apply to this situation. This

may be caused by the asymmetry due to the introduction of δz , which acts like an electric field on z-axis [215].

FIGURE 5.5: Transverse magnetic (TM) mode transition matrix element (TME) for En-H1 transition of CsPbBr₃ nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell

The effect of thickness on the optical properties of NPLs is investigated by analyzing the optical gain, maximum optical gain (MOG) and differential gain (dg/dn). The TE and TM mode of optical gain as a function of photon energy of CsPbBr₃ NPLs with thickness of 3, 5, 7 and 9 unit-cell is shown in Fig. 5.8. The injected carrier density (n) ranges from 1 to $5 \times 10^{19} \text{cm}^{-3}$ for every NPL case. According to equation (5), optical gain is influenced by TME, carrier density, material and so on. A blue shift of peak position can be observed as the thickness decreases at fixed carrier density. When the carrier density is $5 \times 10^{18} \text{cm}^{-3}$, for example, peak positions of optical gain are 2420nm, 2446nm, 2526nm and 2752nm for 9, 7, 5 and 3 unit-cell NPLs, respectively. This is due to the increased quantum confinement introduced by reduction of thickness, which makes the energy levels more separated. Thus, the transitions occur at higher energy.

FIGURE 5.6: Transverse electric (TE) mode transition matrix element (TME) at R-point for transitions between E_n and H_n ($n=1,2,\dots,10$) of CsPbBr_3 nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell

FIGURE 5.7: Transverse magnetic (TM) mode transition matrix element (TME) at R-point for transitions between E_n and H_n ($n=1,2,\dots,10$) of CsPbBr_3 nanoplatelets with thickness of 3, 5, 7, and 9 unit-cell

FIGURE 5.8: The TE (a-d) and TM (e-h) mode optical gain spectrum of CsPbBr₃ nanoplatelets with thickness of (a) (e) 3; (b) (f) 5; (c) (g) 7; and (d) (h) 9 unit-cell

FIGURE 5.9: The TE (a-d) and TM (e-h) mode maximum optical gain (MOG) and differential gain (dg/dn) spectrum of CsPbBr₃ nanoplatelets with thickness of (a) (e) 3; (b) (f) 5; (c) (g) 7; and (d) (h) 9 unit-cell

The TE and TM mode of maximum optical gain (MOG) and differential gain (dg/dn) of CsPbBr₃ nanoplatelets are shown in Fig. 5.9. MOG is highly related with TME, Fermi factor and thickness of NPLs. A positive gain can be reached when the photon energy fulfill the condition of $E_g < \hbar\omega < E_{Fc} - E_{Fv}$. Since E_{Fc} and E_{Fv} depend on carrier density, fewer photon can satisfy the requirement as injected carrier density increases, which brings a saturation point to MOG when the carrier density is high enough. From Fig. 5.9 we can see that as thickness of NPLs increases, the carrier density for MOG to reach saturation decreases. Fig. 5.10 indicates that thick CsPbBr₃ NPLs can only maintain high dg/dn at a certain range of carrier density, while thin NPLs allows dg/dn to increase continuously with carrier density. Differential gain can be used as a measure of how effective the material can transform injected carrier to photon emission in a laser. A high differential gain can lead to a narrow spectral emission width, low-frequency chirp and higher speed of modulation [216, 217].

5.4.2 Experimental Results

We synthesized and characterized 7 unit-cell (around 4 nm) CsPbBr₃ NPLs to certificate our theoretical results. Fig. 5.10 shows the photoluminescence (PL) spectrum and transmission electron microscopy (TEM) image of our synthesized NPL sample. From Fig. 5.10(b) we may notice that most NPLs in the sample have thickness of 4.1 nm, while slight amounts of them appear thicker. This agrees with the PL spectrum in Fig. 5.10(a), where a strong peak at 499 nm is observed, which corresponds to the majority of NPLs, while a "shoulder" at higher wavelength is introduced by the thicker minority. The observation fits well with our theoretical prediction indicated in Fig. 5.1.

5.5 Conclusions

A comprehensive study of the electronic band structure, band mixing probability, optical transitions and gain of CsPbBr₃ nanoplatelets is performed as a function of thickness with the help of $k \cdot p$ method. The band gap of CsPbBr₃ NPLs increases as their thickness decreases. We can predict the band gap of CsPbBr₃ nanoplatelet

FIGURE 5.10: The (a) photoluminescence (PL) spectrum and (b) transmission electron microscopy (TEM) image of CsPbBr₃ nanoplatelets with thickness of 4.1 nm.

with any given thickness using our model, which agrees well with results from our experiment and literature. Band mixing is more obvious for thinner NPLs, which influences the wavefunction and transition matrix element. A blue shift in optical gain peak position can be observed as the thickness of NPLs decreases due to the increase of band gap. As carrier density increases, the maximum optical gain (MOG) of each NPL will reach saturation. Higher density of carrier is needed for MOG of thinner NPL to reach saturation. Thick NPL can only get high differential gain at a small range of carrier density. Overall, the thickness can greatly influence the optoelectronic properties of CsPbBr₃ nanoplatelets. To fulfill the need of different applications and optimize the performance, we need to choose NPLs with proper thickness.

Chapter 6

CsPbBr₃ Quantum Dot: Size effect

6.1 Introduction

CsPbBr₃ quantum dots are materials with great potential in power-generating and lighting devices [82–85]. The photoluminescence yield of such materials can reach 80%, which attracts a lot of interest[90, 91]. Experiments have shown that the band gap of *CsPbBr₃* quantum dots can be manipulated from blue to green spectral regions (410-650)nm [92]. In this chapter, we develop an effective-mass model for the analysis of the size effect on *CsPbBr₃* quantum dots. The model is built based on method. Optoelectronic properties of *CsPbBr₃* quantum dots are analysed and compared with experimental results from the literature. The main content in this chapter is pure theoretical results. Related experiment results from the literature are discussed and compared to verify them.

6.2 Theoretical Framework

Cesium lead halide perovskites are usually synthesized in the form of colloid, where quantum dots of perovskites are surrounded by ligand dielectric medium. The ligand offers the protection against contamination and enhances the optical properties

of quantum dots by passivating the surface electronic states [83]. The 3D atom-by-atom model of a typical CsPbBr₃ quantum dot we applied is shown in Fig. 6.1.

Since physically relevant states are those close to the band extremes (the R-point of the Brillouin zone for CsPbBr₃ [218]), we apply an effective mass envelope function theory approach based on the 8-band $\mathbf{k} \cdot \mathbf{p}$ method in the neighborhood of R-point of the Brillouin zone for each quantum dot geometry. The $\mathbf{k}$ here indicates the wave vector away from the R-point. The method takes into consideration of nonparabolicity of the coupled conduction band (CB) and valence band (VB) simultaneously, which covers the spin-orbit splitting bands, to solve the eigenenergy and obtain its electronic structure in the vicinity of the R-point.

FIGURE 6.1: Three-dimensional atom-by-atom model of typical CsPbBr₃ quantum dots.

As mentioned in Sec. 5.2, the structure phase of halide perovskite is temperature dependent. At temperature below 88°C, CsPbBr₃ has orthorhombic $\mathbf{D}_{2h}^{16} - Pmbn$ structure. As temperature increases, the material tends to have tetragonal $\mathbf{D}_{4h}^5 - P4/mbm$ structure at intermediate-temperature and finally becomes cubic $\mathbf{O}_h^1 - Pm3m$ structure above 133°C [219]. Here we concentrate on modified cubic structure with adjustment on z-axis. The parameter $\Delta z = 500meV$ is added as a

split on z-axis to better fit the real situation. The model can be a good approximation for the higher temperature case. Similar temperature-dependent phase is also observed in hybrid inorganic-organic perovskites such as CH₃NH₃PbI₃ [220]. The model we developed here can also be applied to these materials with proper parameters.

The basis Bloch functions and 8-band Hamiltonian are expressed in details in Sec. 2.3.2. The optical gain and TMEs are calculated using Eq. 2.24 and Eq. 2.25, respectively.

6.3 Results and Discussions

To determine the influence of size on the band structure of cubic CsPbBr₃ quantum dot, we studied quantum dots with size varying from 4nm to 20nm.

Fig. 6.2 shows the energy band gaps between the bottom of conduction band ($E1$) and the top of valence band ($H1$) of cubic quantum dots with sizes of 4nm, 6nm, 8nm, 10nm, 12nm, 16nm and 20nm. The black dots are calculated band gaps ($E1 - H1$) without binding energy.

To calculate the binding energy, commercial software NEXTNANO is applied. NEXTNANO works as a simulator for calculating, in a consistent manner, the realistic electronic structure of three-dimensional heterostructure quantum devices under bias and its current density close to equilibrium. The electronic structure is calculated fully quantum mechanically, whereas the current is determined by employing a semiclassical concept of local Fermi levels that are calculated self-consistently. It can simulate quantum dots, wires, etc. The basic working principle of NEXTNANO include 8-band $\mathbf{k} \cdot \mathbf{p}$ model within a finite differences grid. By sending the required information including the chemical composition, lattice structure, etc. into the software, it will give the needed results after calculation [221]. After considering the binding energy calculated by NEXTNANO, we can obtain the red dots which fit better with experiment results. An increase of band gap can be observed when the quantum dot size decreases, which matches the experiment results from the literature (pink and blue dots) [91, 222] and our own experiment

(green dot). It is noticeable that the dependence of band gap on size has a drastically increase when the size of a quantum dot is about 8nm. For larger quantum dots, such change becomes gradual.

FIGURE 6.2: Band gaps of cubic CsPbBr₃ quantum dots with different sizes.

The square of the wavefunction, also known as spatial charge densities of electron and hole states, of the first 3 conduction bands ($E1 - E3$) and valence bands ($H1 - H3$) of a 4nm-cubic CsPbBr₃ quantum dot are shown in Fig. 6.3. The color gives information of the probability of finding electrons and holes in the space.

The TE and TM mode of transition matrix element (TME) of quantum dots with different sizes are shown in Fig. 6.4 and Fig. 6.5, respectively. The color indicates the strength of stimulated electron transition between different bands. For both TE and TM mode of TME, the transitions happen around the $En - Hn$ ($n=1,2,3,\dots$) diagonal. In the TE mode, $E1 - H1$ transition dominates at smaller quantum dots (4nm and 6nm). But for larger quantum dots (8nm and 10nm), the strongest transition happens at $E2 - H1$ for 8nm and $E5 - H1$ for 10nm. Such phenomenon may be caused by the introduction of Δz , which acts like an electric

FIGURE 6.3: The square of wavefunction of the first 3 conduction bands and valence bands of 4nm cubic CsPbBr₃ quantum dot.

field on z-axis and breaks the symmetry. The asymmetry creates splitting of energy band and the transition rule of $\Delta n = 0$ is broken. For TE mode on x-y plane, the influence of such asymmetry may be similar to perovskite quantum well, which becomes more obvious as quantum dot size increases [223]. For TM mode along z-axis, the asymmetry may have larger influence on smaller quantum dots. Fig. 6.5 indicates that for TM mode, larger quantum dots (8nm and 10nm) still have the strongest transition at $E1 - H1$, while the transition peaks have a small shift for smaller quantum dots (4nm and 6nm).

To better understand the transition process in CsPbBr₃ quantum dots, we studied $f_c - f_v$ shown in Fig. 6.6. It indicates the possibility of transition between conduction band and valence band. The transition can only happen when $f_c - f_v$ is beyond zero. As the size of quantum dot increases, it is reasonable to observe an increase in both value of $f_c - f_v$ and number of available states for transition. The wider band gap of a smaller quantum dot (as shown in Fig. 6.2) makes it harder for electron to transit. Meanwhile, the strong quantum confinement of small quantum dot makes the distance between energy levels so far away from each other that fewer energy levels can be reached by electrons.

FIGURE 6.4: TE mode of transition matrix element of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr₃ quantum dot.

FIGURE 6.5: TM mode of transition matrix element of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr₃ quantum dot.

The product of TME and $f_c - f_v$ can offer more straight-forward and meaningful sight of the transition in CsPbBr₃ quantum dots as shown in Figs. 6.7 and 6.8 for TE and TM mode, respectively. For both TE and TM mode, there are less zones with value beyond zero when the size of quantum dots decreases, which means multi-transition is unlikely to happen in small quantum dot.

FIGURE 6.6: The difference of Fermi distribution between conduction band and valence band $f_c - f_v$ of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr₃ quantum dot.

To look further, we investigated the effect of size on the optical gain of CsPbBr₃ quantum dots. The optical gain spectrum of CsPbBr₃ quantum dots with size of 4nm, 6nm, 8nm and 10nm as a function of photon energy are shown in Fig. 6.9. Varying injected carrier density is set for each quantum dot. It is noticeable that a higher injected carrier density is needed for smaller quantum dot to get positive optical gain. The reason is the wider band gap of smaller quantum dot makes carrier transition harder to occur as mentioned above. The band gap difference caused by quantum dot size also contributes to the blue shift of emission peak when the size decreases.

FIGURE 6.7: The product of TE mode transition matrix element and the difference of Fermi distribution between conduction band and valence band $f_c - f_v$ of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr₃ quantum dot.

FIGURE 6.8: The product of TM mode transition matrix element and the difference of Fermi distribution between conduction band and valence band $f_c - f_v$ of (a) 4nm, (b) 6nm, (c) 8nm, and (d) 10nm cubic CsPbBr₃ quantum dot.

We can also observe a slight blue shift of the emission peak when the carrier density increases for each quantum dot. The blue shift can be explained with the help of band filling effect, also known as Burstein-Moss shift, which was originally discovered to explain the changes of band gap in degenerate InSb with various doping concentrations [224, 225]. The phenomenon is proven to be commonly seen in intrinsic semiconductors including organometal halide perovskite [226–229]. When carriers keep being injected, the states near the bottom of conduction band and top of valence band are quickly occupied. The upcoming carriers have to occupy states with higher energy level due to Pauli exclusion principle. It will cause the broadening of band gap, which can be observed in absorption spectrum [229]. The influence of band filling effect on optical emission is more complicated as electrons from all possible energy states contribute to the recombination process and affect each other. So the carrier-density-dependent blue shift in emission peak is difficult to quantify with current model. Band filling effect is more prominent in bigger quantum dot because the quantum confinement in larger quantum dot is not so strong and induces less split of energy states. Carriers are more likely to occupy higher energy states which are not so far away from the lowest ones. In the smaller quantum dot, on the other hand, the distance between energy states are too far for carriers to cover. Such conclusion is also supported by the Fermi distribution analyze above, which indicates fewer zones with value beyond zero in a smaller quantum dot.

The maximum optical gain (MOG) and differential gain (dg/dn) shown in Fig. 6.10 help us understand the potential of CsPbBr₃ quantum dot in optical devices. To achieve positive gain, the photon energy must meet the requirement of $E_g < \hbar\omega < E_{Fc} - E_{Fv}$, where E_{Fc} and E_{Fv} are influenced by carrier density. As the carrier density increases, fewer photons can meet the requirement, so the maximum optical gain will increase to a certain level and reach saturation. Fig. 6.10 indicates that the carrier density for small quantum dots to get saturation is much higher than large ones, and the differential gain of small quantum dots can reach a rather high level. What's more, the differential gain of small quantum dots can maintain a high level for various carrier densities within a certain range. Such feature can be useful as high differential gain should lead to high modulation bandwidth and low frequency chirp as well as narrow line-width capabilities [230, 231].

FIGURE 6.9: The optical gain spectrum of (a) 4nm, (b) 6nm, (c) 8nm and (d) 10nm CsPbBr₃ quantum dot. n is the carrier density with unit of 10^{18}cm^{-3} .

FIGURE 6.10: The maximum optical gain (MOG) and differential gain(dg/dn) spectrum of (a) 4nm, (b) 6nm, (c) 8nm and (d) 10nm CsPbBr₃ quantum dot.

6.4 Conclusion

A comprehensive study of the effect of size on electronic band structure, optical transition and gain of cubic CsPbBr₃ quantum dot is performed. The band gap of CsPbBr₃ quantum dot increases as the size becomes smaller due to quantum confinement. The analysis of transition matrix element and Fermi distribution indicates that when the QD size decreases, transition to high energy level ($En - H1, n > 2$) is less possible to happen. The peak position of optical gain of cubic CsPbBr₃ quantum dot has blue shift when the size decreases due to the increase of band gap. Band filling effect can lead to a blue shift on emission peak, which is more obvious for large quantum dots. Smaller quantum dot needs higher injected carrier density to have positive gain and reach gain saturation. The differential gain of small quantum dots can reach a high level and maintain such level when the carrier density varies in a certain range. On the whole, the choice of size parameter of CsPbBr₃ quantum dot needs to be made while optimizing the performance for the desired application. The size of quantum dot not only influences the bandstructure, but also affects the position of gain peak and magnitude of differential gain. Since the differential gain is a measure of the efficiency of injected carriers transforming to photon emission in a laser, we suggest more study on the smaller CsPbBr₃ quantum dots for the application in laser-related area.

Chapter 7

Thesis Summary and Conclusions

7.1 Thesis Summary

Semiconductors have been playing a very important role in both scientific research and our daily life throughout the 20th century. When we look around, we would see semiconductors involved in communications, traffic, power generation, lighting, entertainment, power conversion and other fields. It will, not surprisingly, play a critical role in promoting the development of society in the future.

As the feature size of semiconductor devices keeps shrinking, semiconductor nanostructures including quantum dots, quantum wells, quantum rings and nanoplatelets are leading the edge of research areas of semiconductors. Among the wide range of studied semiconductor materials, (i) scandium based MXenes and (ii) cesium lead halide perovskite are two types of semiconductors that have shown their superior properties and potential for novel semiconductor devices. In this thesis, we report studies on the aforementioned two types of semiconductor materials.

In Chapter 1 we introduce the history, background and motivation of the work reported in this thesis followed by a review of relevant literature.

In Chapter 2 we briefly introduce the optoelectronic theory of semiconductors applied in our work from a mathematical view.

In chapter 3 we list the experimental systems and tools applied in our work for the synthesis and characterization of semiconductors.

Chapter 4 introduces in detail of the synthesis process of Sc_2CO_x by magnetron sputtering, which is followed by the characterization of the produced sample.

Chapter 5 discusses the effect of thickness on the electronic bandstructure and optical properties of CsPbBr_3 nanoplatelets using theoretical modeling and experimental measurements.

Chapter 6 studies the effect of size on CsPbBr_3 quantum dots with the help of an 8-band $\mathbf{k} \cdot \mathbf{p}$ model.

7.2 Thesis Conclusion

After giving a brief background of the novel semiconductor materials, this thesis presents studies on two specific materials, which are Sc_2CO_x and CsPbBr_3 . The two materials share the following common features: 1. Both of them are direct band gap materials. 2. They can be synthesized in the form of two-dimensional structures. 3. They are proven or predicted to have great potential in various applications. 4. They are newly discovered and require more study before stepping into commercial applications. The first two properties indicate that both materials may be suitable for opto-electrical applications, while the other two features offer plenty of motivation to learn more about them. The distinctions between the two materials are also obvious. On the one hand, different band structures make them cover separated ranges of wavelength as candidates of opto-electrical applications. On the other hand, the current research progress of the two materials is quite diverse, which suggests dissimilarity in the directions of studying them. For Sc_2CO_x , it is one of the least known members in the big family of MXene because no sample

of it has been studied and reported before. It is also one of the few types of MXene that are predicted to be direct band gap semiconductors. To fulfill the need of revealing the properties of Sc_2CO_x with experimental approaches, the first sample containing Sc_2CO_x is synthesized by magnetron sputtering and the whole procedure is presented in this thesis with all the details. The existence of scandium carbide is confirmed by XRD and XPS spectrum. And the optical properties are measured by XPS, PL and UV-VIS absorptance system. The results indicates that Sc_2CO_x is a direct band gap material which agrees with theoretical predictions. It can give photoluminescence signal in UV range. The first step for Sc_2CO_x to be applied in applications would be solving its oxygen sensitivity problem, which is quite obvious during our study. For CsPbBr_3 , plenty experimental results have been reported about it because of its amazing efficiency in photoelectric conversion. To learn more about the origination of its optical properties and to guide the future work, it is necessary to build an efficient physical model and do a comprehensive theoretical work based on it. Since CsPbBr_3 in the forms of nanoplatelets and quantum dots are both commonly seen in the experimental reports, we create different models for each of them and do a separate study. Here in this thesis, k·p method is applied to build such model. For CsPbBr_3 nanoplatelets, the main variable is the thickness of nanoplatelets. The electronic band structure, band mixing probability, optical transitions and gain as functions of thickness are studied. The variable change to size for CsPbBr_3 quantum dots while the series of study is carried out. Among the findings of the study, two conclusions are worth mentioning. The first one is that the thickness of nanoplatelets and the size of quantum dots can change the band gap of materials, which means the engineering of these dimensional factors can adapt the materials for applications in multiple ranges of wavelength. With the help of our model, it is easier to locate the target material for a specific need. The second one is that thinner CsPbBr_3 nanoplatelets and smaller CsPbBr_3 quantum dots can reach higher differential gain, which is more beneficial for light-emitting related applications.

List of Author's Publications

- **Qiran Chen**, Zhigang Song, Daohua Zhang and Weijun Fan, “Effect of Size on the Electronic Structure and Optical Properties of Cubic $CsPbBr_3$ Quantum Dots,” *IEEE Journal of Quantum Electronics*, vol. 56, no. 1, pp. 1-7, Feb. 2020.
- **Qiran Chen**, Daohua Zhang, Jisheng Pan and Weijun Fan, “Optical properties of two dimensional semi-conductive MXene Sc_2CO_x produced by sputtering,” *Optik*, vol. 219, pp. 165046, Jun. 2020.
- **Qiran Chen**, Zhaojin Wang, Zhigang Song, Weijun Fan, Kai Wang, Munho Kim and Daohua Zhang, “Effect of thickness on the electronic structure and optical properties of quasi two-dimensional perovskite $CsPbBr_3$ nanoplatelets,” to be submitted for review.
- **Qiran Chen**, Weijun Fan, Zhigang Song, Daohua Zhang and Handong Sun, “Band Structure of Perovskite Cubic Quantum Dot,” *the 10th International Conference on Materials for Advanced Technologies.*, Singapore, Jun. 2019.
- **Qiran Chen**, Daohua Zhang and Weijun Fan, “First principles investigation of semiconductor like MXenes,” *the 13th Pacific Rim Conference on Lasers and Electro-Optics (CLEO Pacific Rim, CLEO PR)*, Hong Kong, Jul. 2018.

Bibliography

- [1] G Busch. Early history of the physics and chemistry of semiconductors-from doubts to fact in a hundred years. *European Journal of Physics*, 10(4):254–264, oct 1989. ISSN 0143-0807. doi: 10.1088/0143-0807/10/4/002. URL <https://iopscience.iop.org/article/10.1088/0143-0807/10/4/002>. 1
- [2] Enn Velmre. Thomas Johann Seebeck (1770-1831). *Proceedings of the Estonian Academy of Sciences: Engineering*, 13(4):276–282, 2007. ISSN 14060175. 1
- [3] V. G. Lytovchenko and Maksym V. Strikha. 100 years of semiconductor science: The Ukrainian contribution. *Europhysics News*, 45(1):15–18, 2014. ISSN 05317479. doi: 10.1051/epn/2014101. 1
- [4] E. H. Hall. On a new action of the magnet on electric currents. *American Journal of Mathematics*, 2(3):287–292, 1879. ISSN 00029327, 10806377. URL <http://www.jstor.org/stable/2369245>. 1
- [5] Isobel Falconer. Corpuscles, electrons and cathode rays: J. j. thomson and the 'discovery of the electron'. *The British Journal for the History of Science*, 20(3):241–276, 1987. ISSN 00070874, 1474001X. URL <http://www.jstor.org/stable/4026358>. 1
- [6] J. Buchwald A. Warwick. *Histories of the Electron: The Birth of Microphysics*. 2001. 1
- [7] Willem Hackmann. P. r. morris. a history of the world semiconductor industry. iee history of technology series 12. london: Peter peregrinus on behalf of the institution of electrical engineers, 1990. pp. 171. isbn 0-86341-227-0. £32. *British Journal for the History of Science*, 25(4):495–496, 1992. doi: 10.1017/s0007087400029964. 2
- [8] N. Dasgupta and A. Dasgupta. *Semiconductor Devices: Modelling and Technology*. PHI Learning, 2004. ISBN 9788120323988. URL <https://books.google.com.sg/books?id=PlaC-M50GTUC>. 2
- [9] W. S. Gorton. The genesis of the transistor. *Proceedings of the IEEE*, 86(1): 50–52, 1998. 2

- [10] A.N. Saxena. *Invention of Integrated Circuits: Untold Important Facts*. International series on advances in solid state electronics and technology. World Scientific, 2009. ISBN 9789812814463. URL <https://books.google.com.sg/books?id=z7738Wq-j-8C>. 2
- [11] Mark Fox and Radu Ispasoiu. *Quantum Wells, Superlattices, and Band-Gap Engineering*, pages 1021–1040. 01 2007. doi: 10.1007/978-0-387-29185-7_42. 3
- [12] Karl F. Renk. *GaAs Quantum Well Laser*, pages 457–474. Springer International Publishing, Cham, 2017. ISBN 978-3-319-50651-7. doi: 10.1007/978-3-319-50651-7_22. URL https://doi.org/10.1007/978-3-319-50651-7_22. 4
- [13] R. Rossetti, S. Nakahara, and L. E. Brus. Quantum size effects in the redox potentials, resonance Raman spectra, and electronic spectra of CdS crystallites in aqueous solution. *jcp*, 79(2):1086–1088, July 1983. doi: 10.1063/1.445834. 4
- [14] A. I. Ekimov and A. A. Onushchenko. Quantum size effect in three-dimensional microscopic semiconductor crystals. *JETP Letters*, 34:363–366, 1981. 4
- [15] L. E. Brus. Electron–electron and electron-hole interactions in small semiconductor crystallites: The size dependence of the lowest excited electronic state. *The Journal of Chemical Physics*, 80(9):4403–4409, 1984. doi: 10.1063/1.447218. 4
- [16] Cédric Mongin, Sofia Garakyaraghi, Natalia Razgoniaeva, Mikhail Zamkov, and Felix N. Castellano. Direct observation of triplet energy transfer from semiconductor nanocrystals. *Science*, 351(6271):369–372, 2016. ISSN 0036-8075. doi: 10.1126/science.aad6378. URL <https://science.sciencemag.org/content/351/6271/369>. 5
- [17] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669, 2004. ISSN 0036-8075. doi: 10.1126/science.1102896. URL <https://science.sciencemag.org/content/306/5696/666>. 5, 29
- [18] Michael Ashton, Joshua Paul, Susan B. Sinnott, and Richard G. Hennig. Topology-scaling identification of layered solids and stable exfoliated 2d materials. *Phys. Rev. Lett.*, 118:106101, Mar 2017. doi: 10.1103/PhysRevLett.118.106101. URL <https://link.aps.org/doi/10.1103/PhysRevLett.118.106101>. 6
- [19] Dr. Arno Avela. Graphene market insights 2020, analysis and forecast global and chinese market to 2025, by manufacturers, regions, technology, application, product type. [EB/OL]. https://www.researchandmarkets.com/research/zh8mh8/global_and_china Accessed April 4, 2020. 6

- [20] Michael Naguib, Murat Kurtoglu, Volker Presser, Jun Lu, Junjie Niu, Min Heon, Lars Hultman, Yury Gogotsi, and Michel W. Barsoum. Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2 . *Advanced Materials*, 23(37):4248–4253, 2011. ISSN 09359648. doi: 10.1002/adma.201102306. 7, 30, 31, 42, 45
- [21] Michael Naguib, Olha Mashtalir, Joshua Carle, Volker Presser, Jun Lu, Lars Hultman, Yury Gogotsi, and Michel W. Barsoum. Two-dimensional transition metal carbides. *ACS Nano*, 6(2):1322–1331, 2012. ISSN 19360851. doi: 10.1021/nn204153h. 7, 31, 42
- [22] A L Ivanovskii and A N Enyashin. Graphene-like transition-metal nanocarbides and nanonitrides. *Russian Chemical Reviews*, 82(8):735–746, 2013. ISSN 0036-021X. doi: 10.1070/RC2013v082n08ABEH004398. URL <http://stacks.iop.org/0036-021X/82/i=8/a=735?key=crossref.cbfd3918cd6d2164e9f6de1743d47399>.
- [23] Michael Naguib, Joseph Halim, Jun Lu, Kevin M. Cook, Lars Hultman, Yury Gogotsi, and Michel W. Barsoum. New two-dimensional niobium and vanadium carbides as promising materials for li-ion batteries. *Journal of the American Chemical Society*, 135(43):15966–15969, 2013. ISSN 00027863. doi: 10.1021/ja405735d. 31, 42
- [24] Igor R. Shein and Alexander L. Ivanovskii. Graphene-like nanocarbides and nanonitrides of d metals (MXenes): synthesis, properties and simulation. *Micro & Nano Letters*, 8(2):59–62, 2013. ISSN 1750-0443. doi: 10.1049/mnl.2012.0797. URL <http://digital-library.theiet.org/content/journals/10.1049/mnl.2012.0797>.
- [25] M. Ghidui, M. Naguib, C. Shi, O. Mashtalir, L. M. Pan, B. Zhang, J. Yang, Y. Gogotsi, S. J.L. Billinge, and M. W. Barsoum. Synthesis and characterization of two-dimensional Nb_4C_3 (MXene). *Chemical Communications*, 50(67):9517–9520, 2014. ISSN 1364548X. doi: 10.1039/c4cc03366c. 31
- [26] Olha Mashtalir, Maria R. Lukatskaya, Meng Qiang Zhao, Michel W. Barsoum, and Yury Gogotsi. Amine-assisted delamination of Nb_2C MXene for li-ion energy storage devices. *Advanced Materials*, 27(23):3501–3506, 2015. ISSN 15214095. doi: 10.1002/adma.201500604.
- [27] Michael Ghidui, Maria R. Lukatskaya, Meng Qiang Zhao, Yury Gogotsi, and Michel W. Barsoum. Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. *Nature*, 516(7529):78–81, 2015. ISSN 14764687. doi: 10.1038/nature13970. URL <http://dx.doi.org/10.1038/nature13970>.
- [28] Olha Mashtalir, Michael Naguib, Boris Dyatkin, Yury Gogotsi, and Michel W. Barsoum. Kinetics of aluminum extraction from Ti_3AlC_2 in hydrofluoric acid. *Materials Chemistry and Physics*, 139(1):147–152, 2013.

- ISSN 02540584. doi: 10.1016/j.matchemphys.2013.01.008. URL <http://dx.doi.org/10.1016/j.matchemphys.2013.01.008>. 7
- [29] Xianghua Zhang, Maoquan Xue, Xinghua Yang, Zhiping Wang, Guangsi Luo, Zhide Huang, Xiaoli Sui, and Changsheng Li. Preparation and tribological properties of $\text{Ti}_3\text{C}_2(\text{OH})_2$ nanosheets as additives in base oil. *RSC Advances*, 5(4):2762–2767, 2015. ISSN 20462069. doi: 10.1039/c4ra13800g. 7
- [30] Qing Tang, Zhen Zhou, and Panwen Shen. Are MXenes promising anode materials for Li ion batteries? Computational studies on electronic properties and Li storage capability of Ti_3C_2 and $\text{Ti}_3\text{C}_2\text{X}_2$ ($\text{X} = \text{F}, \text{OH}$) monolayer. *Journal of the American Chemical Society*, 134(40):16909–16916, 2012. ISSN 00027863. doi: 10.1021/ja308463r. 7
- [31] Tao Hu, Jiemin Wang, Hui Zhang, Zhaojin Li, Minmin Hu, and Xiaohui Wang. Vibrational properties of Ti_3C_2 and $\text{Ti}_3\text{C}_2\text{T}_2$ ($\text{T} = \text{O}, \text{F}, \text{OH}$) monosheets by first-principles calculations: A comparative study. *Physical Chemistry Chemical Physics*, 17(15):9997–10003, 2015. ISSN 14639076. doi: 10.1039/c4cp05666c. 7
- [32] A. N. Enyashin and A. L. Ivanovskii. Two-dimensional titanium carbonitrides and their hydroxylated derivatives: Structural, electronic properties and stability of MXenes $\text{Ti}_3\text{C}_{2-x}\text{N}_x(\text{OH})_2$ from DFTB calculations. *Journal of Solid State Chemistry*, 207:42–48, 2013. ISSN 00224596. doi: 10.1016/j.jssc.2013.09.010. URL <http://dx.doi.org/10.1016/j.jssc.2013.09.010>.
- [33] H. Lashgari, M. R. Abolhassani, A. Boochani, S. M. Elahi, and J. Khodadadi. Electronic and optical properties of 2D graphene-like compounds titanium carbides and nitrides: DFT calculations. *Solid State Communications*, 195: 61–69, 2014. ISSN 00381098. doi: 10.1016/j.ssc.2014.06.008. URL <http://dx.doi.org/10.1016/j.ssc.2014.06.008>.
- [34] Mohammad Khazaei, Ahmad Ranjbar, Mahdi Ghorbani-Asl, Masao Arai, Taizo Sasaki, Yunye Liang, and Seiji Yunoki. Nearly free electron states in MXenes. *Physical Review B*, 93(20):1–10, 2016. ISSN 24699969. doi: 10.1103/PhysRevB.93.205125. 7
- [35] Joseph Halim, Maria R. Lukatskaya, Kevin M. Cook, Jun Lu, Cole R. Smith, Lars Åke Näslund, Steven J. May, Lars Hultman, Yury Gogotsi, Per Eklund, and Michel W. Barsoum. Transparent conductive two-dimensional titanium carbide epitaxial thin films. *Chemistry of Materials*, 26(7):2374–2381, 2014. ISSN 15205002. doi: 10.1021/cm500641a. 7, 31, 42
- [36] Michael Naguib, Jérémy Come, Boris Dyatkin, Volker Presser, Pierre Louis Taberna, Patrice Simon, Michel W. Barsoum, and Yury Gogotsi. MXene: A promising transition metal carbide anode for lithium-ion batteries. *Electrochemistry Communications*, 16(1):61–64, 2012. ISSN 13882481. doi: 10.1016/j.elecom.2012.01.002. URL <http://dx.doi.org/10.1016/j.elecom.2012.01.002>.

- [37] Seon Joon Kim, Michael Naguib, Mengqiang Zhao, Chuanfang Zhang, Hee Tae Jung, Michel W. Barsoum, and Yury Gogotsi. High mass loading, binder-free MXene anodes for high areal capacity Li-ion batteries. *Electrochimica Acta*, 163:246–251, 2015. ISSN 00134686. doi: 10.1016/j.electacta.2015.02.132. URL <http://dx.doi.org/10.1016/j.electacta.2015.02.132>.
- [38] Maria R. Lukatskaya, Olha Mashtalir, Chang E. Ren, Yohan Dall’Agnese, Patrick Rozier, Pierre Louis Taberna, Michael Naguib, Patrice Simon, Michel W. Barsoum, Yury Gogotsi, Yohan Dall’Agnese, Michel W. Barsoum, Yury Gogotsi, Yohan Dall’Agnese, Patrick Rozier, Pierre Louis Taberna, Michael Naguib, Patrice Simon, Michel W. Barsoum, Yury Gogotsi, Yohan Dall’Agnese, Michel W. Barsoum, Yury Gogotsi, Yohan Dall’Agnese, Patrick Rozier, Pierre Louis Taberna, Michael Naguib, Patrice Simon, Michel W. Barsoum, Yury Gogotsi, Yohan Dall’Agnese, Michel W. Barsoum, and Yury Gogotsi. Cation Intercalation and High Volumetric Capacitance of Two-Dimensional Titanium Carbide. *Science*, 341(September): 1502–1506, 2013. ISSN 0036-8075, 1095-9203. doi: 10.1557/mrc.2012.25. URL <http://www.sciencemag.org/cgi/doi/10.1126/science.1241488>.
- [39] Yeoheung Yoon, Keunsik Lee, and Hyoyoung Lee. Low-dimensional carbon and MXene-based electrochemical capacitor electrodes. *Nanotechnology*, 27(17), 2016. ISSN 13616528. doi: 10.1088/0957-4484/27/17/172001.
- [40] Xiaohong Xie, Siguo Chen, Wei Ding, Yao Nie, and Zidong Wei. An extraordinarily stable catalyst: Pt NPs supported on two-dimensional $\text{Ti}_3\text{C}_2\text{X}_2$ ($\text{X} = \text{OH}, \text{F}$) nanosheets for oxygen reduction reaction. *Chemical Communications*, 49(86):10112–10114, 2013. ISSN 13597345. doi: 10.1039/c3cc44428g.
- [41] Dandan Sun, Mingshan Wang, Zhengyang Li, Guangxin Fan, Li Zhen Fan, and Aiguo Zhou. Two-dimensional Ti_3C_2 as anode material for Li-ion batteries. *Electrochemistry Communications*, 47:80–83, 2014. ISSN 13882481. doi: 10.1016/j.elecom.2014.07.026. URL <http://dx.doi.org/10.1016/j.elecom.2014.07.026>. 7
- [42] Yorulmaz Uğur, Özden Ayberk, K Perkgöz Nihan, Ay Feridun, and Sevik Cem. Vibrational and mechanical properties of single layer MXene structures: a first-principles investigation. *Nanotechnology*, 27(33):335702, 2016. URL <http://stacks.iop.org/0957-4484/27/i=33/a=335702> <http://iopscience.iop.org/article/10.1088/0957-4484/27/33/335702/meta>. 7
- [43] Mohammad Khazaei, Masao Arai, Taizo Sasaki, Chan-Yeup Chung, Natarajan S. Venkataramanan, Mehdi Estili, Yoshio Sakka, and Yoshiyuki Kawazoe. Novel electronic and magnetic properties of two-dimensional transition metal carbides and nitrides. *Advanced Functional Materials*, 23(17):2185–2192, 2013. ISSN 1616301X. doi: 10.1002/adfm.201202502. 7, 42

- [44] Youngbin Lee, Yubin Hwang, and Yong Chae Chung. Achieving type i, ii, and iii heterojunctions using functionalized mxene. *ACS Applied Materials and Interfaces*, 7(13):7163–7169, 2015. ISSN 19448252. doi: 10.1021/acsami.5b00063. 7
- [45] Kuangwei Xiong, Peihong Wang, Guang Yang, Zhongfei Liu, Haijun Zhang, Shaowei Jin, and Xin Xu. Functional Group Effects on the Photoelectronic Properties of MXene (Sc₂CT₂, T = O, F, OH) and Their Possible Photocatalytic Activities. *Scientific Reports*, 7(1):1–8, 2017. ISSN 20452322. doi: 10.1038/s41598-017-15233-8. URL <http://dx.doi.org/10.1038/s41598-017-15233-8>. 7
- [46] Sarat Kumar Sahoo, Balamurugan Manoharan, and Narendiran Sivakumar. Chapter 1 - introduction: Why perovskite and perovskite solar cells? In Sabu Thomas and Aparna Thankappan, editors, *Perovskite Photovoltaics*, pages 1 – 24. Academic Press, 2018. ISBN 978-0-12-812915-9. doi: <https://doi.org/10.1016/B978-0-12-812915-9.00001-0>. URL <https://www.sciencedirect.com/science/article/pii/B9780128129159000010>. 8
- [47] Shuang Yang, Wenxin Niu, An-Liang Wang, Zhanxi Fan, Bo Chen, Chao-liang Tan, Qipeng Lu, and Hua Zhang. Ultrathin Two-Dimensional Organic-Inorganic Hybrid Perovskite Nanosheets with Bright, Tunable Photoluminescence and High Stability. *Angewandte Chemie*, 129(15):4316–4319, 2017. ISSN 1521-3773. doi: 10.1002/ange.201701134. 8
- [48] Dong Liang, Yuelin Peng, Yongping Fu, Melinda J. Shearer, Jingjing Zhang, Jianyuan Zhai, Yi Zhang, Robert J. Hamers, Trisha L. Andrew, and Song Jin. Color-Pure Violet-Light-Emitting Diodes Based on Layered Lead Halide Perovskite Nanoplates. *ACS Nano*, 10(7):6897–6904, 2016. ISSN 1936086X. doi: 10.1021/acsnano.6b02683.
- [49] Woon Seok Yang, Byung Wook Park, Eui Hyuk Jung, Nam Joong Jeon, Young Chan Kim, Dong Uk Lee, Seong Sik Shin, Jangwon Seo, Eun Kyu Kim, Jun Hong Noh, and Sang Il Seok. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. *Science*, 356(6345): 1376–1379, 2017. ISSN 10959203. doi: 10.1126/science.aan2301.
- [50] Haonan Si, Qingliang Liao, Zheng Zhang, Yong Li, Xuhui Yang, Guangjie Zhang, Zhuo Kang, and Yue Zhang. An innovative design of perovskite solar cells with Al₂O₃ inserting at ZnO/perovskite interface for improving the performance and stability. *Nano Energy*, 22:223–231, 2016. ISSN 22112855. doi: 10.1016/j.nanoen.2016.02.025. URL <http://dx.doi.org/10.1016/j.nanoen.2016.02.025>.
- [51] Constantinos C. Stoumpos and Mercouri G. Kanatzidis. The Renaissance of Halide Perovskites and Their Evolution as Emerging Semiconductors. *Accounts of Chemical Research*, 48(10):2791–2802, 2015. ISSN 15204898. doi: 10.1021/acs.accounts.5b00229.

- [52] Yongping Fu, Fei Meng, Matthew B. Rowley, Blaise J. Thompson, Melinda J. Shearer, Dewei Ma, Robert J. Hamers, John C. Wright, and Song Jin. Solution growth of single crystal methylammonium lead halide perovskite nanostructures for optoelectronic and photovoltaic applications. *Journal of the American Chemical Society*, 137(17):5810–5818, 2015. ISSN 15205126. doi: 10.1021/jacs.5b02651.
- [53] Huanping Zhou, Qi Chen, Gang Li, Song Luo, Tze-bing Song, Hsin-Sheng Duan, Ziruo Hong, Jingbi You, Yongsheng Liu, and Yang Yang. Interface engineering of highly efficient perovskite solar cells. *Science*, 345(6196):542–546, 2014. ISSN 0036-8075. doi: 10.1126/science.1254050. URL <https://science.sciencemag.org/content/345/6196/542>.
- [54] Martin A. Green, Anita Ho-Baillie, and Henry J. Snaith. The emergence of perovskite solar cells. *Nature Photonics*, 8(7):506–514, 2014. ISSN 17494893. doi: 10.1038/nphoton.2014.134.
- [55] Pablo P. Boix, Shweta Agarwala, Teck Ming Koh, Nripan Mathews, and Subodh G. Mhaisalkar. Perovskite solar cells: Beyond methylammonium lead iodide. *Journal of Physical Chemistry Letters*, 6(5):898–907, 2015. ISSN 19487185. doi: 10.1021/jz502547f.
- [56] Yongbo Yuan, Tao Li, Qi Wang, Jie Xing, Alexei Gruverman, and Jinsong Huang. Anomalous photovoltaic effect in organic-inorganic hybrid perovskite solar cells. *Science Advances*, 3(3):1–8, 2017. ISSN 23752548. doi: 10.1126/sciadv.1602164. 8
- [57] Michael Kulbak, David Cahen, and Gary Hodes. How Important Is the Organic Part of Lead Halide Perovskite Photovoltaic Cells? Efficient CsPbBr₃ Cells. *Journal of Physical Chemistry Letters*, 6(13):2452–2456, 2015. ISSN 19487185. doi: 10.1021/acs.jpcclett.5b00968. 8
- [58] Kun Hua Wang, Liang Wu, Lei Li, Hong Bin Yao, Hai Sheng Qian, and Shu Hong Yu. Large-Scale Synthesis of Highly Luminescent Perovskite-Related CsPb₂Br₅Nanoplatelets and Their Fast Anion Exchange. *Angewandte Chemie - International Edition*, 55(29):8328–8332, 2016. ISSN 15213773. doi: 10.1002/anie.201602787. 8, 51
- [59] Jizhong Song, Jianhai Li, Xiaoming Li, Leimeng Xu, Yuhui Dong, and Haibo Zeng. Quantum Dot Light-Emitting Diodes Based on Inorganic Perovskite Cesium Lead Halides (CsPbX₃). *Advanced Materials*, 27(44):7162–7167, 2015. ISSN 15214095. doi: 10.1002/adma.201502567.
- [60] Quinten A. Akkerman, Valerio D’Innocenzo, Sara Accornero, Alice Scarpellini, Annamaria Petrozza, Mirko Prato, and Liberato Manna. Tuning the optical properties of cesium lead halide perovskite nanocrystals by anion exchange reactions. *Journal of the American Chemical Society*, 137(32):10276–10281, 2015. ISSN 15205126. doi: 10.1021/jacs.5b05602.

- [61] Brent A. Koscher, Joseph K. Swabeck, Noah D. Bronstein, and A. Paul Alivisatos. Essentially Trap-Free CsPbBr₃ Colloidal Nanocrystals by Post-synthetic Thiocyanate Surface Treatment. *Journal of the American Chemical Society*, 139(19):6566–6569, 2017. ISSN 15205126. doi: 10.1021/jacs.7b02817.
- [62] Abhishek Swarnkar, Ramya Chulliyil, Vikash Kumar Ravi, Mir Irfanullah, Arindam Chowdhury, and Angshuman Nag. Colloidal CsPbBr₃ Perovskite Nanocrystals: Luminescence beyond Traditional Quantum Dots. *Angewandte Chemie*, 127(51):15644–15648, 2015. ISSN 00448249. doi: 10.1002/ange.201508276. URL <http://doi.wiley.com/10.1002/ange.201508276>. 8, 51
- [63] Abhishek Swarnkar, Ashley R. Marshall, Erin M. Sanehira, Boris D. Chernomordik, David T. Moore, Jeffrey A. Christians, Tamoghna Chakrabarti, and Joseph M. Luther. Quantum dot-induced phase stabilization of α -cs₂pbi₃ perovskite for high-efficiency photovoltaics. *Science*, 354(6308):92–95, 2016. ISSN 0036-8075. doi: 10.1126/science.aag2700. URL <https://science.sciencemag.org/content/354/6308/92>. 8
- [64] Young Shin Park, Shaojun Guo, Nikolay S. Makarov, and Victor I. Klimov. Room Temperature Single-Photon Emission from Individual Perovskite Quantum Dots. *ACS Nano*, 9(10):10386–10393, 2015. ISSN 1936086X. doi: 10.1021/acs.nano.5b04584.
- [65] Fengrui Hu, Huichao Zhang, Chun Sun, Chunyang Yin, Bihu Lv, Chunfeng Zhang, William W. Yu, Xiaoyong Wang, Yu Zhang, and Min Xiao. Superior Optical Properties of Perovskite Nanocrystals as Single Photon Emitters. *ACS Nano*, 9(12):12410–12416, 2015. ISSN 1936086X. doi: 10.1021/acs.nano.5b05769.
- [66] Liuqi Zhang, Xiaolei Yang, Qi Jiang, Pengyang Wang, Zhigang Yin, Xingwang Zhang, Hairen Tan, Yang Michael Yang, Mingyang Wei, Brandon R. Sutherland, Edward H. Sargent, and Jingbi You. Ultra-bright and highly efficient inorganic based perovskite light-emitting diodes. *Nature Communications*, 8:1–8, 2017. ISSN 20411723. doi: 10.1038/ncomms15640. URL <http://dx.doi.org/10.1038/ncomms15640>.
- [67] Sergii Yakunin, Loredana Protesescu, Franziska Krieg, Maryna I. Bodnarchuk, Georgian Nedelcu, Markus Humer, Gabriele De Luca, Manfred Fiebig, Wolfgang Heiss, and Maksym V. Kovalenko. Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites. *Nature Communications*, 6:1–8, 2015. ISSN 20411723. doi: 10.1038/ncomms9056. 8

- [68] Georgian Nedelcu, Loredana Protesescu, Sergii Yakunin, Maryna I. Bodnarchuk, Matthias J. Grotevent, and Maksym V. Kovalenko. Fast Anion-Exchange in Highly Luminescent Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , $X = \text{Cl, Br, I}$). *Nano Letters*, 15(8):5635–5640, 2015. ISSN 15306992. doi: 10.1021/acs.nanolett.5b02404. [8](#)
- [69] Loredana Protesescu, Sergii Yakunin, Maryna I. Bodnarchuk, Franziska Krieg, Riccarda Caputo, Christopher H. Hendon, Ruoxi Yang, Aron Walsh, and Maksym V. Kovalenko. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , $X = \text{Cl, Br, and I}$): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Letters*, 15(6):3692–3696, 2015. ISSN 15306992. doi: 10.1021/nl5048779. [8](#), [51](#)
- [70] Weiwei Zhang, Zhiqiang Su, Ming Gong, Chuan-Feng Li, Guang-Can Guo, and Lixin He. Giant optical anisotropy in cylindrical self-assembled InAs/-GaAs quantum rings. *EPL (Europhysics Letters)*, 83(6):67004, sep 2008. doi: 10.1209/0295-5075/83/67004. [9](#)
- [71] Y. Arakawa and H. Sakaki. Multidimensional quantum well laser and temperature dependence of its threshold current. *Applied Physics Letters*, 40(11):939–941, 1982. ISSN 00036951. doi: 10.1063/1.92959. [9](#)
- [72] Yehonadav Bekenstein, Brent A. Koscher, Samuel W. Eaton, Peidong Yang, and A. Paul Alivisatos. Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies. *Journal of the American Chemical Society*, 137(51):16008–16011, 2015. ISSN 15205126. doi: 10.1021/jacs.5b11199. [9](#)
- [73] Di Yang, Yatao Zou, Pengli Li, Qipeng Liu, Linzhong Wu, Huicheng Hu, Yong Xu, Baoquan Sun, Qiao Zhang, and Shuitong Lee. Large-scale synthesis of ultrathin cesium lead bromide perovskite nanoplates with precisely tunable dimensions and their application in blue light-emitting diodes. *Nano Energy*, 47(February):235–242, 2018. ISSN 22112855. doi: 10.1016/j.nanoen.2018.03.019. URL <https://doi.org/10.1016/j.nanoen.2018.03.019>.
- [74] Quinten A. Akkerman, Silvia Genaro Motti, Ajay Ram Srimath Kandada, Edoardo Mosconi, Valerio D’Innocenzo, Giovanni Bertoni, Sergio Marras, Brett A. Kamino, Laura Miranda, Filippo De Angelis, Annamaria Petrozza, Mirko Prato, and Liberato Manna. Solution Synthesis Approach to Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control. *Journal of the American Chemical Society*, 138(3):1010–1016, 2016. ISSN 15205126. doi: 10.1021/jacs.5b12124.
- [75] Zhi Yang, Minqiang Wang, Hengwei Qiu, Xi Yao, Xiangzhou Lao, Shijie Xu, Zhonghai Lin, Luyi Sun, and Jinyou Shao. Engineering the Exciton Dissociation in Quantum-Confined 2D CsPbBr_3 Nanosheet Films. *Advanced Functional Materials*, 28(14):1–10, 2018. ISSN 16163028. doi: 10.1002/adfm.201705908.

- [76] Shibin Sun, Dan Yuan, Yuan Xu, Aifei Wang, and Zhengtao Deng. Ligand-Mediated Synthesis of Shape-Controlled Cesium Lead Halide Perovskite Nanocrystals via Reprecipitation Process at Room Temperature. *ACS Nano*, 10(3):3648–3657, 2016. ISSN 1936086X. doi: 10.1021/acsnano.5b08193.
- [77] Junjie Si, Yang Liu, Zhuofei He, Hui Du, Kai Du, Dong Chen, Jing Li, Mengmeng Xu, He Tian, Haiping He, Dawei Di, Changqing Lin, Yingchun Cheng, Jianpu Wang, and Yizheng Jin. Efficient and High-Color-Purity Light-Emitting Diodes Based on in Situ Grown Films of CsPbX₃ (X = Br, I) Nanoplates with Controlled Thicknesses. *ACS Nano*, 11(11):11100–11107, 2017. ISSN 1936086X. doi: 10.1021/acsnano.7b05191. 9
- [78] M. D. Tessier, B. Mahler, B. Nadal, H. Heuclin, S. Pedetti, and B. Dubertret. Spectroscopy of colloidal semiconductor core/shell nanoplatelets with high quantum yield. *Nano Letters*, 13(7):3321–3328, 2013. ISSN 15306984. doi: 10.1021/nl401538n. 9
- [79] Daqin Chen and Xiao Chen. Luminescent perovskite quantum dots: synthesis, microstructures, optical properties and applications. *Journal of Materials Chemistry C*, 7(6):1413–1446, 2019. ISSN 20507526. doi: 10.1039/C8TC05545A. 9
- [80] Dan Wang, Dan Wu, Di Dong, Wei Chen, Junjie Hao, Jing Qin, Bing Xu, Kai Wang, and Xiaowei Sun. Polarized emission from CsPbX₃ perovskite quantum dots. *Nanoscale*, 8(22):11565–11570, 2016. ISSN 20403372. doi: 10.1039/c6nr01915c. 9
- [81] Shibin Sun, Dan Yuan, Yuan Xu, Aifei Wang, and Zhengtao Deng. Ligand-Mediated Synthesis of Shape-Controlled Cesium Lead Halide Perovskite Nanocrystals via Reprecipitation Process at Room Temperature. *ACS Nano*, 10(3):3648–3657, 2016. ISSN 1936086X. doi: 10.1021/acsnano.5b08193. 9
- [82] Quinten A. Akkerman, Marina Gandini, Francesco Di Stasio, Prachi Rastogi, Francisco Palazon, Giovanni Bertoni, James M. Ball, Mirko Prato, Annamaria Petrozza, and Liberato Manna. Strongly emissive perovskite nanocrystal inks for high-voltage solar cells. *Nature Energy*, 2(2):1–7, 2017. ISSN 20587546. doi: 10.1038/nenergy.2016.194. 9, 63
- [83] Abhishek Swarnkar, Ashley R. Marshall, Erin M. Sanehira, Boris D. Chernomordik, David T. Moore, Jeffrey A. Christians, Tamoghna Chakrabarti, and Joseph M. Luther. Quantum dot-induced phase stabilization of α -csPbI₃ perovskite for high-efficiency photovoltaics. *Science*, 354(6308):92–95, 2016. ISSN 0036-8075. doi: 10.1126/science.aag2700. URL <https://science.sciencemag.org/content/354/6308/92>. 9, 64
- [84] Jianhai Li, Leimeng Xu, Tao Wang, Jizhong Song, Jiawei Chen, Jie Xue, Yuhui Dong, Bo Cai, Qingsong Shan, Boning Han, and Haibo Zeng. 50-Fold EQE Improvement up to 6.27% of Solution-Processed All-Inorganic

- Perovskite CsPbBr₃ QLEDs via Surface Ligand Density Control. *Advanced Materials*, 29(5), 2017. ISSN 15214095. doi: 10.1002/adma.201603885. [9](#)
- [85] Guangru Li, Florencia Wisnivesky Rocca Rivarola, Nathaniel J.L.K. Davis, Sai Bai, Tom C. Jellicoe, Francisco De La Peña, Shaocong Hou, Caterina Ducati, Feng Gao, Richard H. Friend, Neil C. Greenham, and Zhi Kuang Tan. Highly Efficient Perovskite Nanocrystal Light-Emitting Diodes Enabled by a Universal Crosslinking Method. *Advanced Materials*, 28(18):3528–3534, 2016. ISSN 15214095. doi: 10.1002/adma.201600064. [9](#), [63](#)
- [86] Rui Su, Carole Diederichs, Jun Wang, Timothy C.H. Liew, Jiaxin Zhao, Sheng Liu, Weigao Xu, Zhanghai Chen, and Qihua Xiong. Room-Temperature Polariton Lasing in All-Inorganic Perovskite Nanoplatelets. *Nano Letters*, 17(6):3982–3988, 2017. ISSN 15306992. doi: 10.1021/acs.nanolett.7b01956. [9](#)
- [87] Do Hyun Kwak, Da Hye Lim, Hyun Soo Ra, Parthiban Ramasamy, and Jong Soo Lee. High performance hybrid graphene-CsPbBr₃-: XIx perovskite nanocrystal photodetector. *RSC Advances*, 6(69):65252–65256, 2016. ISSN 20462069. doi: 10.1039/c6ra08699c. [9](#)
- [88] Dmitry N. Dirin, Ihor Cherniukh, Sergii Yakunin, Yevhen Shynkarenko, and Maksym V. Kovalenko. Solution-Grown CsPbBr₃Perovskite Single Crystals for Photon Detection. *Chemistry of Materials*, 28(23):8470–8474, 2016. ISSN 15205002. doi: 10.1021/acs.chemmater.6b04298. [9](#)
- [89] Constantinos C. Stoumpos, Christos D. Malliakas, John A. Peters, Zhifu Liu, Maria Sebastian, Jino Im, Thomas C. Chasapis, Arief C. Wibowo, Duck Young Chung, Arthur J. Freeman, Bruce W. Wessels, and Mercouri G. Kanatzidis. Crystal growth of the perovskite semiconductor CsPbBr₃: A new material for high-energy radiation detection. *Crystal Growth and Design*, 13(7):2722–2727, 2013. ISSN 15287483. doi: 10.1021/cg400645t. [9](#)
- [90] Vikash Kumar Ravi, Abhishek Swarnkar, Rayan Chakraborty, and Angshuman Nag. Excellent Green but Less Impressive Blue Luminescence from CsPbBr₃perovskite nanocubes and nanoplatelets. *Nanotechnology*, 27(32): 1–5, jun 2016. [9](#), [63](#)
- [91] Loredana Protesescu, Sergii Yakunin, Maryna I. Bodnarchuk, Franziska Krieg, Riccarda Caputo, Christopher H. Hendon, Ruoxi Yang, Aron Walsh, and Maksym V. Kovalenko. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX₃, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Letters*, 15(6):3692–3696, 2015. ISSN 15306992. doi: 10.1021/nl5048779. [9](#), [36](#), [63](#), [65](#)
- [92] Yehonadav Bekenstein, Brent A. Koscher, Samuel W. Eaton, Peidong Yang, and A. Paul Alivisatos. Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies. *Journal of the*

- American Chemical Society*, 137(51):16008–16011, 2015. ISSN 15205126. doi: 10.1021/jacs.5b11199. 9, 63
- [93] Yuhui Dong, Yu Gu, Yousheng Zou, Jizhong Song, Leimeng Xu, Jianhai Li, Jie Xue, Xiaoming Li, and Haibo Zeng. Improving All-Inorganic Perovskite Photodetectors by Preferred Orientation and Plasmonic Effect. *Small*, 12(40):5622–5632, 2016. ISSN 16136829. doi: 10.1002/smll.201602366. 9
- [94] Michael Kulbak, David Cahen, and Gary Hodes. How Important Is the Organic Part of Lead Halide Perovskite Photovoltaic Cells? Efficient CsPbBr₃ Cells. *Journal of Physical Chemistry Letters*, 6(13):2452–2456, 2015. ISSN 19487185. doi: 10.1021/acs.jpcclett.5b00968.
- [95] Jizhong Song, Leimeng Xu, Jianhai Li, Jie Xue, Yuhui Dong, Xiaoming Li, and Haibo Zeng. Monolayer and Few-Layer All-Inorganic Perovskites as a New Family of Two-Dimensional Semiconductors for Printable Optoelectronic Devices. *Advanced Materials*, pages 4861–4869, 2016. ISSN 15214095. doi: 10.1002/adma.201600225. 9
- [96] Jonathan De Roo, Maria Ibáñez, Pieter Geiregat, Georgian Nedelcu, Willem Walravens, Jorick Maes, Jose C. Martins, Isabel Van Driessche, Maksym V. Kovalenko, and Zeger Hens. Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano*, 10(2):2071–2081, 2016. ISSN 1936086X. doi: 10.1021/acsnano.5b06295. 9
- [97] Yue Wang, Xiaoming Li, Jizhong Song, Lian Xiao, Haibo Zeng, and Handong Sun. All-Inorganic Colloidal Perovskite Quantum Dots: A New Class of Lasing Materials with Favorable Characteristics. *Advanced Materials*, 27(44):7101–7108, 2015. ISSN 15214095. doi: 10.1002/adma.201503573. 9
- [98] Abhishek Swarnkar, Ramya Chulliyil, Vikash Kumar Ravi, Mir Irfanullah, Arindam Chowdhury, and Angshuman Nag. Colloidal CsPbBr₃ Perovskite Nanocrystals: Luminescence beyond Traditional Quantum Dots. *Angewandte Chemie*, 127(51):15644–15648, 2015. ISSN 00448249. doi: 10.1002/ange.201508276. URL <http://doi.wiley.com/10.1002/ange.201508276>. 9
- [99] Sergii Yakunin, Loredana Protesescu, Franziska Krieg, Maryna I. Bodnarchuk, Georgian Nedelcu, Markus Humer, Gabriele De Luca, Manfred Fiebig, Wolfgang Heiss, and Maksym V. Kovalenko. Low-threshold amplified spontaneous emission and lasing from colloidal nanocrystals of caesium lead halide perovskites. *Nature Communications*, 6:1–8, 2015. ISSN 20411723. doi: 10.1038/ncomms9056. URL <http://dx.doi.org/10.1038/ncomms9056>. 10
- [100] N.W. Ashcroft and N.D. Mermin. *Solid State Physics*. Saunders College, Philadelphia, 1976. 14
- [101] J. Bardeen. An improved calculation of the energies of metallic li and na. *The Journal of Chemical Physics*, 6(7):367–371, 1938. doi: 10.1063/1.1750270. URL <https://doi.org/10.1063/1.1750270>. 14

- [102] Frederick Seitz and R. P. Johnson. Modern theory of solids. i. *Journal of Applied Physics*, 8(2):84–97, 1937. doi: 10.1063/1.1710273. URL <https://doi.org/10.1063/1.1710273>. 14
- [103] G. Dresselhaus, A. F. Kip, and C. Kittel. Cyclotron resonance of electrons and holes in silicon and germanium crystals. *Phys. Rev.*, 98:368–384, Apr 1955. doi: 10.1103/PhysRev.98.368. URL <https://link.aps.org/doi/10.1103/PhysRev.98.368>. 14
- [104] E.O. Kane. Energy band structure in p-type germanium and silicon. *Journal of Physics and Chemistry of Solids*, 1(1):82 – 99, 1956. ISSN 0022-3697. doi: [https://doi.org/10.1016/0022-3697\(56\)90014-2](https://doi.org/10.1016/0022-3697(56)90014-2). URL <http://www.sciencedirect.com/science/article/pii/0022369756900142>. 14
- [105] Evan O. Kane. Band structure of indium antimonide. *Journal of Physics and Chemistry of Solids*, 1(4):249 – 261, 1957. ISSN 0022-3697. doi: [https://doi.org/10.1016/0022-3697\(57\)90013-6](https://doi.org/10.1016/0022-3697(57)90013-6). URL <http://www.sciencedirect.com/science/article/pii/0022369757900136>. 14
- [106] J. M. Luttinger and W. Kohn. Motion of electrons and holes in perturbed periodic fields. *Phys. Rev.*, 97:869–883, Feb 1955. doi: 10.1103/PhysRev.97.869. URL <https://link.aps.org/doi/10.1103/PhysRev.97.869>. 14
- [107] J. Chen, W. J. Fan, Q. Xu, X. W. Zhang, S. S. Li, and J. B. Xia. Electronic structure and optical gain saturation of inas1 xnx/gaas quantum dots. *Journal of Applied Physics*, 105(12):123705, 2009. doi: 10.1063/1.3143025. URL <https://doi.org/10.1063/1.3143025>. 14
- [108] J. Chen, W.J. Fan, Q. Xu, X.W. Zhang, S.S. Li, and J.B. Xia. Shape effects on the electronic structure and the optical gain of inasn/gaas nanostructures: From a quantum lens to a quantum ring. *Superlattices and Microstructures*, 52(4):618 – 631, 2012. ISSN 0749-6036. doi: <https://doi.org/10.1016/j.spmi.2012.06.018>. URL <http://www.sciencedirect.com/science/article/pii/S0749603612001826>.
- [109] W. J. Fan. Tensile-strain and doping enhanced direct bandgap optical transition of n+ doped ge/gesi quantum wells. *Journal of Applied Physics*, 114(18):183106, 2013. doi: 10.1063/1.4831750. URL <https://doi.org/10.1063/1.4831750>. 14, 17
- [110] Craig Pryor. Eight-band calculations of strained inas/gaas quantum dots compared with one-, four-, and six-band approximations. *Phys. Rev. B*, 57:7190–7195, Mar 1998. doi: 10.1103/PhysRevB.57.7190. URL <https://link.aps.org/doi/10.1103/PhysRevB.57.7190>. 15
- [111] Q. Chen, Z. Song, D. Zhang, H. Sun, and W. Fan. Effect of size on the electronic structure and optical properties of cubic cspbbr3 quantum dots. *IEEE Journal of Quantum Electronics*, 56(1):1–7, 2020. 15, 51

- [112] K. Heidrich, W. Schäfer, M. Schreiber, J. Söchtig, G. Trendel, J. Treusch, T. Grandke, and H. J. Stolz. Electronic structure, photoemission spectra, and vacuum-ultraviolet optical spectra of CsPbCl_3 and CsPbBr_3 . *Phys. Rev. B*, 24:5642–5649, Nov 1981. doi: 10.1103/PhysRevB.24.5642. URL <https://link.aps.org/doi/10.1103/PhysRevB.24.5642>. 15, 52
- [113] Kain Lu Low, Yue Yang, Genquan Han, Weijun Fan, and Yee-Chia Yeo. Electronic band structure and effective mass parameters of $\text{Ge}_{1-x}\text{Sn}_x$ alloys. *Journal of Applied Physics*, 112(10):103715, 2012. doi: 10.1063/1.4767381. URL <https://doi.org/10.1063/1.4767381>. 17
- [114] Micheal J. Mehl, David Hicks, Cormac Toher, Ohad Levy, Robert M. Hanson, Gus Hart, and Stefano Curtarolo. The AFLOW Library of Crystallographic Prototypes: Part 1. *Computational Materials Science*, 136:S1–S828, 2017. URL <http://aflow.org/CrystalDatabase/>. 19
- [115] N.S. Pashuk, I.P. and Pidzyrajlo and M.G. Matsko. Exciton absorption, luminescence and resonance raman scattering in CsPbCl_3 and CsPbBr_3 crystals at low temperatures. *Fizika Tverdogo Tela*, 23(7):2162–2165, 1981. 19
- [116] Michael A. Becker, Roman Vaxenburg, Georgian Nedelcu, Peter C. Sercel, Andrew Shabaev, Michael J. Mehl, John G. Michopoulos, Samuel G. Lambrakos, Noam Bernstein, John L. Lyons, Thilo Stöferle, Rainer F. Mahrt, Maksym V. Kovalenko, David J. Norris, Gabriele Rainò, and Alexander L. Efros. Bright triplet excitons in caesium lead halide perovskites. *Nature*, 553(7687):189–193, 2018. ISSN 14764687. doi: 10.1038/nature25147. 19
- [117] Jacky Even, Laurent Pedesseau, Jean Marc Jancu, and Claudine Katan. Importance of spin-orbit coupling in hybrid organic/inorganic perovskites for photovoltaic applications. *Journal of Physical Chemistry Letters*, 4(17):2999–3005, 2013. ISSN 19487185. doi: 10.1021/jz401532q. 19
- [118] S. T. Ng, W. J. Fan, Y. X. Dang, and S. F. Yoon. Comparison of electronic band structure and optical transparency conditions of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ quantum wells calculated by 10-band, 8-band, and 6-band $\mathbf{k} \cdot \mathbf{p}$ models. *Phys. Rev. B*, 72:115341, Sep 2005. doi: 10.1103/PhysRevB.72.115341. URL <https://link.aps.org/doi/10.1103/PhysRevB.72.115341>. 19
- [119] JOACHIM PIPREK. Chapter 5 - photon generation. In JOACHIM PIPREK, editor, *Semiconductor Optoelectronic Devices*, pages 121 – 139. Academic Press, Boston, 2003. ISBN 978-0-08-046978-2. doi: <https://doi.org/10.1016/B978-0-08-046978-2.50030-2>. URL <http://www.sciencedirect.com/science/article/pii/B9780080469782500302>. 23, 24
- [120] M. del CastilloMussot and L. J. Sham. Excitonic effect in the optical spectrum of semiconductors. *Phys. Rev. B*, 31:2092–2098, Feb 1985. doi: 10.1103/PhysRevB.31.2092. URL <https://link.aps.org/doi/10.1103/PhysRevB.31.2092>. 24

- [121] J. Voigt, F. Spiegelberg, and M. Senoner. Band parameters of cds and cdse single crystals determined from optical exciton spectra. *physica status solidi (b)*, 91(1):189–199, 1979. doi: 10.1002/pssb.2220910120. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/pssb.2220910120>. 24
- [122] Ali Naeem, Francesco Masia, Sotirios Christodoulou, Iwan Moreels, Paola Borri, and Wolfgang Langbein. Giant exciton oscillator strength and radiatively limited dephasing in two-dimensional platelets. *Phys. Rev. B*, 91:121302, Mar 2015. doi: 10.1103/PhysRevB.91.121302. URL <https://link.aps.org/doi/10.1103/PhysRevB.91.121302>. 24
- [123] Sandrine Ithurria, Mickael Tessier, Benoit Mahler, R Lobo, B Dubertret, and Alexander Efros. Colloidal nanoplatelets with two-dimensional electronic structure. *Nature materials*, 10:936–41, 12 2011. doi: 10.1038/nmat3145. 25
- [124] J. Chen, W. J. Fan, Q. Xu, X. W. Zhang, S. S. Li, and J. B. Xia. Electronic structure and optical gain saturation of InAs 1-xNx/GaAs quantum dots. *Journal of Applied Physics*, 105(12):0–10, 2009. ISSN 00218979. doi: 10.1063/1.3143025. 26
- [125] Daniel R. Dreyer, Alexander D. Todd, and Christopher W. Bielawski. Harnessing the chemistry of graphene oxide. *Chem. Soc. Rev.*, 43:5288–5301, 2014. doi: 10.1039/C4CS00060A. URL <http://dx.doi.org/10.1039/C4CS00060A>. 29
- [126] Per Joensen, R.F. Frindt, and S.Roy Morrison. Single-layer mos2. *Materials Research Bulletin*, 21(4):457 – 461, 1986. ISSN 0025-5408. doi: [https://doi.org/10.1016/0025-5408\(86\)90011-5](https://doi.org/10.1016/0025-5408(86)90011-5). URL <http://www.sciencedirect.com/science/article/pii/0025540886900115>. 29
- [127] G. F. Walker and W. G. Garrett. Chemical exfoliation of vermiculite and the production of colloidal dispersions. *Science*, 156(3773):385–387, 1967. ISSN 0036-8075. doi: 10.1126/science.156.3773.385. URL <https://science.sciencemag.org/content/156/3773/385>. 29
- [128] Zong-huai Liu, Kenta Ooi, Hirofumi Kanoh, Wei-ping Tang, and Tahei Tomida. Swelling and delamination behaviors of birnessite-type manganese oxide by intercalation of tetraalkylammonium ions. *Langmuir*, 16(9):4154–4164, 2000. doi: 10.1021/la9913755. URL <https://doi.org/10.1021/la9913755>. 29
- [129] Yenny Hernandez, Valeria Nicolosi, Mustafa Lotya, Fiona Blighe, Zhenyu Sun, Sukanta De, I. Mcgovern, Brendan Holland, Michele Byrne, Y. Gun’ko, John Boland, Peter Niraj, Georg Duesberg, Robbie Goodhue, John Hutchison, Vittorio Scardaci, Andrea Ferrari, and Jonathan Coleman. High-yield production of graphene by liquid-phase exfoliation of graphite. *Nature nanotechnology*, 3:563–8, 10 2008. doi: 10.1038/nnano.2008.215. 29

- [130] Louisiane Verger, Chuan Xu, Varun Natu, Hui-Ming Cheng, Wencai Ren, and Michel W. Barsoum. Overview of the synthesis of mxenes and other ultrathin 2d transition metal carbides and nitrides. *Current Opinion in Solid State and Materials Science*, 23(3):149 – 163, 2019. ISSN 1359-0286. doi: <https://doi.org/10.1016/j.cossms.2019.02.001>. URL <https://www.sciencedirect.com/science/article/pii/S1359028618301426>. 29
- [131] M.W. Barsoum. *MAX Phases: Properties of Machinable Ternary Carbides and Nitrides*. Wiley, 2013. ISBN 9783527654604. URL <https://books.google.com.sg/books?id=qMcZAgAAQBAJ>. 30
- [132] Pritishma Lakhe, Evan M. Prehn, Touseef Habib, Jodie L. Lutkenhaus, Miladin Radovic, M. Sam Mannan, and Micah J. Green. Process safety analysis for ti₃c₂tx mxene synthesis and processing. *Industrial & Engineering Chemistry Research*, 58(4):1570–1579, 2019. doi: 10.1021/acs.iecr.8b05416. URL <https://doi.org/10.1021/acs.iecr.8b05416>. 30
- [133] Quanzheng Tao, Martin Dahlqvist, Jun Lu, Sankalp Kota, Rahele Meshkian, Joseph Halim, Justinas Palisaitis, Lars Hultman, Michel Barsoum, Per Persson, and Johanna Rosén. Two-dimensional mo_{1.33}c mxene with divacancy ordering prepared from parent 3d laminate with in-plane chemical ordering. *Nature Communications*, 8:14949, 04 2017. doi: 10.1038/ncomms14949. 31
- [134] Ingemar Persson, Ahmed el Ghazaly, Quanzheng Tao, Joseph Halim, Sankalp Kota, Vanya Darakchieva, Justinas Palisaitis, Michel W. Barsoum, Johanna Rosen, and Per O. Å. Persson. Tailoring structure, composition, and energy storage properties of mxenes from selective etching of in-plane, chemically ordered max phases. *Small*, 14(17):1703676, 2018. doi: 10.1002/smll.201703676. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/smll.201703676>. 31
- [135] Rahele Meshkian, Martin Dahlqvist, Jun Lu, Björn Wickman, Joseph Halim, Jimmy Thörnberg, Quanzheng Tao, Shixuan Li, Saad Intikhab, Joshua Snyder, Michel W. Barsoum, Melike Yildizhan, Justinas Palisaitis, Lars Hultman, Per O. Å. Persson, and Johanna Rosen. W-based atomic laminates and their 2d derivative w_{1.33}c mxene with vacancy ordering. *Advanced Materials*, 30(21):1706409, 2018. doi: 10.1002/adma.201706409. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201706409>. 31
- [136] J. Halim, J. Palisaitis, J. Lu, J. Thörnberg, E. J. Moon, M. Precner, P. Eklund, P. O. Å. Persson, M. W. Barsoum, and J. Rosen. Synthesis of two-dimensional nb_{1.33}c (mxene) with randomly distributed vacancies by etching of the quaternary solid solution (nb₂/3sc₁/3)2alc max phase. *ACS Applied Nano Materials*, 1(6):2455–2460, 2018. doi: 10.1021/acsanm.8b00332. URL <https://doi.org/10.1021/acsanm.8b00332>. 31
- [137] Guobing Ying, Andrew D. Dillon, Aaron T. Fafarman, and Michel W. Barsoum. Transparent, conductive solution processed spincoat 2d ti₂ctx (mxene)

- films. *Materials Research Letters*, 5(6):391–398, 2017. doi: 10.1080/21663831.2017.1296043. URL <https://doi.org/10.1080/21663831.2017.1296043>. 31
- [138] Fanfan Liu, Aiguo Zhou, Jinfeng Chen, Jin Jia, Weijia Zhou, Libo Wang, and Qianku Hu. Preparation of Ti_3C_2 and Ti_2C mxenes by fluoride salts etching and methane adsorptive properties. *Applied Surface Science*, 416: 781 – 789, 2017. ISSN 0169-4332. doi: <https://doi.org/10.1016/j.apsusc.2017.04.239>. URL <http://www.sciencedirect.com/science/article/pii/S0169433217312850>. 31
- [139] W. Sun, S. A. Shah, Y. Chen, Z. Tan, H. Gao, T. Habib, M. Radovic, and M. J. Green. Electrochemical etching of Ti_2AlC to Ti_2CTx (mxene) in low-concentration hydrochloric acid solution. *J. Mater. Chem. A*, 5:21663–21668, 2017. doi: 10.1039/C7TA05574A. URL <http://dx.doi.org/10.1039/C7TA05574A>. 31
- [140] J. Lu, I. Persson, H. Lind, J. Palisaitis, M. Li, Y. Li, K. Chen, J. Zhou, S. Du, Z. Chai, Z. Huang, L. Hultman, P. Eklund, J. Rosen, Q. Huang, and P. O. Å. Persson. $\text{Ti}_{n+1}\text{C}_n$ mxenes with fully saturated and thermally stable cl terminations. *Nanoscale Adv.*, 1:3680–3685, 2019. doi: 10.1039/C9NA00324J. URL <http://dx.doi.org/10.1039/C9NA00324J>. 31
- [141] Fanfan Liu, Jie Zhou, Shuwei Wang, Bingxin Wang, Cai Shen, Libo Wang, Qianku Hu, Qing Huang, and Aiguo Zhou. Preparation of high-purity v_2c MXene and electrochemical properties as li-ion batteries. *Journal of The Electrochemical Society*, 164(4):A709–A713, 2017. doi: 10.1149/2.0641704jes. URL <https://doi.org/10.11492F2.0641704jes>. 31
- [142] Bhuvaneswari Soundiraraju and Benny Kattikkanal George. Two-dimensional titanium nitride (Ti_2N) mxene: Synthesis, characterization, and potential application as surface-enhanced raman scattering substrate. *ACS Nano*, 11(9):8892–8900, 2017. doi: 10.1021/acsnano.7b03129. URL <https://doi.org/10.1021/acsnano.7b03129>. PMID: 28846394. 31
- [143] Michael Abdelmalak. Mxenes: A new family of two-dimensional materials and its application as electrodes for li-ion batteries. 2014. 31
- [144] Joseph Halim, Sankalp Kota, Maria R. Lukatskaya, Michael Naguib, Meng-Qiang Zhao, Eun Ju Moon, Jeremy Pitock, Jagjit Nanda, Steven J. May, Yury Gogotsi, and Michel W. Barsoum. Synthesis and characterization of 2d molybdenum carbide (mxene). *Advanced Functional Materials*, 26(18):3118–3127, 2016. doi: 10.1002/adfm.201505328. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adfm.201505328>. 31, 32
- [145] Michael Ghidui, Maria Lukatskaya, Meng-Qiang Zhao, Yury Gogotsi, and Michel Barsoum. Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. *Nature*, advance online publication, 11 2014. doi: 10.1038/nature13970. 31

- [146] Linda H. Karlsson, Jens Birch, Joseph Halim, Michel W. Barsoum, and Per O. Å. Persson. Atomically resolved structural and chemical investigation of single mxene sheets. *Nano Letters*, 15(8):4955–4960, 2015. doi: 10.1021/acs.nanolett.5b00737. URL <https://doi.org/10.1021/acs.nanolett.5b00737>. PMID: 26177010. 31, 32
- [147] Tengfei Li, Lulu Yao, Qinglei Liu, Jiajun Gu, Ruichun Luo, Jinghan Li, Xudong Yan, Weiqiang Wang, Pan Liu, Bin Chen, Wang Zhang, Waseem Abbas, Raheela Naz, and Di Zhang. Fluorine-free synthesis of high-purity $\text{ti}_3\text{c}_2\text{tx}$ ($\text{t}=\text{oh}$, o) via alkali treatment. *Angewandte Chemie International Edition*, 57(21):6115–6119, 2018. doi: 10.1002/anie.201800887. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.201800887>. 31
- [148] Sheng Yang, Panpan Zhang, Faxing Wang, Antonio Gaetano Ricciardulli, Martin Lohe, Paul Blom, and Xinliang Feng. Fluoride-free synthesis of two-dimensional titanium carbide (mxene) using a binary aqueous system. *Angewandte Chemie International Edition in English*, 57, 10 2018. doi: 10.1002/anie.201809662. 31
- [149] Mohamed Alhabeb, Kathleen Maleski, Tyler Mathis, Asia Sarycheva, Christine Hatter, Simge Uzun, Ariana Levitt, and Yury Gogotsi. Selective etching of silicon from ti_3sic_2 (max) to obtain 2d titanium carbide (mxene). *Angewandte Chemie International Edition*, 57, 03 2018. doi: 10.1002/anie.201802232. 31
- [150] Babak Anasori, Yu Xie, Majid Beidaghi, Jun Lu, Brian C. Hosler, Lars Hultman, Paul R. C. Kent, Yury Gogotsi, and Michel W. Barsoum. Two-dimensional, ordered, double transition metals carbides (mxenes). *ACS Nano*, 9(10):9507–9516, 2015. doi: 10.1021/acsnano.5b03591. URL <https://doi.org/10.1021/acsnano.5b03591>. PMID: 26208121. 31
- [151] Jie Zhou, Xianhu Zha, Fan Y. Chen, Qun Ye, Per Eklund, Shiyu Du, and Qing Huang. A two-dimensional zirconium carbide by selective etching of al_3c_3 from nanolaminated $\text{zr}_3\text{al}_3\text{c}_5$. *Angewandte Chemie International Edition*, 55(16):5008–5013, 2016. doi: 10.1002/anie.201510432. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/anie.201510432>. 31
- [152] Jie Zhou, Xianhu Zha, Xiaobing Zhou, Fanyan Chen, Guoliang Gao, Shuwei Wang, Cai Shen, Tao Chen, Chunyi Zhi, Per Eklund, Shiyu Du, Jianming Xue, Weiqun Shi, Zhifang Chai, and Qing Huang. Synthesis and electrochemical properties of two-dimensional hafnium carbide. *ACS Nano*, 11(4):3841–3850, 2017. doi: 10.1021/acsnano.7b00030. URL <https://doi.org/10.1021/acsnano.7b00030>. PMID: 28375599. 31
- [153] Patrick Urbankowski, Babak Anasori, Taron Makaryan, Dequan Er, Sankalp Kota, Patrick L. Walsh, Mengqiang Zhao, Vivek B. Shenoy, Michel W. Barsoum, and Yury Gogotsi. Synthesis of two-dimensional titanium nitride ti_4n_3 (mxene). *Nanoscale*, 8:11385–11391, 2016. doi: 10.1039/C6NR02253G. URL <http://dx.doi.org/10.1039/C6NR02253G>. 31

- [154] Minh H. Tran, Timo Schäfer, Ali Shahraei, Michael Dürrschnabel, Leopoldo Molina-Luna, Ulrike I. Kramm, and Christina S. Birkel. Adding a new member to the mxene family: Synthesis, structure, and electrocatalytic activity for the hydrogen evolution reaction of v4c3tx. *ACS Applied Energy Materials*, 1(8):3908–3914, 2018. doi: 10.1021/acsaem.8b00652. URL <https://doi.org/10.1021/acsaem.8b00652>. 31
- [155] Jian Yang, Michael Naguib, Michael Ghidui, Li-Mei Pan, Jian Gu, Jagjit Nanda, Joseph Halim, Yury Gogotsi, and Michel W. Barsoum. Two-dimensional nb-based m4c3 solid solutions (mxenes). *Journal of the American Ceramic Society*, 99(2):660–666, 2016. doi: 10.1111/jace.13922. URL <https://ceramics.onlinelibrary.wiley.com/doi/abs/10.1111/jace.13922>. 31
- [156] Michael Ghidui, Joseph Halim, Sankalp Kota, David Bish, Yury Gogotsi, and Michel W. Barsoum. Ion-exchange and cation solvation reactions in ti3c2 mxene. *Chemistry of Materials*, 28(10):3507–3514, 2016. doi: 10.1021/acs.chemmater.6b01275. URL <https://doi.org/10.1021/acs.chemmater.6b01275>. 31
- [157] Michael Ghidui, Sankalp Kota, Joseph Halim, Alexander W. Sherwood, Nils Nedfors, Johanna Rosen, Vadym N. Mochalin, and Michel W. Barsoum. Alkylammonium cation intercalation into ti3c2 (mxene): Effects on properties and ion-exchange capacity estimation. *Chemistry of Materials*, 29(3):1099–1106, 2017. doi: 10.1021/acs.chemmater.6b04234. URL <https://doi.org/10.1021/acs.chemmater.6b04234>.
- [158] Olha Mashtalir, Michael Naguib, Vadym Mochalin, Yohan Dall’Agnese, Min Heon, Michel Barsoum, and Yury Gogotsi. Intercalation and delamination of layered carbides and carbonitrides. *Nature communications*, 4:1716, 04 2013. doi: 10.1038/ncomms2664. 31
- [159] Xiahan Sang, Yu Xie, Ming-Wei Lin, Mohamed Alhabeb, Katherine L. Van Aken, Yury Gogotsi, Paul R. C. Kent, Kai Xiao, and Raymond R. Unocic. Atomic defects in monolayer titanium carbide (ti3c2tx) mxene. *ACS Nano*, 10(10):9193–9200, 2016. doi: 10.1021/acsnano.6b05240. URL <https://doi.org/10.1021/acsnano.6b05240>. PMID: 27598326. 32
- [160] Chuan Xu, Libin Wang, Zhibo Liu, Long Chen, Jingkun Guo, Ning Kang, Xiu-Liang Ma, Hui-Ming Cheng, and Wencai Ren. Large-area high-quality 2D ultrathin Mo₃C superconducting crystals. *Nature materials*, 14(11):1135–1141, 2015. ISSN 1476-1122. doi: 10.1038/nmat4374. URL <http://dx.doi.org/10.1038/nmat4374>. 32, 42
- [161] Yury Gogotsi. Chemical vapour deposition: Transition metal carbides go 2d. *Nature materials*, 14, 08 2015. doi: 10.1038/nmat4386.
- [162] Dechao Geng, Xiaoxu Zhao, Linjun Li, Peng Song, Bingbing Tian, Wei Liu, Jianyi Chen, Dong Shi, Ming Lin, Wu Zhou, and Kian Ping Loh. Controlled

- growth of ultrathin Mo_2C superconducting crystals on liquid Cu surface. *2D Materials*, 4(1):011012, Dec 2016. doi: 10.1088/2053-1583/aa51b7. URL <https://doi.org/10.1088/2053-1583/aa51b7>. 32
- [163] Xu Xiao, Huimin Yu, Huanyu Jin, Menghao Wu, Yunsheng Fang, Jiyu Sun, Zhimi Hu, Tianqi Li, Jiabin Wu, Liang Huang, Yury Gogotsi, and Jun Zhou. Salt-templated synthesis of 2d metallic mon and other nitrides. *ACS Nano*, 11(2):2180–2186, 2017. doi: 10.1021/acsnano.6b08534. URL <https://doi.org/10.1021/acsnano.6b08534>. PMID: 28157328. 32
- [164] Siddharth Joshi, Qi Wang, Ajinkya Puntambekar, and Vidhya Chakrapani. Facile synthesis of large area two-dimensional layers of transition-metal nitride and their use as insertion electrodes. *ACS Energy Letters*, 2(6):1257–1262, 2017. doi: 10.1021/acsenenergylett.7b00240. URL <https://doi.org/10.1021/acsenenergylett.7b00240>.
- [165] Jin Jia, Tanli Xiong, Lili Zhao, Fulei Wang, Hong Liu, Renzong Hu, Jian Zhou, Weijia Zhou, and Shaowei Chen. Ultrathin n-doped Mo_2C nanosheets with exposed active sites as efficient electrocatalyst for hydrogen evolution reactions. *ACS Nano*, 11(12):12509–12518, 2017. doi: 10.1021/acsnano.7b06607. URL <https://doi.org/10.1021/acsnano.7b06607>. PMID: 29220156. 32
- [166] Fan Zhang, Zhi Zhang, Huichao Wang, Cheuk Ho Chan, Ngai Yui Chan, Xin Xin Chen, and Ji-Yan Dai. Plasma-enhanced pulsed-laser deposition of single-crystalline Mo_2C ultrathin superconducting films. *Phys. Rev. Materials*, 1:034002, Aug 2017. doi: 10.1103/PhysRevMaterials.1.034002. URL <https://link.aps.org/doi/10.1103/PhysRevMaterials.1.034002>. 32
- [167] Zhi Zhang, Fan Zhang, Huichao Wang, Cheuk Chan, Wei Lu, and Jiyan Dai. Substrate orientation-induced epitaxial growth of face centered cubic Mo_2C superconductive thin film. *J. Mater. Chem. C*, 5, 09 2017. doi: 10.1039/C7TC03652C. 32
- [168] Bendjerad Adel, S. Boukhtache, A. Benhaya, Dominique Luneau, Hak El, and Kaddour Benyahia. Modeling of magnetic properties of iron thin films deposited by rf magnetron sputtering using preisach model. *Serbian Journal of Electrical Engineering*, 13:229–238, 06 2016. doi: 10.2298/SJEE1602229B. 32
- [169] Jon Tomas Gudmundsson and Daniel Lundin. 1 - introduction to magnetron sputtering. In Daniel Lundin, Tiberiu Minea, and Jon Tomas Gudmundsson, editors, *High Power Impulse Magnetron Sputtering*, pages 1 – 48. Elsevier, 2020. ISBN 978-0-12-812454-3. doi: <https://doi.org/10.1016/B978-0-12-812454-3.00006-1>. URL <https://www.sciencedirect.com/science/article/pii/B9780128124543000061>. 32
- [170] J. E. Greene. Review article: Tracing the recorded history of thin-film sputter deposition: From the 1800s to 2017. *Journal of Vacuum Science & Technology*

- A, 35(5):05C204, 2017. doi: 10.1116/1.4998940. URL <https://doi.org/10.1116/1.4998940>. 33
- [171] A. W. Hull. The magnetron. *Journal of the American Institute of Electrical Engineers*, 40(9):715–723, 1921. doi: 10.1109/JoAIEE.1921.6594005. 33
- [172] M. Shandilya, R. Rai, and J. Singh. Review: hydrothermal technology for smart materials. *Advances in Applied Ceramics*, 115(6):354–376, 2016. doi: 10.1080/17436753.2016.1157131. URL <https://doi.org/10.1080/17436753.2016.1157131>. 34
- [173] Santander Nieto, Ramón Polanco, and Rolando Roque-Malherbe. Absorption kinetics of hydrogen in nanocrystals of $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ proton-conducting perovskite. *The Journal of Physical Chemistry C*, 111(6):2809–2818, 2007. doi: 10.1021/jp067389i. URL <https://doi.org/10.1021/jp067389i>. 34
- [174] Ekram El-Ads. *Perovskite Nanomaterials – Synthesis, Characterization, and Applications*, pages 107–151. 02 2016. ISBN 978-953-51-2245-6. doi: 10.5772/61280. 34
- [175] E. Martínez, E. Sánchez Viches, A. Beltrán-Porter, and D. Beltrán-Porter. Low temperature synthesis of ba-fe mixed oxides having perovskite type structures. *Materials Research Bulletin*, 21(5):511 – 514, 1986. ISSN 0025-5408. doi: [https://doi.org/10.1016/0025-5408\(86\)90103-0](https://doi.org/10.1016/0025-5408(86)90103-0). URL <http://www.sciencedirect.com/science/article/pii/0025540886901030>. 34
- [176] Z. Zakhariev. *Polycrystalline Materials: Theoretical and Practical Aspects*. IntechOpen, 2012. ISBN 9789533079349. URL <https://books.google.com.sg/books?id=pjCaDwAAQBAJ>. 34
- [177] D. Dijkkamp, T. Venkatesan, X. D. Wu, S. A. Shaheen, N. Jisrawi, Y. H. Min-Lee, W. L. McLean, and M. Croft. Preparation of y-ba-cu oxide superconductor thin films using pulsed laser evaporation from high tc bulk material. *Applied Physics Letters*, 51(8):619–621, 1987. doi: 10.1063/1.98366. URL <https://doi.org/10.1063/1.98366>. 34
- [178] C. Webb, S.-L. Weng, J. N. Eckstein, N. Missert, K. Char, D. G. Schlom, E. S. Hellman, M. R. Beasley, A. Kapitulnik, and J. S. Harris. Growth of high tc superconducting thin films using molecular beam epitaxy techniques. *Applied Physics Letters*, 51(15):1191–1193, 1987. doi: 10.1063/1.98729. URL <https://doi.org/10.1063/1.98729>. 34
- [179] Andre Croteau, Shogo Matsubara, Yoichi Miyasaka, and Nobuaki Shohata. Ferroelectric $\text{pb}(\text{zr}, \text{ti})\text{o}_3$ thin films prepared by metal target sputtering. *Japanese Journal of Applied Physics*, 26(S2):18, jan 1987. doi: 10.7567/jjaps.26s2.18. URL <https://doi.org/10.75672Fjjaps.26s2.18>. 34
- [180] Z. Han, L. Bourget, H. Li, M. Ulla, W. S. Millman, H. P. Baum, M. F. Xu, B. K. Sarma, M. Levy, and B. P. Tonner. Single-target sputter deposition,

- post-processing and electron spectroscopy of perovskite superconductor thin films. *AIP Conference Proceedings*, 165(1):66–70, 1988. doi: 10.1063/1.37082. URL <https://aip.scitation.org/doi/abs/10.1063/1.37082>. 34
- [181] M. Naito, R. H. Hammond, B. Oh, M. R. Hahn, J. W. P. Hsu, P. Rosenthal, A. F. Marshall, M. R. Beasley, T. H. Geballe, A. Kapitulnik, and et al. Thin-film synthesis of the high- T_c oxide superconductor $YBa_2Cu_3O_7$ by electron-beam codeposition. *Journal of Materials Research*, 2(6):713–725, 1987. doi: 10.1557/JMR.1987.0713. 34
- [182] P. M. Mankiewich, J. H. Scofield, W. J. Skocpol, R. E. Howard, A. H. Dayem, and E. Good. Reproducible technique for fabrication of thin films of high transition temperature superconductors. *Applied Physics Letters*, 51(21):1753–1755, 1987. doi: 10.1063/1.98513. URL <https://doi.org/10.1063/1.98513>. 34, 35
- [183] R. Rossetti, S. Nakahara, and L. E. Brus. Quantum size effects in the redox potentials, resonance raman spectra, and electronic spectra of cds crystallites in aqueous solution. *The Journal of Chemical Physics*, 79(2):1086–1088, 1983. doi: 10.1063/1.445834. URL <https://doi.org/10.1063/1.445834>. 35
- [184] Louis Brus. Electronic wave functions in semiconductor clusters: experiment and theory. *The Journal of Physical Chemistry*, 90(12):2555–2560, 1986. doi: 10.1021/j100403a003. URL <https://doi.org/10.1021/j100403a003>. 35
- [185] Ning Wang, Wenbo Liu, and Qichun Zhang. Perovskite-based nanocrystals: Synthesis and applications beyond solar cells. *Small Methods*, 2(6):1700380, 2018. doi: 10.1002/smtd.201700380. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/smtd.201700380>. 35
- [186] Chris de Weerd, Tom Gregorkiewicz, and Leyre Gomez. All-inorganic perovskite nanocrystals: Microscopy insights in structure and optical properties. *Advanced Optical Materials*, 6(16):1800289, 2018. doi: 10.1002/adom.201800289. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adom.201800289>. 35
- [187] Hung-Chia Wang, Zhen Bao, Hsin-Yu Tsai, An-Cih Tang, and Ru-Shi Liu. Perovskite quantum dots and their application in light-emitting diodes. *Small*, 14(1):1702433, 2018. doi: 10.1002/smll.201702433. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/smll.201702433>. 35
- [188] Chi Yang, Yihui Wu, Qingshan Ma, and Wen-Hua Zhang. Nanocrystals of halide perovskite: Synthesis, properties, and applications. *Journal of Energy Chemistry*, 27(3):622 – 636, 2018. ISSN 2095-4956. doi: <https://doi.org/10.1016/j.jechem.2017.12.007>. URL <http://www.sciencedirect.com/science/article/pii/S2095495617309713>. 35
- [189] Maksym V. Kovalenko, Liberato Manna, Andreu Cabot, Zeger Hens, Dmitri V. Talapin, Cherie R. Kagan, Victor I. Klimov, Andrey L. Rogach,

- Peter Reiss, Delia J. Milliron, Philippe Guyot-Sionnest, Gerasimos Konstantatos, Wolfgang J. Parak, Taeghwan Hyeon, Brian A. Korgel, Christopher B. Murray, and Wolfgang Heiss. Prospects of nanoscience with nanocrystals. *ACS Nano*, 9(2):1012–1057, 2015. doi: 10.1021/nm506223h. URL <https://doi.org/10.1021/nm506223h>. PMID: 25608730. 35
- [190] Xiaoming Li, Fei Cao, Dejian Yu, Jun Chen, Zhiguo Sun, Yalong Shen, Ying Zhu, Lin Wang, Yi Wei, Ye Wu, and Haibo Zeng. All inorganic halide perovskites nanosystem: Synthesis, structural features, optical properties and optoelectronic applications. *Small*, 13(9):1603996, 2017. doi: 10.1002/smll.201603996. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/smll.201603996>. 35
- [191] C. B. Murray, D. J. Norris, and M. G. Bawendi. Synthesis and characterization of nearly monodisperse cde (e = sulfur, selenium, tellurium) semiconductor nanocrystallites. *Journal of the American Chemical Society*, 115(19):8706–8715, 1993. doi: 10.1021/ja00072a025. URL <https://doi.org/10.1021/ja00072a025>. 35
- [192] L. Manna, D. Milliron, A. Meisel, E. Scher, and A. Alivisatos. Controlled growth of tetrapod-branched inorganic nanocrystals. *Nature Materials*, 2: 382–385, 2003. 35
- [193] Javad Shamsi, Alexander S. Urban, Muhammad Imran, Luca De Trizio, and Liberato Manna. Metal halide perovskite nanocrystals: Synthesis, post-synthesis modifications, and their optical properties. *Chemical Reviews*, 119(5):3296–3348, 2019. doi: 10.1021/acs.chemrev.8b00644. URL <https://doi.org/10.1021/acs.chemrev.8b00644>. PMID: 30758194. 36, 37
- [194] Oleh Vybornyi, Sergii Yakunin, and Maksym V. Kovalenko. Polar-solvent-free colloidal synthesis of highly luminescent alkylammonium lead halide perovskite nanocrystals. *Nanoscale*, 8:6278–6283, 2016. doi: 10.1039/C5NR06890H. URL <http://dx.doi.org/10.1039/C5NR06890H>. 36
- [195] M. Kurlansky and S.D. Schindler. *The Story of Salt*. Penguin Young Readers Group, 2014. ISBN 9780147511669. URL <https://books.google.com.sg/books?id=a2gLngEACAAJ>. 37
- [196] Ioannis Lignos, Stavros Stavrakis, Georgian Nedelcu, Loredana Protesescu, Andrew J. deMello, and Maksym V. Kovalenko. Synthesis of cesium lead halide perovskite nanocrystals in a droplet-based microfluidic platform: Fast parametric space mapping. *Nano Letters*, 16(3):1869–1877, 2016. doi: 10.1021/acs.nanolett.5b04981. URL <https://doi.org/10.1021/acs.nanolett.5b04981>. PMID: 26836149. 38
- [197] Kun-Hua Wang, Liang Wu, Lei Li, Hong-Bin Yao, Hai-sheng Qian, and Shu-Hong Yu. Large-scale synthesis of highly luminescent perovskite-related cs pb

- 2 br 5 nanoplatelets and their fast anion exchange. *Angewandte Chemie*, 128, 05 2016. doi: 10.1002/ange.201602787. 38
- [198] Song Wei, Yanchun Yang, Xiaojiao Kang, Lan Wang, Lijian Huang, and Daocheng Pan. Room-temperature and gram-scale synthesis of cspb_x3 (x = cl, br, i) perovskite nanocrystals with 50–85 *Chem. Commun.*, 52:7265–7268, 2016. doi: 10.1039/C6CC01500J. URL <http://dx.doi.org/10.1039/C6CC01500J>.
- [199] Javad Shamsi, Prachi Rastogi, Vincenzo Caligiuri, Ahmed L. Abdelhady, Davide Spirito, Liberato Manna, and Roman Krahne. Bright-emitting perovskite films by large-scale synthesis and photoinduced solid-state transformation of cspbbr3 nanoplatelets. *ACS Nano*, 11(10):10206–10213, 2017. doi: 10.1021/acsnano.7b04761. URL <https://doi.org/10.1021/acsnano.7b04761>. PMID: 28945960. 38
- [200] George C. Papavassiliou, Georgia Pagona, Nikos Karousis, George A. Mousdis, Ioannis Koutselas, and Anastasia Vassilakopoulou. Nanocrystalline/microcrystalline materials based on lead-halide units. *J. Mater. Chem.*, 22: 8271–8280, 2012. doi: 10.1039/C2JM15783G. URL <http://dx.doi.org/10.1039/C2JM15783G>. 38
- [201] Feng Zhang, Haizheng Zhong, Cheng Chen, Xian-gang Wu, Xiangmin Hu, Hailong Huang, Junbo Han, Bingsuo Zou, and Yuping Dong. Brightly luminescent and color-tunable colloidal ch₃nh₃pbx₃ (x = br, i, cl) quantum dots: Potential alternatives for display technology. *ACS Nano*, 9(4):4533–4542, 2015. doi: 10.1021/acsnano.5b01154. URL <https://doi.org/10.1021/acsnano.5b01154>. PMID: 25824283. 38
- [202] Xiaoming Li, Ye Wu, Shengli Zhang, Bo Cai, Yu Gu, Jizhong Song, and Haibo Zeng. Cspb_x3 quantum dots for lighting and displays: Room-temperature synthesis, photoluminescence superiorities, underlying origins and white light-emitting diodes. *Advanced Functional Materials*, 26(15):2435–2445, 2016. doi: 10.1002/adfm.201600109. URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/adfm.201600109>. 38
- [203] Sudipta Seth and Anunay Samanta. A facile methodology for engineering the morphology of cspb_x 3 perovskite nanocrystals under ambient condition. *Scientific Reports*, 6:37693, 12 2016. doi: 10.1038/srep37693. 38
- [204] Shun Wang, Yu Lei Du, and Wen He Liao. Tunable band gap and optical properties of surface functionalized Sc₂C monolayer. *Chinese Physics B*, 26(1):1–5, 2017. ISSN 20583834. doi: 10.1088/1674-1056/26/1/017806. 42
- [205] Michel W Barsoum. The m_{n+1}ax_n phases: A new class of solids;thermodynamically stable nanolaminates. *Frog. Solid St. Chem.*, 28: 201–281, 2000. ISSN 0079-6786. doi: 10.1016/S0079-6786(00)00006-6. 42

- [206] Martin Magnuson, Maurizio Mattesini, Carina Höglund, Igor A. Abrikosov, Jens Birch, and Lars Hultman. Electronic structure investigation of the cubic inverse perovskite sc_3AlN . *Phys. Rev. B*, 78:235102, Dec 2008. doi: 10.1103/PhysRevB.78.235102. URL <https://link.aps.org/doi/10.1103/PhysRevB.78.235102>. 42
- [207] Mdi. jade 6 (computer software), materials data, livermore, ca, usa. 2004. 44
- [208] D. A. Permin, E. M. Gavrishchuk, O. N. Klyusik, S. V. Egorov, and A. A. Sorokin. Self-propagating high-temperature synthesis of Sc_2O_3 nanopowders using different precursors. *Advanced Powder Technology*, 27(6):2457–2461, 2016. ISSN 15685527. doi: 10.1016/j.appt.2016.08.025. URL <http://dx.doi.org/10.1016/j.appt.2016.08.025>. 44
- [209] D. Briggs. X-ray photoelectron spectroscopy (XPS). *Handbook of Adhesion: Second Edition*, pages 621–622, 2005. doi: 10.1002/0470014229.ch22. 45
- [210] V. V. Afanas'ev, S. Shamulia, M. Badylevich, A. Stesmans, L. F. Edge, W. Tian, D. G. Schlom, J. M.J. Lopes, M. Roeckerath, and J. Schubert. Electronic structure of silicon interfaces with amorphous and epitaxial insulating oxides: Sc_2O_3 , Lu_2O_3 , LaLuO_3 . *Microelectronic Engineering*, 84(9-10):2278–2281, 2007. ISSN 01679317. doi: 10.1016/j.mee.2007.04.113. 45
- [211] J.Tauc. OPTICAL PROPERTIES AND ELECTRONIC STRUCTURE OF AMORPHOUS Ge AND Si. *Mat. Res. Bull.*, 3(2):37–46, 1968. 48
- [212] Tariq Abbas, L. Slewa, Hersh Khizir, and Shaida Kakil. Synthesis of cobalt oxide (Co_3O_4) thin films by electrostatic spray pyrolysis technique (esp). *Journal of Materials Science: Materials in Electronics*, 28, 10 2016. doi: 10.1007/s10854-016-5748-y. 48
- [213] Z. G. Yu. Effective-mass model and magneto-optical properties in hybrid perovskites. *Scientific Reports*, 6(April):1–14, 2016. ISSN 20452322. doi: 10.1038/srep28576. 52
- [214] Shunsuke Hirotsu, Jimpei Harada, Masashi Iizumi, and Kazuo Gesi. Structural phase transitions in CsPbBr_3 . *Journal of the Physical Society of Japan*, 37(5):1393–1398, 1974. doi: 10.1143/JPSJ.37.1393. URL <https://doi.org/10.1143/JPSJ.37.1393>. 52
- [215] W. J. Fan. Bulk inversion asymmetry effect on band structure and optical transition of a new class all-inorganic cubic perovskite nanoplatelet. *AIP Advances*, 8(9), 2018. ISSN 21583226. doi: 10.1063/1.5048349. 57
- [216] H. Riane, F. Hamdache, S. Bahloul, and N. Benharrats. Alloy composition effects on the gain and the differential gain for CdZnTe based II-VI semiconductor lasers. *Superlattices and Microstructures*, 40(1):19–28, 2006. ISSN 07496036. doi: 10.1016/j.spmi.2006.01.004. 61

- [217] S. A. Anson, J. T. Olesberg, Michael E. Flatté, T. C. Hasenberg, and Thomas F. Boggess. Differential gain, differential index, and linewidth enhancement factor for a 4 μm superlattice laser active layer. *Journal of Applied Physics*, 86(2):713–718, 1999. ISSN 00218979. doi: 10.1063/1.370793. [61](#)
- [218] K. Heidrich, W. Schäfer, M. Schreiber, J. Söchtig, G. Trendel, J. Treusch, T. Grandke, and H. J. Stolz. Electronic structure, photoemission spectra, and vacuum-ultraviolet optical spectra of CsPbCl_3 and CsPbBr_3 . *Physical Review B*, 24(10):5642–5649, 1981. ISSN 01631829. doi: 10.1103/PhysRevB.24.5642. [64](#)
- [219] Shunsuke Hirotsu, Jimpei Harada, Masashi Iizumi, and Kazuo Gesi. Structural phase transitions in csPbBr_3 . *Journal of the Physical Society of Japan*, 37(5):1393–1398, 1974. doi: 10.1143/JPSJ.37.1393. URL <https://doi.org/10.1143/JPSJ.37.1393>. [64](#)
- [220] Z. G. Yu. Effective-mass model and magneto-optical properties in hybrid perovskites. *Scientific Reports*, 6(April):1–14, 2016. ISSN 20452322. doi: 10.1038/srep28576. [65](#)
- [221] Stefan Birner, Tobias Zibold, Till Andlauer, Tillmann Kubis, Matthias Sabathil, Alex Trellakis, and Peter Vogl. nextnano: General purpose 3-d simulations. *IEEE Transactions on Electron Devices*, 54(9):2137–2142, 2007. doi: 10.1109/TED.2007.902871. [65](#)
- [222] Junhao Lin, Leyre Gomez, Chris De Weerd, Yasufumi Fujiwara, Tom Gregorkiewicz, and Kazutomo Suenaga. Direct Observation of Band Structure Modifications in Nanocrystals of CsPbBr_3 Perovskite. *Nano Letters*, 16(11):7198–7202, 2016. ISSN 15306992. doi: 10.1021/acs.nanolett.6b03552. [65](#)
- [223] W. J. Fan. Bulk inversion asymmetry effect on band structure and optical transition of a new class all-inorganic cubic perovskite nanoplatelet. *AIP Advances*, 8(9), 2018. ISSN 21583226. doi: 10.1063/1.5048349. [67](#)
- [224] Elias Burstein. Anomalous optical absorption limit in InSb [4]. *Physical Review*, 93(3):632–633, 1954. ISSN 0031899X. doi: 10.1103/PhysRev.93.632. [71](#)
- [225] T. S. Moss. The interpretation of the properties of indium antimonide. *Proceedings of the Physical Society. Section B*, 67(10):775–782, 1954. ISSN 03701301. doi: 10.1088/0370-1301/67/10/306. [71](#)
- [226] Prashant V. Kamat, Nada M. Dimitrijevic, and A. J. Nozik. Dynamic Burstein-Moss shift in semiconductor colloids. *Journal of physical chemistry*, 93(8):2873–2875, 1989. ISSN 00223654. doi: 10.1021/j100345a003. [71](#)
- [227] Stephen G. Hickey, D. Jason Riley, and Elizabeth J. Tull. Photoelectrochemical studies of CdS nanoparticle modified electrodes: Absorption and photocurrent investigations. *Journal of Physical Chemistry B*, 104(32):7623–7626, 2000. ISSN 15206106. doi: 10.1021/jp993858n.

-
- [228] Ken Ichi Kawamura, Keisuke Maekawa, Hiroshi Yanagi, Masahiro Hirano, and Hideo Hosono. Observation of carrier dynamics in CdO thin films by excitation with femtosecond laser pulse. *Thin Solid Films*, 445(2):182–185, 2003. ISSN 00406090. doi: 10.1016/S0040-6090(03)01172-6.
- [229] Joseph S. Manser and Prashant V. Kamat. Band filling with free charge carriers in organometal halide perovskites. *Nature Photonics*, 8(9):737–743, 2014. ISSN 17494893. doi: 10.1038/nphoton.2014.171. URL <http://dx.doi.org/10.1038/nphoton.2014.171>. [71](#)
- [230] H. Riane, F. Hamdache, S. Bahlouli, and N. Benharrats. Alloy composition effects on the gain and the differential gain for CdZnTe based II-VI semiconductor lasers. *Superlattices and Microstructures*, 40(1):19–28, 2006. ISSN 07496036. doi: 10.1016/j.spmi.2006.01.004. [71](#)
- [231] S. A. Anson, J. T. Olesberg, Michael E. Flatté, T. C. Hasenberg, and Thomas F. Boggess. Differential gain, differential index, and linewidth enhancement factor for a 4 μm superlattice laser active layer. *Journal of Applied Physics*, 86(2):713–718, 1999. ISSN 00218979. doi: 10.1063/1.370793. [71](#)